Research Paper

The effect of chloride and orthophosphate on the release of iron from a cast iron pipe section

D. A. Lytle, P. Sarin and V. L. Snoeyink

ABSTRACT

"Colored water" resulting from suspended iron particles is a common drinking water consumer complaint which is largely impacted by water chemistry. A bench scale study, performed on a 90-year-old corroded cast-iron pipe section removed from a drinking water distribution system, was used to evaluate the effects of orthophosphate and chloride on iron release, color and turbidity. Experiments showed that an increase in chloride concentration of 100 mg/L significantly increased the concentration of iron released from the pipe section while the presence of orthophosphate at 3 mg/L decreased iron release. Chloride increased and orthophosphate decreased the water color and turbidity caused by the release of iron, but there was not a linear relationship with respect to the concentration of iron released. The control of chloride and orthophosphate concentrations is important in controlling the problem of colored water.

Key words | iron, chloride, red water, orthophosphate

D. A. Lytle (corresponding author)
US Environmental Protection Agency, ORD,
   NRMRL, WSWRD, TTEB,
26 W. Martin Luther King Drive
Cincinnati OH 45268,
USA
Tel: +1 513 569 7132
Fax: +1 513 569 7172
E-mail: lytle.darren@epa.gov

P. Sarin
Materials Science & Engineering Department,
   University of Illinois,
1304 W. Green St.,
Urbana IL 61801,
USA

V. L. Snoeyink
Department of Civil and Environmental
   Engineering,
University of Illinois,
205 N. Mathews
Urbana, IL 61801,
USA

INTRODUCTION

"Colored water" describes the appearance of drinking water that contains suspended particulate iron where the actual suspension color may range from light yellow to red due to water chemistry and particle properties. This iron can originate from the source water and from distribution system materials. The relatively soluble +2 oxidation state is the dominant form of iron found in anoxic environments, which include some groundwaters, the hypolimnion of eutrophic reservoirs, drinking water distribution system dead ends and beneath thick iron corrosion scales. When exposed to oxygen or disinfectant during water treatment and distribution, Fe(II) is oxidized to the insoluble Fe(III) form, which readily precipitates and causes colored water.

The release of iron from distribution system materials such as cast iron water mains is a complex process which involves mass transfer and many interactions. These include corrosion, reduction–oxidation (redox) reactions, precipitation, dissolution, solid phase reactions and microbiological activity. The consumer's perception of the quality of water containing suspended iron is dependent upon the properties of the iron particles which are again an important function of water chemistry. Colored water problems originating from distribution system materials may be reduced by controlling corrosion, iron release from corrosion scales and the form and properties of the iron particles. Iron release may be reduced by proper control of pH, alkalinity and hardness, and possibly through the addition of corrosion inhibitors (i.e.

orthophosphate). Chemicals, such as silicates and polyphosphates, reduce the visible appearance of iron particles in suspension by impacting the particle properties but their interactions at the iron scale–water interface are less understood. The objective of this research was to evaluate the effects of two water quality parameters, chloride and orthophosphate, on the release of iron from an old cast-iron pipe section removed from a drinking water distribution system and to study the properties of the resulting suspensions.

BACKGROUND

Water chemistry and the properties of the scale and corrosion deposits that cover the iron pipe wall are important factors that affect iron release[1] from drinking water distribution systems. The structure and chemical composition of iron corrosion scales are particularly important in understanding iron release (Sarin *et al.* 1999, 2000). Iron corrosion scales are complex structures that typically consist of layers of ferrous, ferric and mixed (ferrous and ferric) oxides and oxy-hydroxides. The inner layer (closest to the pipe wall) often consists of relatively porous ferric oxy-hydroxide (goethite, α-FeOOH). Ferrous mineral phases such as $Fe(OH)_2$ and $FeCO_3$ are also thought to be present, but are difficult to identify due to their sensitivity to the oxygen introduced during handling and analysis. The inner layer serves as a large source of soluble Fe^{2+}. The porous layer is covered by a dense "shell-like" layer consisting of relatively insoluble ferric phases such as α-FeOOH and β-FeOOH (lepidocrocite) and mixed oxides such as Fe_3O_4. Electrically conductive solid phases in the porous and shell-like layer, such as Fe_3O_4, could provide a pathway for the Kuch mechanism (Kuch *et al.* 1983), leading to the generation of Fe^{2+} and the degradation of the shell-like layer. In accordance with the iron release model proposed by Sarin *et al.* (2004), the properties of the pores in the dense layer are important in controlling the diffusion of Fe^{2+} and other ions in and out of the scale. The dense layer may be covered by a relatively thin precipitated ferric

layer. The presence of an oxidant at the scale surface has an important effect on the scale: under flowing conditions oxygen and disinfectants are continually supplied to the scale surface where oxidation of ferrous iron occurs. Ferric iron precipitates primarily within the scale, which is thought to reinforce the scale structure and reduce porosity. Ferric iron solubility is low at typical pH values and thus iron release is relatively small. Under stagnant conditions that follow flow, dissolved oxygen is reduced via reaction with ferrous iron. Diffusion of oxygen to the surface in response to the concentration gradient is slow relative to the Fe^{2+}–oxygen reaction and an anoxic zone is created at or near the scale surface. The rate of formation of this zone depends upon the nature of the scale and water chemistry. With prolonged periods of stagnation, ferrous iron is released from the scale, causing dissolution of ferrous solids and reduction of ferric phases. As a result, the scale is believed to weaken and porosity increases, allowing more ferrous iron to diffuse into bulk water. The scale breakdown process can be reversed by increasing the flow rate and the concentration of disinfectants at the surface (Sarin *et al.* 2004).

Iron release is greatly affected by water chemistry including pH, alkalinity and corrosion inhibitors. The effects of chloride and orthophosphate on iron release are of interest to many drinking water systems. Changes in chloride concentration may be an issue for water utilities that are considering ion exchange treatment, changing to a more saline source or using a source that fluctuates in chloride content. Orthophosphate corrosion inhibitors are widely used to reduce lead and copper solubility (Schock *et al.* 1995*a,b*; Schock *et al.* 1996; Schock & Clement 1998) in drinking water distribution systems, but it is not widely recognized for iron release or red water control. Despite the interest, very little work has examined the effects of chloride and orthophosphate on the release of iron from drinking water distribution system pipe materials.

