

ORIGINAL RESEARCH

Full-scale demonstration testing of hexavalent chromium reduction via stannous chloride application

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The best available technologies for hexavalent chromium [Cr(VI)] treatment can be cost prohibitive and operationally complex. Direct stannous [Sn(II)] chloride application to reduce Cr(VI) to trivalent chromium is an alternative treatment approach that could substantially decrease treatment costs. A full-scale demonstration was conducted at the Coachella Valley Water District to investigate the ability of Sn(II) to reduce Cr(VI) in a chlorinated groundwater system. An average Sn(II) dose of 0.5 mg-Sn/L, which corresponds to ~7.3 times the stoichiometric dose ratio for Cr(VI) reduction, was able to maintain Cr(VI) at <10 µg/L throughout the distribution system over a 30-day period. Tin (Sn) and chromium (Cr) concentrations decreased with increasing distance from stannous feed locations, suggesting accumulation in the distribution system. Distribution system pipe-scale analysis after the demonstration found the presence of Sn and Cr in pipe scales; however, minimal Sn and Cr release was observed during main flushing at the end of the demonstration.

KEY WORDS

chlorine reoxidation, energy-dispersive X-ray spectroscopy, scale analysis, scanning electron microscopy, tubercle

1 | INTRODUCTION

Hexavalent chromium [Cr(VI)] is generated from both naturally occurring and anthropogenic sources (Chebeir, Chen, & Liu, 2016; Chebeir & Liu, 2016, 2018; Gonzalez, Ndung'u, & Flegal, 2005; McKinley, Pratt, & McPhillips, 1992). Cr(VI) is an unregulated contaminant, with several treatability, mode-of-action, and risk assessment studies conducted over the course of the last two decades to assess the public health risk of Cr(VI) exposure via drinking water; these were summarized in a recent Journal AWWA article (Moffat, Martinova, Seidel, & Thompson, 2018). In April 2014, the California State Water Resource Control Board (SWRCB) Division of Drinking Water (DDW) issued a final maximum contaminant level (MCL) for Cr(VI) at 10 µg/L (California Department of Public Health [CDPH], 2014a).

This Cr(VI) standard was substantially lower than the federal and California total chromium (Cr) MCLs of 100 and 50 µg/L, respectively. Senate Bill No. 385 (SB-385), signed by Governor Brown in September 2015, provided water agencies the ability to satisfy the regulation while implementing compliance plans at the earliest feasible date no later than January 1, 2020 (SB-385, 2015).

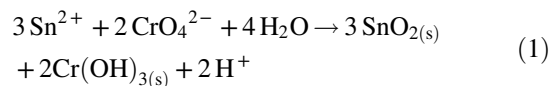
On May 31, 2017, the Superior Court of California, County of Sacramento, issued a Peremptory Writ of Mandate to the California SWRCB for withdrawal of the 10 µg/L Cr(VI) MCL and establishment of a new MCL. This is a result of the *California Manufacturers and Technology Association and Solano County Taxpayers Association v. State Water Resources Control Board* (2017) ruling, which determined that the Water Board failed to demonstrate Cr(VI) compliance as economically feasible. On September

11, 2017, the Cr(VI) MCL was officially withdrawn, and only the total Cr MCL of 50 µg/L is currently in effect (SWRCB, 2017). While no Cr(VI) MCL is in effect in California, the California Office of Environmental Health Hazard Assessment maintains the Cr(VI) public health goal of 0.02 µg/L (2011), and the SWRCB is currently proceeding with the establishment of a new Cr(VI) MCL. As such, advances in Cr(VI) treatment alternatives could impact utilities' ability and costs to comply with future Cr(VI) regulations.

Best available technologies for Cr(VI) treatment include strong-base anion exchange (SBA-IX), weak-base anion exchange (WBA-IX), reduction coagulation filtration (RCF), and reverse osmosis (RO) (CDPH, 2014b). These Cr(VI) treatment alternatives can result in significant capital and operational costs and are operationally complex, requiring residual waste management for SBA-IX and RO (Plummer et al., 2018), on-site sewer access for backwash discharge for RCF, and pH adjustment for WBA-IX (Blute, Wu, Visosky, & DeWolfe, 2012; Brandhuber et al., 2004; Najm et al., 2014; Seidel, Najm, Blute, Corwin, & Wu, 2013). Direct application of stannous chloride (SnCl₂) for Cr(VI) reduction to trivalent chromium [Cr(III)] is a treatment alternative that could substantially decrease capital and O&M costs, as well as waste residuals, relative to most other Cr(VI) treatment technologies (e.g., SBA-IX) (Plummer et al., 2018).

1.1 | SnCl₂ overview

Stannous chloride is a reducing agent that has been used in only a few drinking water distribution systems as a corrosion inhibitor (Hozalski, Tan, & Chen, 2005; Hozalski, Tan, & Dai, 2010). Although the use of SnCl₂ at full scale is limited, it has achieved NSF/ANSI 60 certification from Underwriters Laboratories. Stannous [Sn(II)] is one of the two main oxidation states of tin (Sn), along with stannic [Sn(IV)]. There is no current federal or state MCL for Sn. Acting as an electron donor, SnCl₂ reduces Cr(VI) to Cr(III), which is regulated under the California total Cr MCL of 50 µg/L. The stoichiometric equation for Cr(VI) reduction by SnCl₂ is given in Equation (1) (Brandhuber et al., 2004):



Previous bench-scale research conducted on Cr(VI) reduction in drinking water in Glendale, California, demonstrated complete SnCl₂ reduction of Cr(VI) in Glendale water within the first measurement at 30 min. The studies conducted on Cr(VI)-spiked distilled water and Glendale water concluded that SnCl₂ is a more effective reductant compared with sulfides and sulfites (Brandhuber et al.,

2004; Lai & McNeill, 2006). The investigation of stannous-reduced Cr(III) reoxidation in Glendale water resulted in 25–40% reoxidation by chloramine for doses between 0.5 and 10 mg/L of total chlorine. No testing of stannous-reduced Cr(III) reoxidation in chlorinated water was conducted (Brandhuber et al., 2004).

More recent bench testing of Cr(VI) reduction via SnCl₂ demonstrated complete Cr(VI) reduction within the first sample time of 10 min. In the presence of 1 mg/L chlorine residual, only 1 µg/L (6%) Cr reoxidation occurred over the 5-day sampling period (Gorman et al., 2017). Additional bench testing of Cr(VI) reduction via stannous application for three waters also demonstrated complete reduction of Cr(VI) by the first measurement at 6 min and partial reoxidation to Cr(VI) in the presence of chlorine (Kennedy, Korak, Flint, Hoffman, & Arias-Paic, 2018).

Pilot testing of RCF with stannous as an alternative reductant, in lieu of ferrous, resulted in complete Cr removal and extended filter run time, with stannous resulting in more than double the unit filter run volume than that of ferrous (Gorman, Plummer, Samson, Townsend, & Seidel, 2019). Stannous pilot testing conducted by Kennedy et al. (2018) on Cr(VI)-reduced waters also demonstrated Cr removal with sand filtration, although little or no Cr removal occurred with depth or pleated cartridge filtration. Kennedy et al. (2018) used a stannous stock solution made from reagent-grade SnCl₂ with diluted deionized water that resulted in a pH of ~2, which is in the pH range where stannic hydroxide can form and precipitate out of solution (Al-Hinai, Al-Hinai, & Dutta, 2014). Throughout their testing, stability issues were observed, and the diluted stock was regularly remade because, as the stock age increased, its Cr(VI) reduction potential decreased, it gained a yellow color, and turbidity increased, indicating that Sn(II) was oxidized in air-saturated water and precipitated out of solution.

1.2 | Water system background

The Coachella Valley Water District (CVWD), located in Riverside County, California, is the largest provider of drinking water in the Coachella Valley. Of its more than 100 wells, CVWD has over 30 wells that required treatment to comply with the remanded Cr(VI) MCL. In July 2016, when the remanded Cr(VI) MCL was still in effect, the CVWD Board of Directors approved entering into a \$250 million agreement for the construction of SBA-IX treatment facilities at 29 drinking water wells throughout the service area, as well as construction of a Central Resin Regeneration Facility and pipelines to support these treatment facilities.

In October 2016, before construction of treatment facilities started, preliminary bench tests performed at CVWD's water quality laboratory demonstrated that stannous was

effective in reducing Cr(VI) concentrations below the 10 µg/L withdrawn Cr(VI) MCL, had the potential to provide a more simple treatment alternative at the wellhead, and would have less impact on the community. As a result, the CVWD Board of Directors temporarily stopped construction of Cr(VI) treatment facilities and approved launching a bench-scale and full-scale demonstration study to evaluate the feasibility and effectiveness of direct SnCl₂ application at representative CVWD wells (CVWD, 2018).

2 | BENCH TESTING APPROACH

Bench testing of Cr(VI) reduction via stannous and investigation of Cr(VI) reoxidation potential in chlorinated water were conducted at CVWD's state-certified water quality laboratory; 1-L amber glass bottles containing raw Well 3408 water, detailed subsequently, were dosed using a 5% stannous stock solution (PAS-8105; Guard Products Inc., Pleasanton, CA) with 0.1, 0.3, and 0.6 mg-Sn/L corresponding to 1.5, 4.4, and 8.8 times the stoichiometric dose ratio, respectively, to reduce Cr(VI). Sn was dosed directly to raw well water from the 5% stannous stock solutions, which is composed of 4% HCl (pH < 1), to prevent Sn oxidation and precipitation (Al-Hinai et al., 2014; Kennedy et al., 2018). After dosing with SnCl₂, each bottle was mixed using a stir plate for 10–15 s at 270 rpm, followed immediately by chlorine addition ranging from 0 to 1.5 mg/L. Bottles were stored in the dark at room temperature between sampling events. Cr(VI), turbidity, total Cr, and total Sn samples were collected at 1, 6, 24, 48, 96, and 360 h (15 days) and analyzed using standard methods, detailed subsequently. The total Sn method is used to analyze for all Sn oxidation states, including Sn(II) and Sn(IV).

3 | MATERIALS AND METHODS

3.1 | Full-scale demonstration approach

CVWD owns and operates an isolated distribution system, identified as Improvement District No. 8 (ID-8), which

comprises four wells that serve a population of 4,200. All four wells have Cr(VI) concentrations over the previous 10 µg/L MCL, with water quality and site constraints making treatment cost prohibitive for approaches such as SBA-IX, WBA-IX, and RCF. Historical Cr(VI) concentrations and production data for the ID-8 wells are listed in Table 1. Raw Cr(VI) concentrations range between 11 and 24 µg/L for all four wells.

The ID-8 distribution system map, showing where the water main (predominantly 8–18 in. in diameter) exists along Dillon Road and noting the demonstration sampling locations, is given in Figure 1. Hydraulic modeling in the distribution system estimated the maximal water age in the system to be approximately 10 days, assuming 50% turnover in the tanks. Throughout the duration of the full-scale demonstration, Well 3405 was not operated and, as a result, is not shown in Figure 1. As the ID-8 system is small, isolated, and semilinear with respect to piping and the distribution system, and contains wells of similar water quality, it was selected for full-scale demonstration.

3.2 | Testing and water quality objectives

The primary objectives of the full-scale demonstration are to validate the bench test results and determine: (a) the extent to which Cr(VI) is reduced to Cr(III) by stannous and (b) the extent of Cr(III) reoxidation once chlorine is applied. Previous Cr(VI) regulation set the compliance monitoring location for the MCL at the point of entry (POE) to the distribution system; as such, several water quality goals were identified to be achieved at the POE(s): Cr(VI) ≤ 10 µg/L on the basis of the withdrawn MCL; total Cr and turbidity below California's 50 µg/L MCL and 5 ntu secondary MCL, respectively; and total Sn ≤ 0.63 mg-Sn/L on the basis of the NSF 60 maximum use level.

In addition to evaluating the similitude of the full-scale demonstration to bench test results, the demonstration was also a proactive investigation to evaluate water quality conditions within the distribution system, such as Cr(III) reoxidation and the fate of Sn and Cr. These accompanying

TABLE 1 Summary of ID-8 system well production, Cr(VI) concentrations, and total Cr concentrations (2012–2017)

Well ID	Design capacity (gpm)	Pump test capacity (gpm)	Utilization (%)	Cr(VI) range (µg/L)	Cr(VI) average (µg/L)	Total Cr range (µg/L)	Total Cr average (µg/L)
3405	1,500	940	52	11–14 (9)	13	12–14 (3)	13
3408	1,500	1,493	43	19–20 (10)	20	18–21 (8)	19
3409	1,500	1,860	26	15–24 (5)	21	21–23 (2)	22
3410	2,000	1,975	32	14–16 (5)	15	n/a (1) ^a	16

Note. Values in parentheses in the range columns indicate the number of samples.

Abbreviations: Cr(VI), hexavalent chromium; ID-8, Improvement District No. 8.

^aSingle sample.