Chloride

Chloride has long been associated with increased corrosion rate and pitting corrosion of iron materials (Nakama & Sasa 1976; Mansfeld & Kenkel 1979; Szklarska-Smialowska 1986; Jones 1996). Some work has suggested that chloride breaks down passive iron corrosion films (Heusler & Fischer 1976;

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[1]"Iron release" describes the transport of iron, either soluble or particulate, from the pipe wall or scale to the bulk water. Iron corrosion differs from iron release in that corrosion refers to the specific process where electrons are transferred from the iron metal to an electron acceptor such as oxygen. Iron corrosion can be a source of iron release.

Jones 1982). Chloride was thought to catalyze the generation of Fe^{3+} from FeOOH films. Anodic production of Fe^{2+} attracts negative anions to the surface of the corroding metal. Anions are necessary to maintain electroneutrality and complete the electrical circuit of the corrosion cell. Chloride is expected to have greater mobility through water and layers of corrosion deposits as compared to other major anions (Benjamin *et al.* 1996; Jones 1996). Chloride reacts in the corrosion pit to form a strong acid according to

$$Fe^{2+} + 2H_2O + Cl^- \rightarrow Fe(OH)_2 + 2HCl \qquad (1)$$
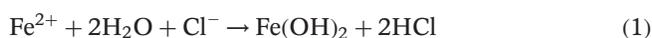
The acid /chloride solution increases iron corrosion which further attracts more chloride into the pit.

The impact of chloride on iron release is of special interest. Madsen (see Madsen 1973; Benjamin *et al.* 1996) reported that an increase in chloride concentration resulted in immediate changes in the iron content of distributed water in Germany. Indirectly, chloride may influence iron release by affecting Fe^{2+} oxygenation kinetics. The effect of chloride on Fe(II) oxygenation kinetics in slightly acidic and neutral solutions has been reported by several workers. Millero (1985) reported that anions such as Br^-, NO_3^- and ClO_4^- increased the rate of Fe(II) oxygenation slightly and the effect of anions on the rate constant decreased in the order $HCO_3^- >> Br^- > NO_3^- > ClO_4^- > Cl^- >> SO_4^{2-} > > B(OH)_4^-$. In another study, Tamura *et al.* (1976) found that the effect of anions on the Fe(II) oxygenation rate constant decreased in order ClO_4^-, NO_3^-, Cl^-, $H_3SiO_4^-$, Br^-, I^-, SO_4^{2-}. Similarly, Sung & Morgan (1980) found the order ClO_4^-, Cl^-, SO_4^{2-}.

Orthophosphate

Orthophosphate has been shown to be effective at reducing the solubility of lead by encouraging the formation of the relatively insoluble, basic lead orthophosphate (Schock, 1980, 1981, 1989; Sheiham & Jackson, 1981). Solubility reduction is dependent on orthophosphate concentration, pH and dissolved inorganic concentration, with the greatest benefits observed between pH 7.2 and 7.8 (Schock *et al.* 1996). Orthophosphate may also be beneficial at reducing copper (II) solubility in some conditions (Schock *et al.* 1994, 1995*a,b*; Schock and Clement 1998).

It has been suggested that orthophosphate will reduce the corrosion rate of steel and iron release rate (Benjamin *et al.* 1996). One report found that the corrosion rate of mild steel and scale accumulation was reduced by two-thirds following the addition of 5 mg/L orthophosphate, while 1 mg/L had no effect (Benjamin *et al.* 1990). The formation and precipitation of sparingly soluble metal phosphate salts, such as calcium phosphate phases, may form protective diffusion barriers (Nancollas 1983). Studies using cyclic voltammetry showed that the main component of films formed on iron in phosphate solutions was vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$ (Melendres *et al.* 1989). Similar observations were made with films developed on mild steel in 1 N sodium phosphate solution adjusted to pH 6 (Smart *et al.* 1990). The pitting of carbon steel by chloride was to be reduced by phosphate addition, which was thought to result from the competitive adsorption of anions on the metal surface reported (Ergun & Turan 1991).

Recently, pipe loop studies using corroded cast iron pipes removed from the drinking water distribution system of the Massachusetts Water Resources Authority (MWRA) showed that orthophosphate at a residual of 3 mg PO_4/L (pH 7.3–7.8, alkalinity 30–35 mg $CaCO_3$/L) reduced iron levels over a 6 month period (Clement *et al.* 2002). However, in the same study short-term testing conducted at the University of Illinois (Champaign-Urbana, IL) in higher alkalinity water did not show an effect of orthophosphate on iron release. The investigators suggested that the discrepancies were a result of differences in scale composition.

MATERIALS AND METHODS

Pipe section

Experiments were conducted using a section of cast-iron pipe (approximately 90 years old) removed from the drinking water distribution system in the City of Cincinnati, OH (Figure 1). The pipe was approximately 8 cm (3.15 in) in height and 10.2 cm (4 in) in diameter. Approximately 1.3 cm (0.5 in) of the original effective inside diameter was lost to corrosion deposits. One end of the pipe was closed with a rubber seal and hose clamp fastener.

Figure 1 │ Photograph of 4 inch diameter cast-iron pipe section used in study.

Test water

Cincinnati tap water (Cincinnati, OH) served as the base water for the experiments (Table 1). The pipe section was "conditioned" with Cincinnati tap water for nearly one year prior to the start of data collection. Conditioning was established by emptying and immediately refilling the pipe section with Cincinnati tap water on a daily basis.

Chemicals

Unless otherwise specified, all chemicals used in this study were Analytical Reagent (AR) grade. Ultrapure nitric acid,

Table 1 │ Chemistry of test water used in this study. Chemistry variables are listed as the average initial (before stagnation) values

Analyte	Concentration or units	Standard deviation
Calcium (mg/L)	32.9	4.7
Iron (mg/L)	0.002	0.005
Potassium (mg/L)	2.74	0.56
Manganese (mg/L)	9.03	1.4
Chloride (mg/L)	34[***]	9
Sulfate (mg SO_4/L)	65.1	9.7
Silicate (mg SiO_2/L)	5.19	0.58
Sodium (mg/L)	16.1 (82.4[*], 91.4[**])	1.17 (5.68[*], 2.76[**])
Phosphate (mg PO_4/L)	<0.2 (3.17[**])	<0.2 (0.39[**])
Alkalinity (mg $CaCO_3$/L)	73[***]	15
pH (units)	8.65 (8.69[*], 8.79[**])	0.1 (0.08[*], 0.17[**])
Temperature (°C)	18.2	2.1
Dissolved oxygen (mg/L)	6.09 (6.85[*], 8.22[**])	2.87 (1.48[*], 1.62[**])
Redox potential (mV)	609 (573[*], 489[**])	45.9 (35.9[*], 52.0[**])
Free chlorine (mg Cl_2/L)	0.85	0.11

[*]NaCl was added to the base water
[**]NaCl and Na_3PO_4 were added to the base water
[***]Report values based on finished water measurements provided by the Cincinnati Water Works during the study period

HNO_3, (Ultrex, J T Baker Chemical Company, Phillipsburg, NJ) was used to preserve samples for metals analysis and sodium chloride (Fisher Scientific, Fairlawn, NJ) and sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) (Fisher Scientific, Fairlawn, NJ) were used to adjust water chemistry.