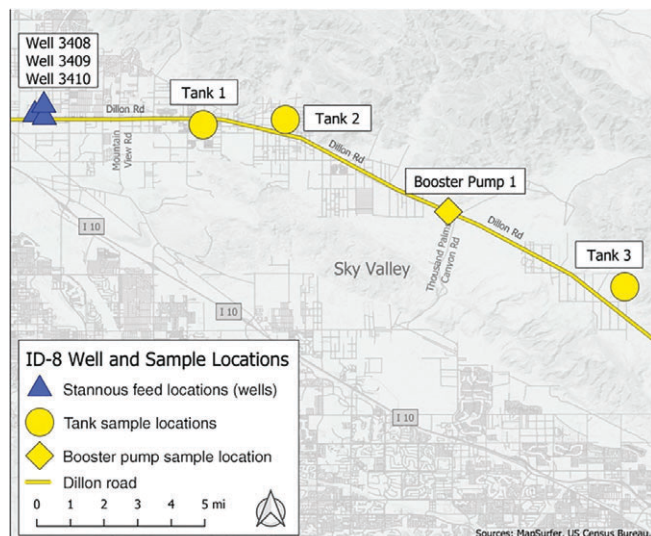


FIGURE 1 ID-8 distribution system map. Abbreviation: ID-8, Improvement District No. 8

objectives were part of a cursory evaluation of distribution system interactions during short-term direct SnCl_2 application for Cr(VI) treatment.

3.3 | Stannous application

On the basis of the results of bench testing, detailed subsequently, an applied stannous dose of 0.5 mg-Sn/L, corresponding to approximately 7.3 times the stoichiometric dose ratio needed to reduce Cr(VI) , was targeted using a 50% SnCl_2 solution, which is >4% HCl and has a pH <1 (PAS-8150, Guard Products Inc.). For the duration of the 10-week demonstration, stannous was applied directly via metering pumps (Grundfos DDA Metering Pump) at Wells 3408, 3409, and 3410. No static mixers or reaction time pipelines or vessels were used. Because of stability challenges encountered with diluted stannous stock solution in previous research (Gorman et al., 2019; Kennedy et al., 2018), the dilution of the stock solution was not conducted to prevent stannous oxidation to stannic in the presence of oxygen.

3.4 | Sample locations

As noted previously, Wells 3408, 3409, and 3410 were operated during the demonstration period. Residence time after Sn addition and before chlorine addition was about 4 s. The POE sample point locations were approximately 5–20 ft. downstream of the chlorine addition point, with water velocities in the manifold of approximately 5–20 fps. Chlorine was dosed to achieve detectable chlorine residuals throughout the distribution system: average system levels of 0.3 mg/L were targeted, with elevated levels close to

1.0 mg/L used at times in the distribution system. The sample location points were before the hydropneumatic tanks at Wells 3409 and 3410, with no hydropneumatic tank at Well 3408.

Additional locations were also selected to monitor water quality throughout the distribution system, including Cr(VI) , Cr, total metals, total Sn, color turbidity, chlorine residual, pH, and temperature. A summary of all sample locations is given in Table 2. Tanks 2 and 3 have the highest residence times. Daily exercising of the tanks with a 50% turnover target began on December 21, 2017. ID-8 hydraulic modeling results concluded a 10-day maximum residence time at Tank 3.

3.5 | Sample collection and analysis

Total Cr, total Sn, Cr(VI) , chlorine residual, temperature, and pH samples were collected thrice a week for the duration of the demonstration, with turbidity and heterotrophic plate count (HPC) samples collected on a weekly basis. Chlorine residual, temperature, and pH samples were measured in the field, with total Cr, Sn, Cr(VI) , HPC, and turbidity samples analyzed in-house at CVWD's water quality laboratory. All other analytical samples were analyzed by a third-party certified laboratory. All analytes were sampled and analyzed according to U.S. Environmental Protection Agency (USEPA)-approved methods (USEPA Method 218.7 for Cr(VI) and USEPA Method 200.8 for total Cr, SM 2130B for turbidity, SM 4500- H^+B for pH, and SM 9215B for HPC, 1994). USEPA Method 200.7 was modified for Sn analysis. Method 200.7 calls for acid preservation of samples at pH < 2. Further investigation on Sn speciation indicates that, unlike most metals, Sn is not acid soluble at pH 2 but base soluble under most oxidative conditions (Al-Hinai et al., 2014). Acid preservation per USEPA Method 200.7 could result in Sn precipitation in the sample bottle and less total Sn recovery during analysis. To validate base preservation of Sn samples, a comparison of measured Sn concentrations with base versus acid preservation of samples was conducted. Method detection limits for total Cr, Cr(VI) , and Sn were 0.5 $\mu\text{g/L}$, 0.05 $\mu\text{g/L}$, and 0.01 mg/L, respectively. It should also be noted that acid digestion was not performed on Sn samples as the turbidity was low (<1 ntu), and they were directly injected at the pH used during their preservation. All Sn samples were for total Sn, except the flushing experiment discussed in the following section.

3.6 | Flushing experiment

Additional sampling during two flushing events was carried out at a hydrant located near Tank 2. The flushing events before stannous addition (pre-stannous) and during addition (stannous feed) were conducted to determine the potential for accumulation of Sn, Cr, and iron within the distribution

TABLE 2 ID-8 sample locations and naming convention

Location I.D.	Sample I.D.	Description
Downstream of chemical injection at Wells 3408, 3409, and 3410	Avg. weighted wells	Dose and reoxidation sampling, anticipated compliance points
Storage tank 3501	Tank 1	First of a series of storage tanks. Evaluate potential for reoxidation to Cr(VI) or precipitation of Cr(III)
Booster pump 3603	Booster pump 1	Single 8" transmission main on Dillion Road. Representative of water entering the southwest portion of the system
Storage tank 4711	Tank 2	Terminal tank in the distribution system
Storage tank 3602	Tank 3	Representative of maximum residence time. Evaluate potential for reoxidation to Cr(VI) or precipitation of Cr(III)

Abbreviations: Cr(III), trivalent chromium; Cr(VI), hexavalent chromium; ID-8, Improvement District No. 8.

system. The flushing experiments were performed on November 29, 2017, and January 30, 2018, with five samples collected per flush event. Flushing velocity was not targeted, and the velocity was not measured. CVWD performed this flush following its standard procedure. One-gallon cubitainers were used to collect samples continuously throughout the 10-min flushes. For the November 2017 flush, flow from the hydrant was directed through a pilot unit for cartridge filtration: unfiltered, 0.35 μm -filtered (Harmsco HC/40 0.35 μm pleated cartridge filter), and 1- μm -filtered (Harmsco HC/40 1 μm pleated cartridge filter) samples were collected from the unit. Between flush events, the pilot unit used for the November flush became inaccessible, and flush samples from January 2018 were manually filtered with 0.45- μm (Millipore Express PLUS Membrane Filter 0.45 μm , 90 mm) and 1- μm (Millipore White PTFE Fluoropore Hydrophobic Membrane Filter 1 μm , 90 mm) filters on site using a vacuum filtration apparatus.