Analytical methods

The pH was measured with a Hach Company (Loveland, CO) EC40 benchtop pH/ISE meter (model 50125). The instrument was standardized daily using a two-point calibration with pH 7 and 10 standard solutions (Whatman, Hillsboro, OR). Dissolved oxygen (DO) was measured with a Hach Company (Loveland, CO) Model DO175 dissolved oxygen meter and a Model 50180 dissolved oxygen probe. Reduction–oxidation (redox) potential was measured with a Corning pH/ion meter 450 (Corning Incorporated, Corning, NY) with two Orion® combination redox electrodes (Orion Research, Inc., Beverly, MA). Metals were analyzed with a Thermo Jarrel Ash (Franklin, MA) 61E® purged inductively coupled argon plasma spectrometer (ICAPS). Color, total iron, orthophosphate and free chlorine were measured with a Hach DR/2000 spectrophotometer (Loveland, CO) and a Hach DR/2010 spectrometer (Loveland, CO). Total iron was measured using the 1, 10 phenanthroline method (Hach Company 1990; APHA-AWWA-WEF 1995). The method measures ferrous iron so a reducing reagent was also included in the reagent powder pillow provided by the Hach Company to convert Fe(III) to Fe(II). Orthophosphate was measured with molybdate in an acid medium provided by the Hach Company, while free chlorine levels were measured by the reaction with the DPD (N, N-diethyl-*p*-phenylenediamine) indicator provided by the Hach Company. Turbidity was measured using a Hach 2100N turbidimeter. Syringe filters (0.45, 0.2 μm) (Whatman, Inc., Clifton, NJ) were used to separate colloidal iron during color and iron measurements.

Other

Glassware (excluding pipettes) used for the preparation of standards and solutions was cleaned using a 5% solution of Contrad 70©. The glassware was thoroughly rinsed with deionized water. Reused glassware was immediately cleaned by soaking in 10% (v/v) concentrated HNO_3 and rinsed with DDI H_2O. Air displacement micropipettes with disposable tips were used for handling and transferring solutions.

Experimental procedure

Two liters of Cincinnati tap water were collected in glass beakers after flushing the laboratory faucet for 5 minutes. If applicable, sodium chloride and sodium phosphate were added at this time and the water was mixed. The pH, redox potential, orthophosphate and free chlorine in the tap water were immediately measured and a water sample was collected for metals analysis by ICAPS. The remaining volume of test water was then pumped through 6.4 mm (0.25 in) plastic tubing into the pipe section (standing vertically) at a slow rate of 50 mL/min from the bottom of the pipe. Excess water was allowed to overflow from the pipe section. Dissolved oxygen (DO) was measured with a dissolved oxygen probe suspended at the center of the pipe during flushing. The pipe section was loosely covered with a glass plate to reduce interaction with the outside environment and allowed to sit undisturbed for approximately 23.5 h during weekdays and 72 or 96 h over weekends. The glass cover was carefully removed at the end of stagnation. Following this process, the first measurements of ferrous iron were taken by drawing 20 mL of water from the center of the pipe section using a 25 mL syringe prefilled with 5 mL 0.6% nitric acid, which preserves the oxygen-sensitive ferrous iron. The dissolved oxygen was then measured as before. Finally, samples were carefully drawn for pH, redox potential, turbidity, color, total iron (ferric and ferrous), orthophosphate and free chlorine and measured immediately and an additional sample was taken for ICAPS analysis. Filtered color and total iron measurements were also made using 0.45 μm syringe filters.

Statistical analysis

Statistical comparisons between means of treatment groups were made using unpaired *t*-test when data sets passed the normality test or the Mann–Whitney Rank Sum Test when data sets failed the normality test ($\alpha = 0.05$) (Daniel 1987; Glantz 1992). Normality was tested using the Kolmogorov–Smirnov test. All statistical calculations were made using Sigmastat™ (version 2.0) (SPSS Inc.)

RESULTS

After conditioning the 90-year-old pipe section for 1 year, evaluations were made over a 223 d period to determine the effects of chloride and orthophosphate on iron release, and the color and turbidity of the resulting suspensions. The following results pertain to data collected after water was in contact with the pipe for approximately 23.5 h unless otherwise noted.

Iron release

The pipe was exposed to untreated Cincinnati tap water for the first 20 d of the study to establish a baseline. Total iron release levels averaged 1.8 ($\pm$ 0.12) mg/L ($\pm$ 95% confidence interval) and remained relatively consistent over the entire period (Figure 2, Table 2). Ferrous iron was measured regularly during the study and, although at times measurable concentrations were detected, the results were sporadic and trends could not be confidently identified. Variability was attributed to the oxidation of ferrous iron during sampling and the sensitivity of ferrous iron to oxidant concentration. Ferrous iron diffusing away from the pipe

wall encounters oxygen or chlorine, and then is rapidly oxidized to ferric iron. Ferrous iron is soluble and therefore is not responsible for color and turbidity in water. Iron released from corroded pipes has been shown to be in the ferrous form when oxygen in the water has been removed (Sarin *et al.* 1999, 2000).

Sodium chloride addition to a concentration of 100 mg/L Cl^- above the natural water level (40 mg/L) was initiated at day 20. Total iron release almost immediately responded by increasing 0.7 mg/L to an average of 2.5 ($\pm$ 0.20) mg/L (Figure 2, Table 2). The effect of chloride on total iron release was statistically significant (Table 3).