3.7 | Main pipeline analysis

A pipe section was retrieved from the ID-8 system upstream of Booster Pump 1 after the 10-week stannous application. The inner wall of the pipe section has corrosion products accumulated as tubercles. Three corrosion scale samples were collected from the tubercle outer layer, and one sample was collected from the tubercle inner layer. The three outer-layer samples showed distinct coloration: red–brown, white, and black,

and black indicating iron-rich, calcium-rich, and manganese-rich sites, respectively, as shown in Figure 2. To quantify background metal concentrations because of pipe corrosion, additional experiments were conducted by electrochemically corroding a fresh pipe surface using an electrochemical station (Pine Instrument Inc., Durham, NC). Specifically, two 3" $\times$ 3" plates of the pipe were cut and sanded until the fresh metal surface was exposed on all sides. The two plates were submerged in treated groundwater collected from the ID-8 system and connected as anode and cathode. A constant current of 500 mA was applied for 12 h, which is equivalent to 5 years of natural corrosion under electrochemical conditions typically found in drinking water distribution systems to generate corrosion products representative of a distribution system not exposed to Sn treatment, but it does not account for microbial or hydraulic influences (Smart, Blackwood, & Werme, 2001).

Corrosion scale samples collected from both the distribution system and the corroded fresh metal plate were ground to homogeneity and sieved through a 95- μm sieve. Samples were digested using USEPA method 3050B acid digestion and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for total metals (USEPA, 1996). A 97% Sn recovery rate with this method was validated using Sn spike tests. Remaining solid samples were analyzed with a scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) for crystal structure and elemental composition, respectively.

FIGURE 2 Pipe inner-wall samples collected post-Sn addition showing all three different collected samples: red–brown, white, and black.

Abbreviation: Sn, tin



4 | BENCH TESTING RESULTS

Time series graphs of Cr(VI) concentrations as a function of stannous dose and target chlorine dose are provided in Figure 3, and free chlorine concentrations measured in the same samples are shown in the Supplementary Information Figure S1. The source water Cr(VI) concentration was 20 µg/L. Total Cr concentrations remained stable over the range of Sn and chlorine doses tested as the average concentrations were 21 µg/L, and the standard deviation was 3 µg/L. Before chlorine addition (time = 0 min), all stannous doses tested resulted in Cr(VI) concentrations <10 µg/L, with doses ≥ 0.3 mg-Sn/L yielding Cr(VI) concentrations <2 µg/L. After chlorine addition, reoxidation of Cr(III) to Cr(VI) was observed primarily within the first 4 h. Reoxidation tests performed previously with Cr(III) chloride in deionized water containing salts showed that reoxidation reactions were complete within approximately 20 h (Brandhuber, McNeill, McLean, Rogers, & Bukhari, 2017). However, in a natural

water containing dissolved organic matter (DOM), Cr(III) reoxidation rates were more similar to what was observed here as reoxidation was complete within a few hours. Reoxidation occurred faster in the natural water possibly because there was little dissolved Cr(III) that could be reoxidized as most of the Cr(III) either precipitated out of solution or may have complexed with DOM (Brandhuber et al., 2017).

For both a 0.3 and 1.5 mg/L target chlorine dose, stannous doses ≥ 0.3 mg-Sn/L maintained Cr(VI) below the withdrawn 10 µg/L MCL for the duration of the 15-day test period. At a lower stannous dose of 0.1 mg-Sn/L, Cr(VI) was above the previous Cr(VI) MCL of 10 µg/L after 4 h. As shown in Figure 4a, there is a correlation between the extent of Cr reoxidation and stannous dose. At a 0.6 mg-Sn/L stannous dose, minimal reoxidation occurs with Cr(VI) concentrations <5 µg/L, despite an average raw Cr(VI) concentration of 20 µg/L and a target chlorine dose up to 1.5 mg/L. Figure 4b indicates that the degree of reoxidation is insensitive to target chlorine dose in the range