Sodium orthophosphate was added to Cincinnati tap water at a concentration of 3 mg PO_4/L approximately 54 d into the study, while maintaining chloride addition. Total iron concentration decreased almost immediately after the orthophosphate feed was initiated and appeared to gradually decrease over the 45 d feed period (Figure 2). Total iron averaged 1.74 ($\pm$ 0.12) mg/L (Table 2) for the entire period, which was a 30% decrease from the average observed during the period when only chloride was fed.
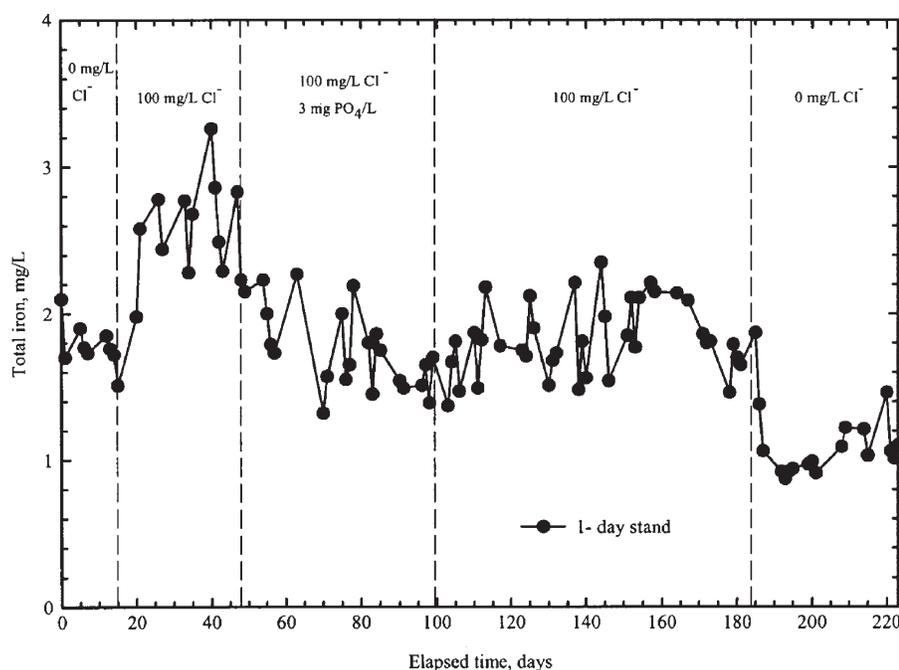

Figure 2 │ The effect of chloride and orthophosphate on the amount of iron released from pipe section.

Table 2 | Mean water quality parameters during treatment periods ($\pm$ 95% confidence interval)

Period	Days	Total iron (mg/L)	Ferrous iron (mg/L)	Turbidity (NTU)	Apparent color (PtCo Units)	NTU/Fe	Color/Fe
Baseline (start-up)	0–20	1.8 ($\pm$0.12)	0.15 ($\pm$0.07)	8.3 ($\pm$2.0)	116.8 ($\pm$17.3)	4.2 ($\pm$0.6)	59.8 ($\pm$5.9)
Chloride	21–54	2.5 ($\pm$0.20)	0.31 ($\pm$0.09)	16.6 ($\pm$1.3)	171.9 ($\pm$12.1)	6.6 ($\pm$0.5)	67.8 ($\pm$2.7)
Chloride and phosphate	55–99	1.74 ($\pm$0.12)	0.16 ($\pm$0.05)	9.43 ($\pm$1.0)	76.7 ($\pm$9.5)	5.4 ($\pm$0.4)	44.0 ($\pm$3.7)
Chloride	100–181	1.82 ($\pm$0.08)	0.09 ($\pm$0.03)	10.4 ($\pm$0.6)	112.6 ($\pm$8.6)	5.7 ($\pm$0.2)	61.5 ($\pm$3.7)
No chemical	182–223	1.11 ($\pm$0.12)	0.11 ($\pm$0.06)	4.8 ($\pm$0.9)	63.2 ($\pm$7.7)	4.4 ($\pm$0.3)	57.0 ($\pm$3.2)

Orthophosphate addition was stopped after 99 d while chloride addition continued. Total iron levels appeared to gradually increase over most of the time period and averaged 1.82 ($\pm$0.08) mg/L (Figure 2, Table 2). However, the change was not significant statistically, based on a comparison of period averages (Table 3). Total iron never returned to the pre-orthophosphate iron levels.

Total iron release significantly dropped almost immediately (Table 3) and averaged 1.11 ($\pm$0.12) mg/L (Figure 2, Table 2) after chloride feed was terminated at 181 d. During the period of the first several sampling points, the total iron levels dropped rapidly to a minimum. After this period, the iron levels appeared to gradually increase as they did in the period following orthophosphate feed termination. Total iron levels did not return to baseline values. These observations suggested that some of the benefit of orthophosphate was maintained long after the orthophosphate feed was discontinued.

Total iron levels of 0.45 μm filtered samples collected following stagnation were generally very low,

averaging 0.15 ($\pm$0.1) mg Fe/L. There were no obvious trends in filtered iron with treatment changes (data not shown).

Turbidity

Although total iron release is important, turbidity and color due to suspended ferric iron may better reflect visual appearance and the perceived water quality by consumers. A turbidity baseline was established over the first 20 d of the study. Turbidity values averaged 8.3 ($\pm$2.0) NTU ($\pm$95% confidence interval) and remained relatively consistent over the entire period (Figure 3). Chloride addition of 100 mg/L Cl^- at day 20 caused the turbidity to immediately increase by a factor of 2. The turbidity increased significantly (Table 3) to an average of 16.6 ($\pm$1.3) NTU (Figure 3, Table 2) during the 34 d period when only chloride was added. Turbidity decreased almost immediately after orthophosphate feed started (54 d into study) and appeared to gradually decrease over the first 20 d of the orthophosphate feed (Figure 3, Table 2). The turbidity significantly

Table 3 | Statistical differences between the means of treatment changes

Period	Total iron	Turbidity	Apparent color	NTU/Fe	Color/Fe
Baseline to chloride	Yes	Yes	Yes	Yes	Yes
Chloried to Chloride/PO_4	Yes	Yes	Yes	Yes	Yes
Chloride/PO_4 to chloride	No	No	Yes	No	Yes
Chloride to Nothing	Yes*	Yes	Yes*	Yes	No

Yes–there is a statistically significant difference between the means of the parameters of sequential treatment periods ($P < 0.05$)
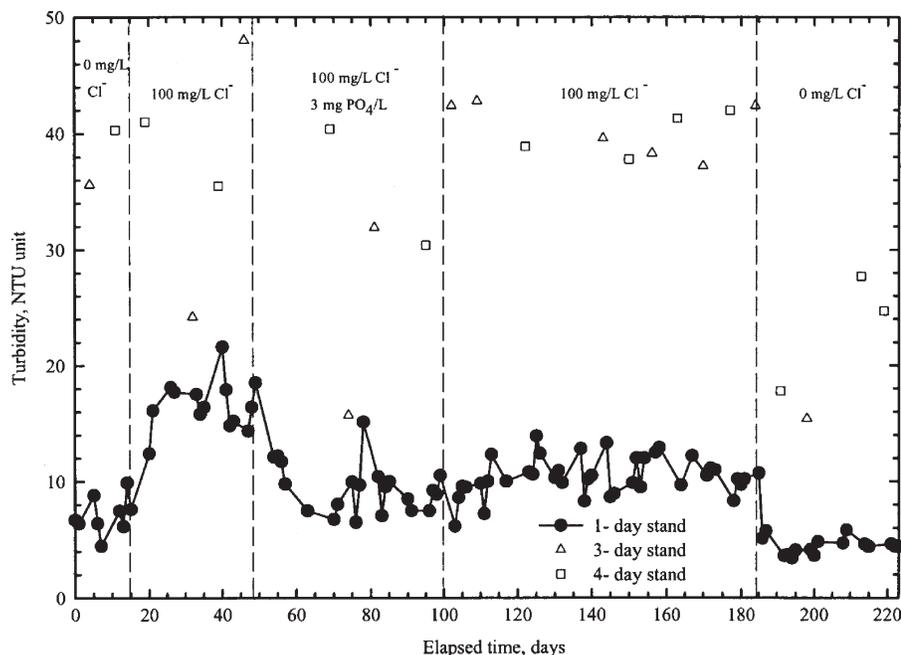*Failed normality test or equal variance test, comparisons run with Mann–Whitney Rank Sum Test

Figure 3 | The effect of chloride and orthophosphate on the turbidity of iron suspensions collected from pipe section.

decreased (Table 3) to an average of 9.4 ($\pm$ 1.0) NTU during this period. Turbidity levels appeared to gradually increase after orthophosphate addition was stopped (99 d) and chloride addition continued, although the means of the two periods were not statistically different (Table 3). The turbidity averaged 10.4 ($\pm$ 0.6) NTU during this time. Turbidity never completely returned to the pre-orthophosphate levels. Turbidity levels dropped almost immediately following chloride feed termination (181 d) and remained relatively constant over the remainder of the study, averaging 4.8 ($\pm$ 0.9) NTU (Table 2).

Changes in turbidity corresponded directly to changes in total iron resulting from water chemistry adjustments. The ratio of turbidity to particulate or ferric iron concentration (total iron minus measured ferrous iron) reflected the effect of water chemistry changes on the properties of the resulting particles and was closely examined in Figure 4. The ratio of turbidity to iron concentration (expressed as NTU/mg Fe/L) during the initial 20 d of the study averaged 4.2 ($\pm$ 0.6) NTU/mg Fe/L (Table 2). The ratio immediately increased significantly (Table 3) to an average of 6.6 ($\pm$ 0.5) NTU/mg Fe/L following the start-up of chloride addition. The ratio decreased slightly following orthophosphate

addition to an average of 5.4 ($\pm$ 0.4) NTU/mg Fe/L (the decrease was statistically significant). The ratio averaged 5.7 ($\pm$ 0.2) NTU/mg Fe/L following orthophosphate termination, which was not a significant change. Finally, the termination of chloride addition after 181 d significantly dropped the ratio average to 4.4 ($\pm$ 0.3) NTU/mg Fe/L. The relationship between particulate iron concentration and turbidity was not linear across the experimental conditions of the study. The results indicate that the particle properties which impact turbidity are affected by water quality. Interestingly, stagnation time had a much greater impact on the ratio. The NTU/mg Fe/L ratio of water collected after 3 and 4 d stagnation periods were typically more than twice the values after 1 d stagnation.

Color

Apparent color (non-filtered color) averaged 116.8 ($\pm$ 17.3) PtCo units (Table 2) and remained relatively constant over the initial 20 d baseline data collection period (Figure 5). The addition of sodium chloride (100 mg/L Cl$^-$) after 20 d caused the color to immediately increase to an average of 171.9 ($\pm$ 12.1) PtCo units (Figure 5) over the 34 d period
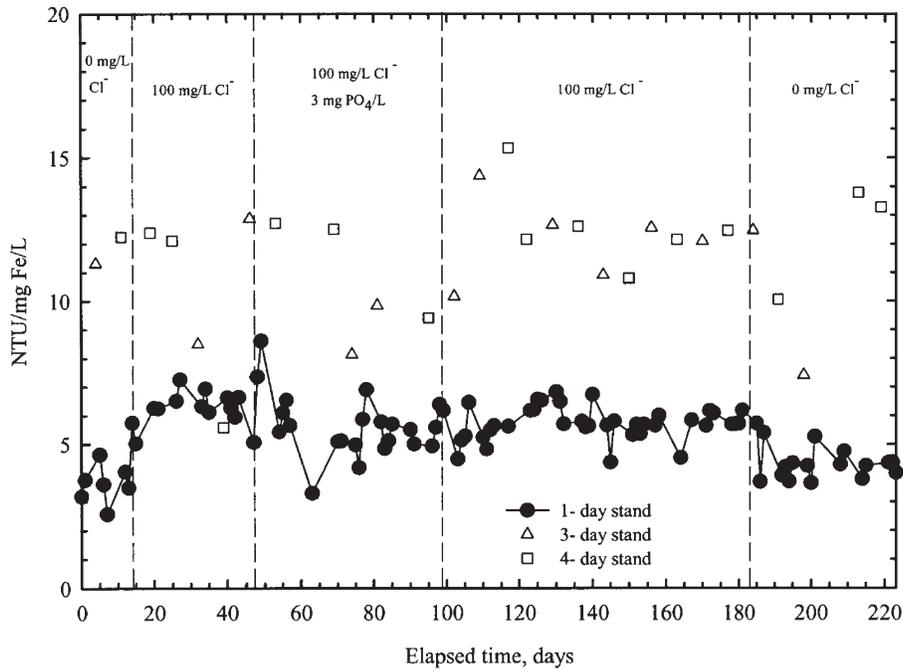
Figure 4 | The effect of chloride and orthophosphate on the relationship between ferric iron and turbidity of iron suspensions collected from iron pipe section.

when only chloride was added. Color decreased almost immediately after the start of the orthophosphate feed (54 d into study) and gradually decreased over the first 20 d of the orthophosphate feed (Figure 5). The color averaged 76.7