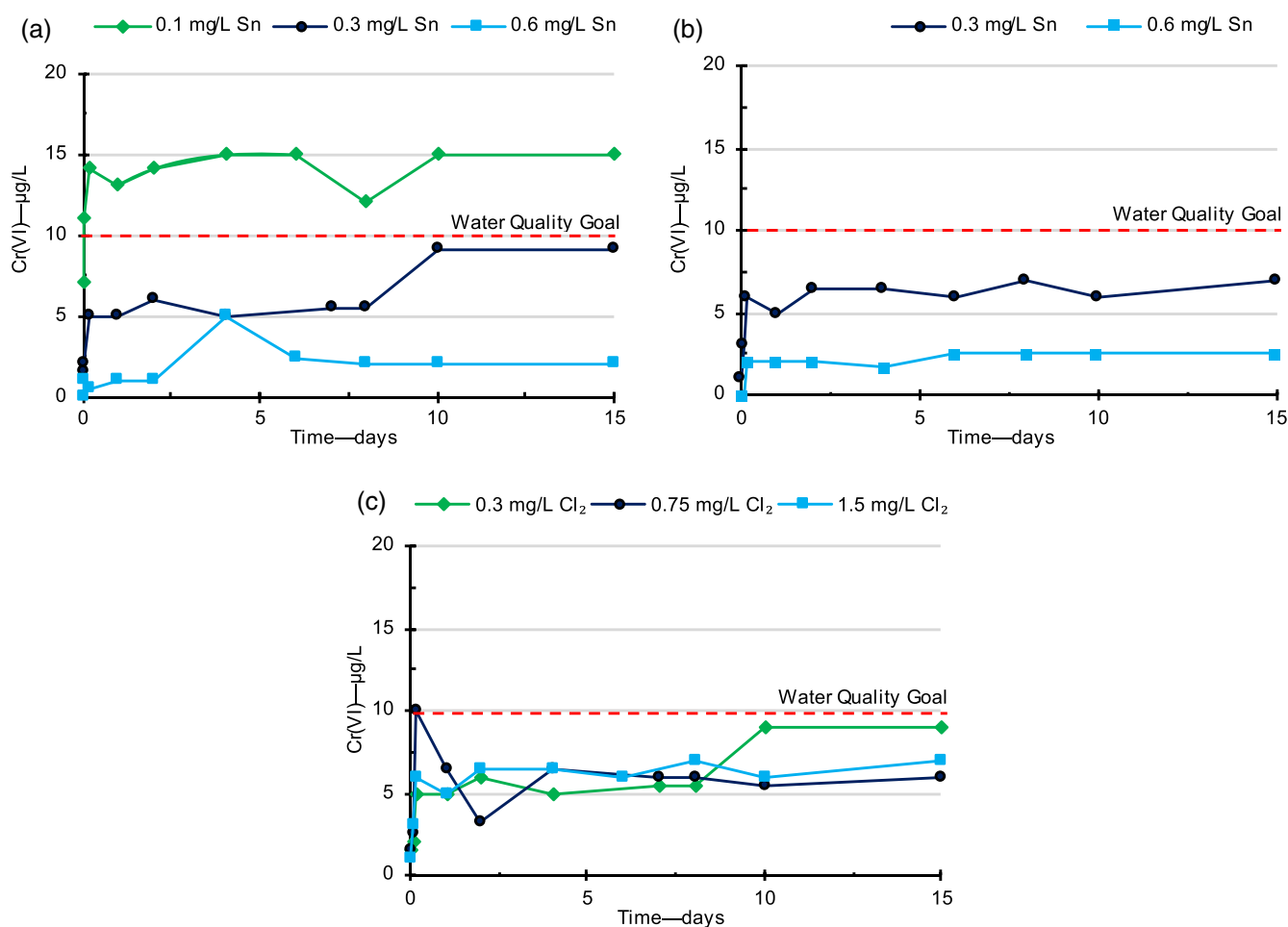


FIGURE 3 Cr(VI) reduction and reoxidation over time during bench-scale tests. (a) 0.3 mg/L target chlorine residual. (b) 1.5 mg/L target chlorine residual. (c) 0.3 mg/L target Sn dose. Abbreviations: Cl₂, chlorine; Cr(VI), hexavalent chromium; MCL, maximum contaminant level; Sn, tin

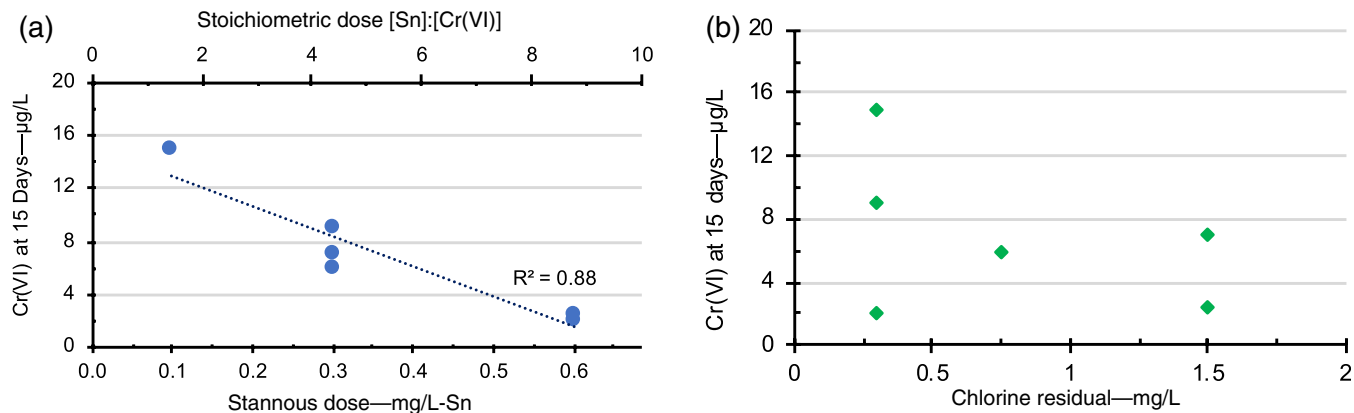


FIGURE 4 Impact of stannous and chlorine dosing on Cr(VI) reduction and reoxidation. (a) Cr(VI) as a function of Sn dose and stoichiometric dose. (b) Cr(VI) as a function of chlorine residual. Abbreviations: Cr(VI), hexavalent chromium; MCL, maximum contaminant level; Sn, tin

of doses applied. Brandhuber et al. (2017) showed that only soluble Cr(III) can be oxidized by chlorine at doses up to 4 mg/L. Thus, higher Sn doses may not only reduce more Cr(VI) to Cr(III) but also decrease soluble Cr(III) by either causing it to precipitate as $\text{Cr}(\text{OH})_{3(s)}$ or by forming stannic solids that incorporate Cr(III) and shield it from reoxidation. The filtration of distribution system water collected after flushing tests described under Section 3.6 showed that most of the Sn and Cr(III) were removed by a 0.45-µm filter, indicating that Sn particulates formed that may have associated with Cr(III). Therefore, direct stannous application for Cr(VI) reduction could be viable for both chlorinated and unchlorinated systems, but Sn doses >1.5 times the stoichiometric dose ratio for Cr(VI) reduction should be used to limit Cr(III) reoxidation in the presence of chlorine. However, the effect of a higher chlorine dose associated with, for example, a “superchlorination” event was not evaluated, and the effect on Cr(III) reoxidation is unknown.

5 | FULL-SCALE DEMONSTRATION RESULTS

5.1 | Base preservation of Sn samples

A comparison of base- versus acid-preserved Sn samples was conducted before beginning the full-scale demonstration. Four stannous doses of 0.3, 0.45, 0.6, and 1.2 mg-Sn/L were applied to DI water with either base or acid preservation. Acid preservation was achieved using 50% (v/v) nitric acid in accordance with USEPA Method 200.8. For base preservation, 50% (w/w) sodium hydroxide was applied to achieve a $\text{pH} \geq 12$.

As illustrated in Figure 5, ICP-MS analysis of base-preserved samples resulted in almost 100% Sn recovery. In comparison, acid preservation yielded less than 50% recovery for Sn doses ≥ 0.45 mg-Sn/L. Thus, base preservation

was used for all total Sn samples collected during the demonstration. Stannous stock solution testing conducted at the end of the full-scale demonstration by spiking Sn from the 50% stock solution into base-preserved deionized water (Figure 5) demonstrated no dissolution or stability issues after the 10-week testing period. The application of the undiluted stannous stock solution and use of the base preservation method throughout the demonstration resulted in no stannous stability challenges, such as those observed in the Kennedy et al. (2018) pilot testing.

5.2 | Distribution system water quality

Time series graphs of Sn, Cr(VI), and total Cr by sample location are shown in Figures 6–8, respectively. In lieu of individual results for Wells 3408, 3409, and 3410, flow-weighted average concentrations of all three wells are used. For each figure, sample locations are listed in the legend, left to right, in order of increasing residence time from the POE to the distribution system. Water quality data are summarized in Table 3, which shows that several water quality parameters, such as pH, remained stable throughout this test.