($\pm$9.5) PtCo units during the orthophosphate feed period. Color gradually increased after orthophosphate addition was stopped (99 d) and chloride addition was maintained. The color averaged 112.6 ($\pm$8.6) PtCo units during the
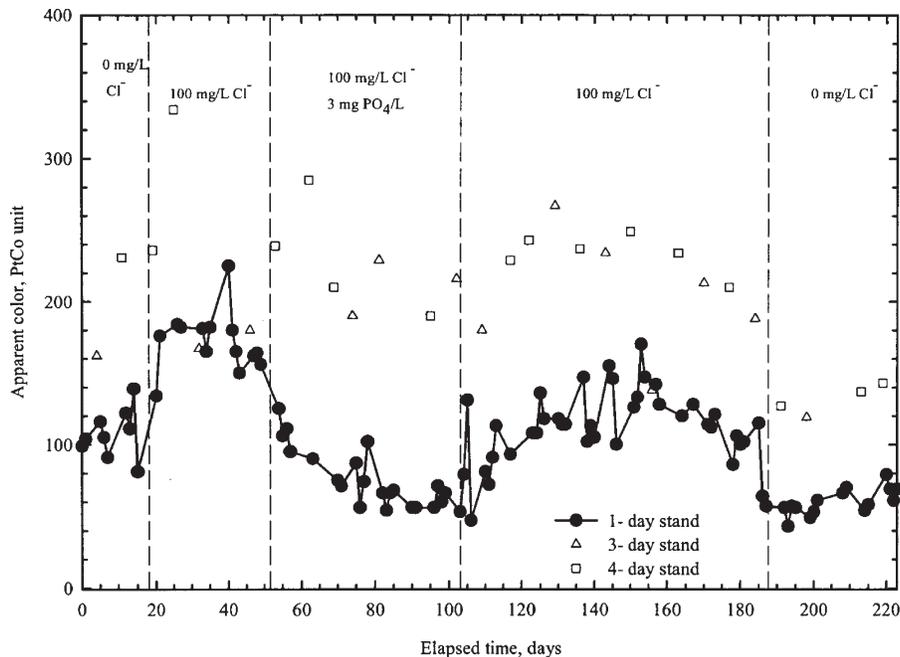

Figure 5 | The effect of chloride and orthophosphate on the apparent color of iron suspensions collected from pipe section.

period and never completely returned to the pre-orthophosphate iron levels. Color dropped almost immediately following the termination of chloride feed (181 d) and remained relatively constant over the remainder of the study averaging 63.2 ($\pm$7.7) PtCo units. All treatment changes resulted in statistically significant changes in color based on comparisons between the means of consecutive groups (Table 3).

Apparent color changes directly reflected changes in total iron. The ratio of color to particulate or ferric iron (total iron minus ferrous iron) shows the effect of water chemistry changes on the aesthetic properties of the resulting particles. The ratio of color to iron (expressed as PtCo units/mg Fe/L) during the initial 20 d of the study averaged 59.8 ($\pm$5.9) PtCo units/mg Fe/L (Figure 6). The ratio immediately increased to 67.8 ($\pm$2.7) PtCo units/mg Fe/L following the start-up of chloride addition. The increase was statistically significant (*t*-test, difference means, 95% confidence). The ratio decreased slightly following orthophosphate addition to an average of 44.0 ($\pm$3.7) PtCo units/mg Fe/L (decrease was statistically significant). The termination of orthophosphate caused a significant rise in the ratio to an average of 61.5 ($\pm$3.7) PtCo

units/mg Fe/L. Finally, following chloride termination, the ratio averaged 57.0 ($\pm$3.2) PtCo units/mg Fe/L and was not a significant change from the preceding period. Like turbidity, the PtCo units/mg Fe/L ratio of water collected after 3 and 4 d stagnation periods were typically more than twice the values after 1 day stagnation.

Loss of ions during stagnation

Calcium, aluminum, sodium, silica and orthophosphate levels in the fill and standing waters were monitored daily starting 65 d into the study. Calcium levels in the fill water ranged from 28 to 45 mg/L, which reflected the natural variability in Ohio River water (the source of Cincinnati tap water) and averaged 33 mg/L (Table 1). Calcium loss to the pipe surface during stagnation ranged from 1 to 14 mg/L (average 5 mg/L). Calcium loss increased as water concentration increased and was not affected by treatment conditions. Calculations of the Langelier Saturation Index (LI + 0.55) and the calcium carbonate precipitation potential (CCPP, 8.6 mg $CaCO_3$/L) showed that the fill water was oversaturated, based on average calcium, pH,
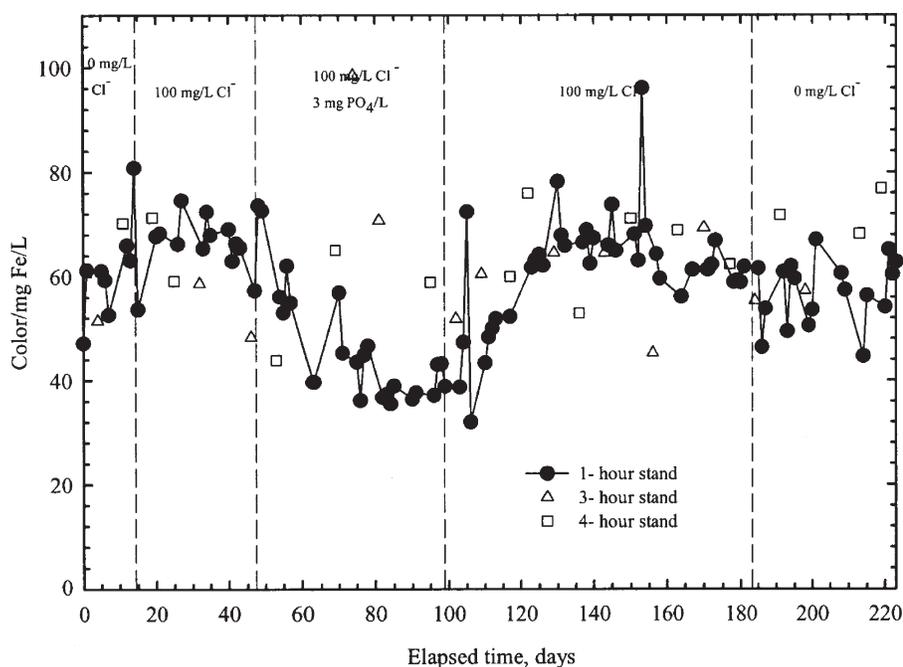

Figure 6 | The effect of chloride and orthophosphate on the relationship between ferric iron and apparent color of iron suspensions collected from iron pipe section.

temperature and historical alkalinity average, with calcium carbonate.

Measurable levels of aluminum were not detected in Cincinnati tap water until day 123, at which time measurable levels of aluminum were regularly detected. Aluminum concentrations averaged approximately 0.07 mg/L (as high as 0.15 mg/L) were consistently measured in the initial water. In every case when aluminum was in the initial tap water, it was all lost to the pipe wall and corrosion deposits (no measurable aluminum was detected) by the end of the stand period.

Sodium levels in the fill water averaged 82 mg/L (Table 1) when sodium chloride was added to the water and 16 mg/L when not added. Sodium loss to the pipe wall during stagnation was not significant at any time during the study.