As shown in Figure 6, weighted average Sn concentrations at the POEs varied from 0.4 to 0.7 mg/L. After the demonstration began on November 29, 2017, increased Sn at Tank 1 and Booster Pump 1 was observed within a few days. At Tank 3, it took more than 10 days for measurable Sn concentrations to be observed. This can be attributed to limited tank exercising before December 21, 2017. After ceasing stannous addition on January 31, 2018, Sn concentrations at all locations returned to ≤ 0.05 mg/L within 10 days. A singular spike of Sn was also observed after Sn addition was discontinued, which could have been the result of main pipe harvesting that was performed upstream of this sample point at Booster Pump 1 on the same day.

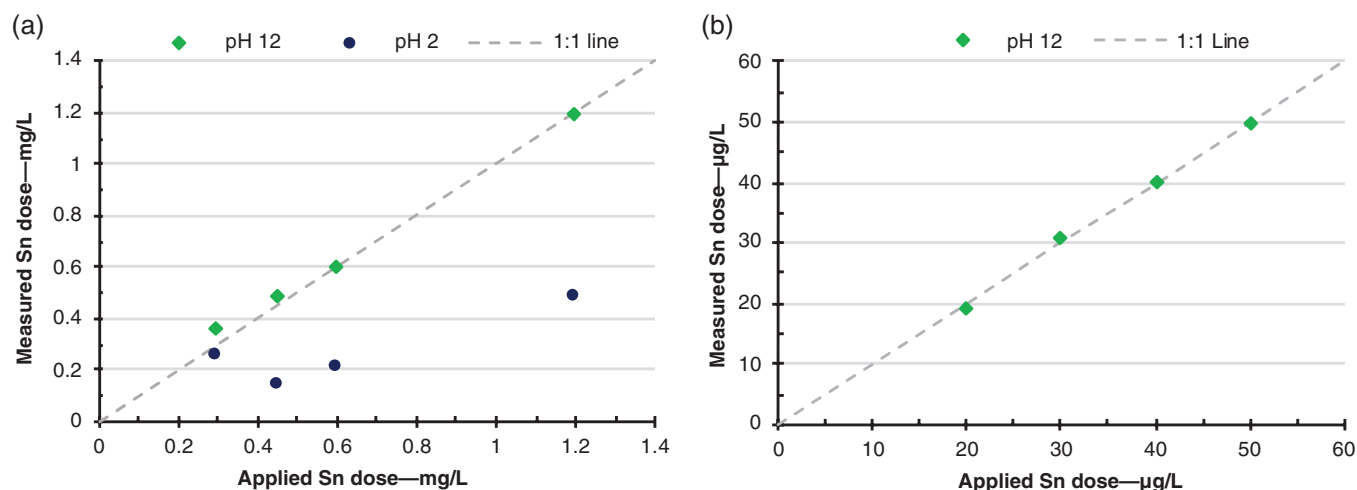


FIGURE 5 Sn recovery in acid- versus base-preserved samples. (a) Acid- versus base-preserved Sn samples. (b) 50% SnCl₂ stock solution stability at end of demonstration. Abbreviations: Cr(VI), hexavalent chromium; MCL, maximum contaminant level; Sn, tin; SnCl₂, stannous chloride

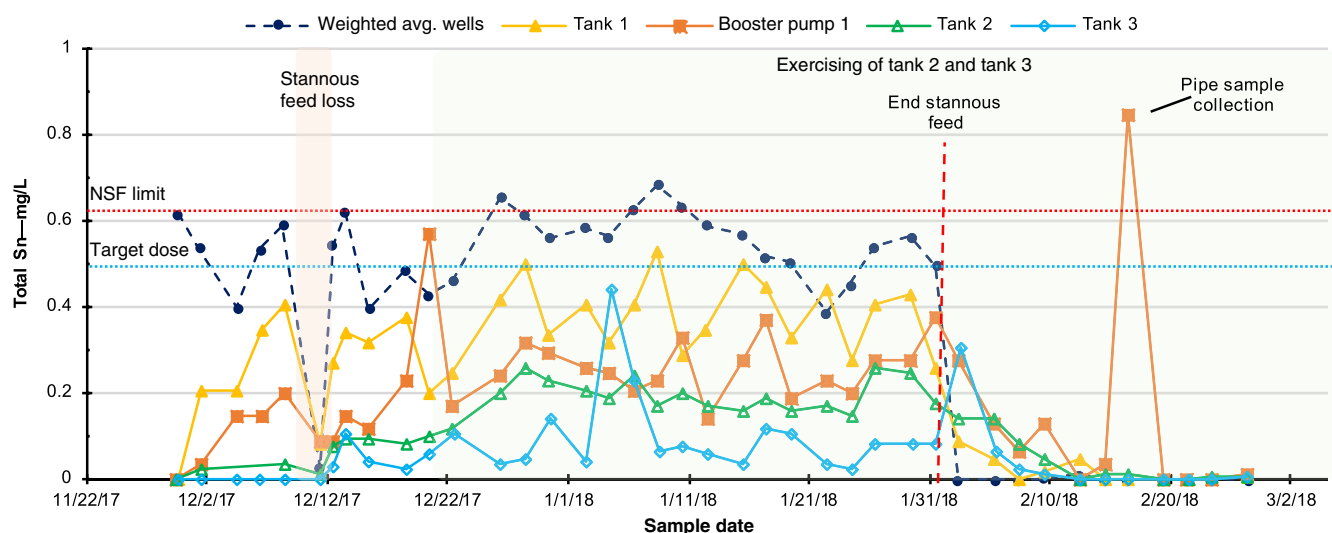


FIGURE 6 Time series of total Sn throughout the ID-8 distribution system. The increased tank exercising period corresponds to when tank turnover increased to 50% daily. Abbreviations: Cr(VI), hexavalent chromium; ID-8, Improvement District No. 8; MCL, maximum contaminant level; Sn, tin

As shown in Figure 7, after increased tank exercising began on December 21, 2017, the full-scale demonstration consistently achieved Cr(VI) concentrations less than the previous Cr(VI) MCL of 10 μg/L at all sample locations for more than 30 days. Only one sampling event, Booster Pump 1 on January 12, exceeded the water quality objective after tank exercising began. It is suspected that there were spikes in Cr(VI) before increased tank exercising because older water that did not undergo Sn reduction remained in the tanks. After ending the stannous feed, Cr(VI) concentrations returned to baseline levels within 2–12 days depending on sample location distance from the POE.