Silica levels in the fill water averaged 5.2 mg SiO_2/L. Silica levels ranging from 0.5 to 2 mg SiO_2/L were lost to the pipe wall during stagnation. These losses increased as fill water concentration increased and were not related to the treatment condition.

Orthophosphate monitoring began 15 d after initiation of the orthophosphate feed. There was no measurable orthophosphate in the Cincinnati tap water and an average

of 3.2 mg PO_4/L was measured after dosing. An average of 2.0 ($\pm$0.2) mg PO_4/L was lost to the pipe wall and corrosion deposits during stagnation (Figure 7, difference between initial and final, non-filtered phosphate). Nearly all of the remaining orthophosphate (0.92 $\pm$ 0.1 mg PO_4/L) was removed with the suspended iron particles following filtration through a 0.45 μm filter. The molar ratio of Fe/P in the suspended particles averaged 2.8 $\pm$ 0.4. On several occasions after phosphate addition was discontinued, measurable levels of orthophosphate were released from the pipe wall (i.e., higher levels were detected after stagnation than in the fill water). Nearly all of the adsorbed phosphorus remained incorporated in the scale for the remainder of the study.

pH, dissolved oxygen, chlorine and redox potential changes during stagnation

The pH of the initial fill water was constant throughout the study and averaged 8.7 ($\pm$0.1) units. After 24 h of stagnation, the pH dropped by 1.1 units to an average of 7.6 ($\pm$0.3). The addition of chloride and phosphate showed no notable effect on the final pH. The dissolved oxygen
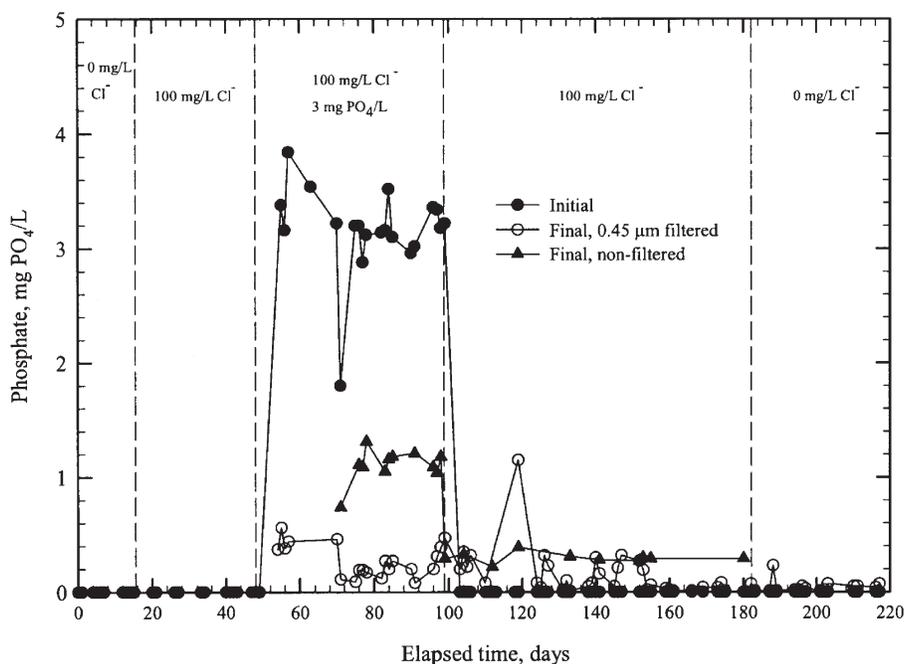

Figure 7 | Comaprison between initial and final (following 24 h stagnation) phosphate concentrations.

concentration of the fill water ranged between 5 and 10 mg O_2/L (average 6.9 [± 2.9] mg/L) and reflected seasonal variability in the source water. Dissolved oxygen levels at the end of 24 h of stagnation were consistently between 2 and 3 mg O_2/L (average 2.4 [± 0.7] mg/L). The final dissolved oxygen concentration was independent of both the initial dissolved oxygen concentration and chloride and phosphate additions. It should be noted, however, that the glass plate cover was not sealed, which allowed oxygen to enter the water and this may have affected the final oxygen concentration. The initial chlorine concentration averaged 0.85 mg Cl_2/L and no measurable chlorine was ever detected after 24 h of stagnation. The redox potential of the initial fill water averaged 562 (± 61) mV over the entire run and the final redox potential averaged 284 (± 98) mV. Again, there were no obvious differences in the final redox potential with treatment change. The oxidant demand is due in part to the oxidation of ferrous iron in the corrosion scale, as reported by others (Baylis, 1926; Benjamin *et al.* 1996; Sarin *et al.* 1999, 2000, 2004). The amounts of oxygen and chlorine needed to oxidize 1 mg Fe(II)/L are 0.14 O_2/L and 0.64 mg Cl_2/L. Given a limited mass of ferrous corrosion scale and the long-term, continual consumption of oxidants, active corrosion of the iron pipe surface below the layers of corrosion deposits must be a major factor. It should be noted that, although the pipe section was covered during stagnation, it was not airtight. As a result, oxygen and CO_2 exchange between the atmosphere and fill water during stagnation was likely and this possibly was the reason that final dissolved oxygen levels and redox potential were independent of treatment. The transfer of CO_2 could also contribute to the pH drop observed during stagnation.

DISCUSSION

Before discussing the experimental study results, several points regarding the experimental approach should be considered. First, the experimental approach used in this study was not intended to necessarily represent conditions present in a drinking water distribution system for a number of reasons. Water flow patterns in drinking water distribution systems vary significantly and somewhat unpredictably, and

regular long water stagnation (24 h) periods are not normal (i.e. water flows in the distribution system whereas the experimental flow design is stagnant and in a batch mode). Drinking water distribution system pipes are positioned horizontally rather than vertically, are under pressure and are not exposed to the atmosphere. The levels of chloride and phosphate examined in this study are possible but extreme. Given the time frame over which corrosion and iron release reactions take place, the range of variable concentrations had to be limited to extremes so the likelihood of any effects would be greatest. The experimental system used in this study was designed to reduce variables and produce measurable changes, by which the effect of water chemistry on iron release could be systematically evaluated. The test water (City of Cincinnati tap water) quality however, is seasonably variable. Changes in important source water quality parameters (e.g. sulfur, chloride, alkalinity, temperature, etc.) were closely monitored and compared to experimental trends to ensure that natural water quality variability was not responsible for observed effects. Given that the pipe was exposed to Cincinnati tap water for over 90 years, the impacts of using any exposure water other than Cincinnati tap water (e.g. controlled synthetically prepared water) on the pipe scale and results would be considered highly likely and detrimental. Therefore using an alternative test exposure water was not an acceptable alternative. Finally, the results of this study exclude the role of microorganisms. Microbial activity could potentially play an important role in this work but, given their complexity, beyond the scope of this project and expertise of the investigators. The study findings will be useful to qualitatively predict how full scale distribution systems will likely respond to similar water quality changes and will also validate and enhance iron release models. The work may also serve as the foundation for future research in this area.