At the bench scale, a stannous dose of 0.6 mg-Sn/L (corresponding to 8.8 times the stoichiometric ratio for

Cr(VI) reduction) achieved Cr(VI) concentrations <1 μg/L before chlorine addition and ≤5 μg/L for up to 15 days in the presence of chlorine. The 0.5 mg-Sn/L dose (corresponding to 7.3 times the stoichiometric ratio) during the full-scale demonstration resulted in average Cr(VI) concentrations between 5 and 8.5 μg/L. Additional sampling of Well 3409 immediately after stannous dosing yielded <1 μg/L of Cr(VI), with upward of 5 μg/L reoxidation after chlorine addition. Therefore, full- and bench-scale testing results were similar.

Figure 8 shows that total Cr levels in samples collected during and immediately after Sn addition were lower than the total Cr MCL of 50 μg/L, with four instances of total Cr >30 μg/L observed. The occurrence of Cr peaking events

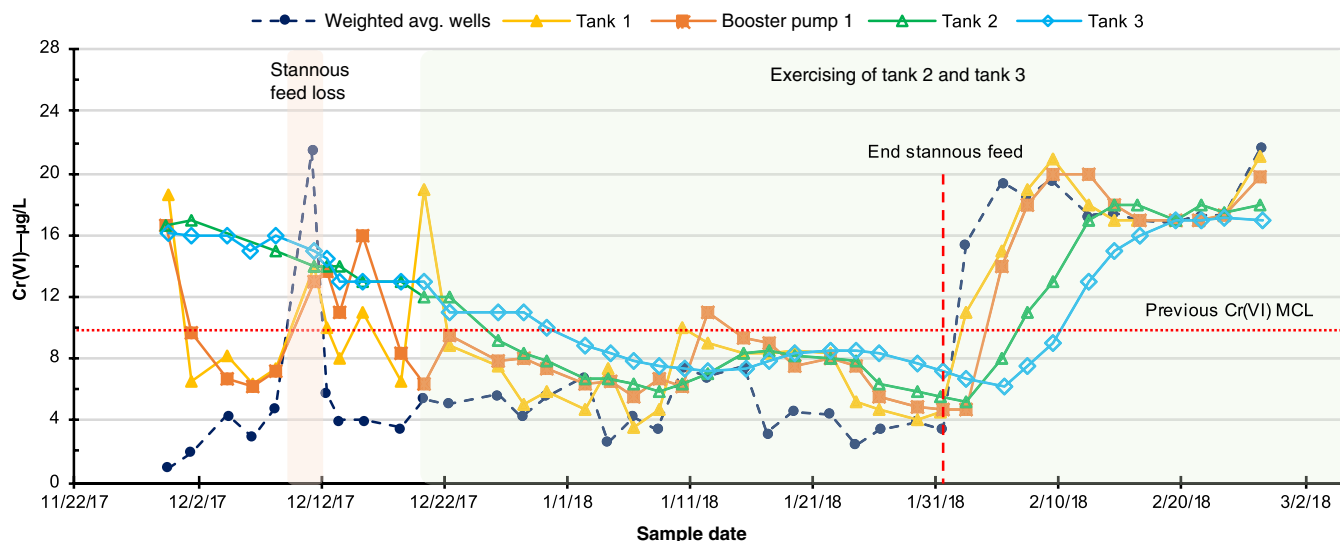


FIGURE 7 Time series of Cr(VI) throughout the ID-8 distribution system. Source water-weighted average well Cr(VI) concentrations before Sn addition are likely equivalent to weighted average well total Cr concentrations plotted in Figure 8. The increased tank exercising period corresponds to when tank turnover increased to 50% daily. Abbreviations: Cr, chromium; Cr(VI), hexavalent chromium; ID-8, Improvement District No. 8; MCL, maximum contaminant level; Sn, tin

(i.e., when total Cr levels exceeded average raw water total Cr concentrations of $\sim 19.5 \mu\text{g/L}$) suggests that total Cr accumulation and release occurred in the distribution system, which is discussed further in the following sections. However, total Cr spikes were not concerning from a regulatory perspective as they represented increased Cr(III) rather than Cr(VI) and remained lower than the $50 \mu\text{g/L}$ MCL for total Cr. Increased total Cr measured at Booster Pump 1 in February 2018 could have been caused by pipeline sampling that occurred on the same day.

5.3 | Sn and Cr accumulation

Boxplots of total Sn, total Cr, Cr(VI), and Cr(III) by sample location and during and after stannous addition are shown in Figure 9. Cr(III) concentrations were calculated by subtracting Cr(VI) from total Cr concentrations. Data included in the boxplots were collected after: (a) Cr(VI) first met the water quality objective of $<10 \mu\text{g/L}$ during Sn feed (Sn feed) and (b) Cr(VI) concentrations returned to $>10 \mu\text{g/L}$ post-Sn addition (post-Sn feed). These data take into account the time required for operational changes to reach each sample location and remove transitional data between test conditions.

As illustrated in Figure 9a, measured Sn concentrations during the Sn feed decreased as sampling distance from the POEs increased, indicating an accumulation of Sn in the distribution system. For example, a median concentration between 0.5 and 0.6 mg-Sn/L was measured at the POEs from the three wells, and the median Sn concentration at Tank 2 was $<0.1 \text{ mg-Sn/L}$. Loss of Sn through the distribution system can be attributed to stannous oxidation causing

precipitation of $\text{SnO}_{2(s)}$ on pipe walls and/or the formation of particles that settled out of solution (Brandhuber et al., 2004; Hozalski et al., 2005, 2010). Once Sn is oxidized, it would be expected to remain in an oxidized state. Sn scaling of pipe walls, which was confirmed to occur through pipe-scale analysis (see Section 3.7), was expected because Sn is a corrosion inhibitor known to coat pipe walls (Hozalski et al., 2005, 2010). As the full-scale demonstration spanned only 60 days, it is unknown if Sn concentrations at the end of the distribution system would remain constant if equilibrium was achieved after Sn further coated pipe walls. After the conclusion of stannous addition and when Cr(VI) concentrations increased to $>10 \mu\text{g/L}$, median Sn in the distribution system was nondetect at all sample locations with the exception of Booster Pump 1, most likely because of the nearby pipeline sampling event that may have fractured and resuspended Sn-containing scales.