Iron corrosion scale and iron release models (Benjamin *et al.* 1996; Sarin *et al.* 1999, 2000, 2004) give a basis for explaining the observed behavior. These models are based on the common observation that most iron corrosion scales consist of three structural regions: a porous interior, a dense shell-like layer and an outer layer. The porous interior region serves as a reservoir for Fe^{2+} ions that are produced from the corrosion of the base iron metal, dissolution of ferrous iron phases and reduction of ferric iron phases.

The porous interior also concentrates anions such as chloride and sulfate in order to maintain the basic requirement for electroneutrality. The shell-like layer (there may be multiple shell-like layers) consists primarily of a thin band of magnetite and goethite. Scales with thick and dense shell-like layers are considered to be more protective against corrosion and iron release. A thin outer layer containing primarily goethite covers the shell-like layer and is directly in contact with the bulk water. Using the simple iron corrosion scale structure description provided above, the observed effects of orthophosphate and chloride can be explained as follows.

Chloride is a relatively small anion and would likely readily diffuse through porous iron corrosion scales, particularly the shell-like layer. Therefore, increasing the chloride concentration in the bulk water will increase the rate of chloride diffusion to the porous interior region. The hydrolysis of Fe^{2+} ions in the pit decreases the aqueous solution pH. The increase in hydrogen ion concentration will attract chloride as well as other anions to the region so electroneutrality requirements can be maintained. The acidic/chloride pore solution accelerates the anodic dissolution of Fe^{2+} during the corrosion of the pipe wall, which attracts even more chloride to the pit. The acidic pore water will also increase the solubility of iron corrosion deposits and the concentration of chloride may also enhance the formation of iron-chloride compounds such as green rust ($[Fe_3^{II}Fe^{III}(OH)_8]^+ \cdot [Cl \cdot nH_2O]^-$). An increase in ferrous iron in the porous interior of the scale will drive the diffusion of iron away from the pipe surface into the bulk water, resulting in increased iron release. The build-up of ions in the scale pore water may also create a pressure build-up within the scale which can eventually lead to a break in the scale (Baylis 1926). An additional possible role of chloride is that it decreases the oxygenation rate of ferrous iron (Tamura *et al.* 1976; Sung & Morgan 1980; Millero 1985). A slower oxidation rate will allow Fe^{2+} to persist longer and extend its concentration gradient across the scale. The effect of a change in chloride concentration on iron release both at the start-up and termination of the chloride feed was immediately observed, which suggests that chloride has little effect on the scale structure. Processes that affect scale structure (density, dissolution, etc.) are slower.

Orthophosphate was very effective in reducing iron release and was incorporated into the iron corrosion scale in some way. The adsorption of orthophosphate onto the surface of iron minerals is well known (Hsu 1973, 1976; Atkinson *et al.* 1974; Parfitt *et al.* 1975; Sposito 1984; Von Gunten & Schneider 1991; Stumm & Sulzberger 1992; Yamaguchi *et al.* 1996) and could be important in this work. Phosphate surface groups have been shown to inhibit EDTA-promoted dissolution and reduction dissolution of iron (hydr)oxides (Bondietti *et al.* 1993; Biber *et al.* 1994). Dissolution of iron (hydr)oxides can be a significant factor on iron release (Sarin *et al.* 1999, 2000, 2004). An alternative possibility is that the addition of phosphate caused the precipitation of iron phosphate solids within the corrosion scale layers. The precipitation and dissolution of iron phosphate minerals are important in controlling the mobility of phosphate in aquatic ecosystems (Nriagu 1972, 1974; Gshwend & Reynolds 1986; Odum 1988; Buffle *et al.* 1989; Chambers & Odum 1990; Seamon *et al.* 1997). Vivianite has been found in drinking water distribution system iron pipe scales (Benjamin *et al.* 1996), although its role in reducing iron release, if any, is not known. The formation of iron phosphate solids in the corrosion scales could reduce iron release by reducing the solubility of ferrous iron and/or decreasing the permeability of the scales. Due to the fact that the experimental pipe section is still in use, detailed scale analysis could not be conducted to better understand the role of phosphate.

Orthophosphate also affected color and turbidity of iron suspensions and the properties of suspended particles based on changes in the ratios of color/Fe and NTU/Fe. Previous benchscale work on iron particles in water (Lytle & Snoeyink 2003) showed that the ratios of color/Fe and NTU/Fe were independent of iron concentration for a given water. The ratios changed when the properties of the particles (e.g. size, shape, crystallinity, etc.) and light scattering and absorption properties changed in response to a water quality change. For example, increasing the pH and dissolved inorganic carbon concentration increased the color and turbidity of 5 mg Fe/L suspensions (Lytle & Snoeyink 2003). Phosphate was incorporated into the suspended particles collected in this study. The effects of orthophosphate on color and turbidity observed in this study were in agreement with the findings of Lytle &

Snoeyink (2002). Turbidity reduction per unit of iron was attributed to a decrease in particle size and changes in particle density and shape. Color reduction was a direct result of a shift in light absorption characteristics due to the presence of phosphate–iron bonds at the particle surface. Iron particle size did not change as a result of orthophosphate addition in this study, based upon comparisons of filtered 0.45 and 0.2 μm samples (data not shown). This suggests that other properties, such as shape and density changes, were responsible for turbidity differences.

The impact of chloride on the suspension color and turbidity was also significant. The effect of chloride on the properties of iron particles and suspensions had not been previously reported. Loss of chloride to the pipe wall, corrosion deposits during stagnation and incorporation of chloride into suspended iron particles were not determined during this study. Therefore it can only be speculated that chloride impacted color, turbidity and the particle properties by similar mechanisms as phosphate.

CONCLUSION

The results of this study showed how chloride and orthophosphate affected the release of iron from a corroded cast-iron pipe section and presented their effects upon the color and turbidity of the resulting suspensions. Experiments revealed that an increase in chloride concentration of 100 mg/L significantly increased the concentration of iron released from the pipe section, while the presence of orthophosphate at 3 mg/L reduced the iron release. Chloride increased and orthophosphate decreased the water color and turbidity caused by the release of iron, but there was not a linear relationship with respect to the concentration of iron released.

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