Figure 9b shows that total Cr concentrations also decreased through the distribution system during Sn feed, which shows that total Cr accumulation arose in the distribution system. In addition, total Cr spikes above the raw flow-weighted average concentration, $19.5 \mu\text{g/L}$, occurred on three separate occasions. The broad whiskers shown in Figure 9 indicate variability in measured total Cr concentrations in the distribution system. These results suggest that accumulated total Cr was released. A spike in total Cr also occurred after the pipeline was harvested upstream of Booster Pump 1. This finding could indicate that total Cr associated with Sn scales which may have been fractured during pipe harvesting was released into the distribution system. Poststannous feed, total Cr

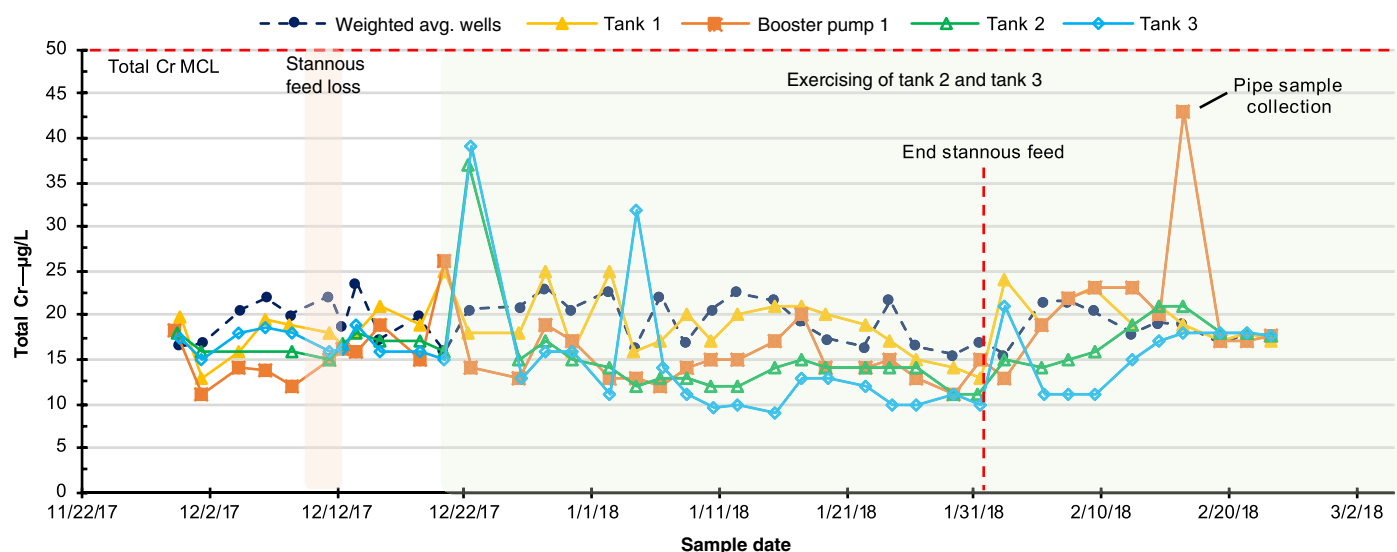


FIGURE 8 Time series of total Cr throughout the ID-8 distribution system. The increased tank exercising period corresponds to when tank turnover increased to 50% daily. Abbreviations: Cr, chromium; ID-8, Improvement District No. 8; MCL, maximum contaminant level

TABLE 3 Average ID-8 distribution system water quality during demonstration testing

Sample location	Sn (mg/L)	Cr(VI) (µg/L)	Total Cr (µg/L)	Turbidity (ntu)	pH	Temperature (°C)	HPC (cfu/mL)
Weighted Average wells	0.52 ± 0.12 (29)	5.0 ± 3.5 (29)	19.5 ± 2.6 (29)	0.27 ± 0.11 (9)	7.9 ± 0.3 (24)	25.3 ± 1.6 (24)	<1 (24)
Tank 1	0.35 ± 0.10 (28)	7.7 ± 3.2 (28)	18.5 ± 3.2 (28)	0.22 ± 0.07 (9)	8.0 ± 0.2 (24)	25.3 ± 1.5 (24)	399 ± 296 (9)
Booster pump 1	0.23 ± 0.11 (28)	8.2 ± 2.7 (28)	15.1 ± 3.1 (28)	0.22 ± 0.07 (9)	8.0 ± 0.2 (24)	24.5 ± 1.2 (24)	2 ± 2 (9)
Tank 2	0.19 ± 0.04 (19)	7.2 ± 1.2 (19)	13.6 ± 1.5 (19)	0.16 ± 0.08 (8)	8.0 ± 0.1 (17)	22.3 ± 1.3 (17)	<1 (6)
Tank 3	0.11 ± 0.10 (15)	8.1 ± 0.8 (15)	12.8 ± 5.7 (15)	0.34 ± 0.26 (9)	8.1 ± 0.2 (15)	22.5 ± 1.3 (15)	1 ± 0.4 (5)

Note. The error represents standard deviations. Values in parentheses are the number of data points.

Abbreviations: Cr, chromium; Cr(VI), hexavalent chromium; HPC, heterotrophic plate count; ID-8, Improvement District No. 8; Sn, tin.

accumulation ceased as total Cr returned to baseline levels (Figure 9b).

Tank sampling during an accelerated drawdown was conducted on January 25 at Tanks 2 and 3 to determine if Sn and Cr accumulation occurred in the tanks. As tanks were turned over by approximately 50% every day, a substantial amount of Cr and Sn entered the tank that could have accumulated and increased concentrations. However, total Cr and Sn concentrations decreased only slightly as Tank 2 drained, and concentrations remained constant in Tank 3. These results suggest that there was minimal Cr and Sn accumulation in these tanks that could be released by an accelerated drawdown, but it is possible there could be additional Cr and Sn released over a longer period of time (Figure 10).

Cr(III) concentrations, calculated by subtracting Cr(VI) from total Cr, were plotted against total Sn concentrations at each sampling location as shown in Figure 11. It can be seen that there is a linear relationship between Cr(III) and total Sn concentrations. In general, data sets further collected from the POE to the distribution system have lower total Sn and Cr(III) levels, which illustrates that these

constituents accumulated as they traveled through the distribution system. The slope of the regression shows that, for each 0.1 mg/L of Sn deposited, ~3 µg/L of Cr(III) was also deposited. The near-zero intercept implies Cr(III) would be nondetect when total Sn is nondetect.

As discussed subsequently, Cr(III) and Sn particles were present in the distribution system. One possible scenario that could explain the linear relationship in Figure 11 between Cr(III) and Sn is that separate Cr(III) and Sn particles formed that had similar settling rates. However, this scenario would require Cr(III) particles to settle at the same rate as a portion of the Sn that formed scales as it was confirmed that Sn coated pipe walls (see Section 3.7). It is more probable that the linear relationship in Figure 11 developed because both Cr(III) and Sn(IV) were incorporated into scales and possibly formed particles together that settled out of solution. Previous research has shown that Cr(III) and Fe(III) can be incorporated as a mixed hydroxide phase in drinking water distribution systems (Chebeir & Liu, 2018). It is possible that a similar Cr(III)/Sn(IV)-mixed oxide phase exists in the corrosion scales.

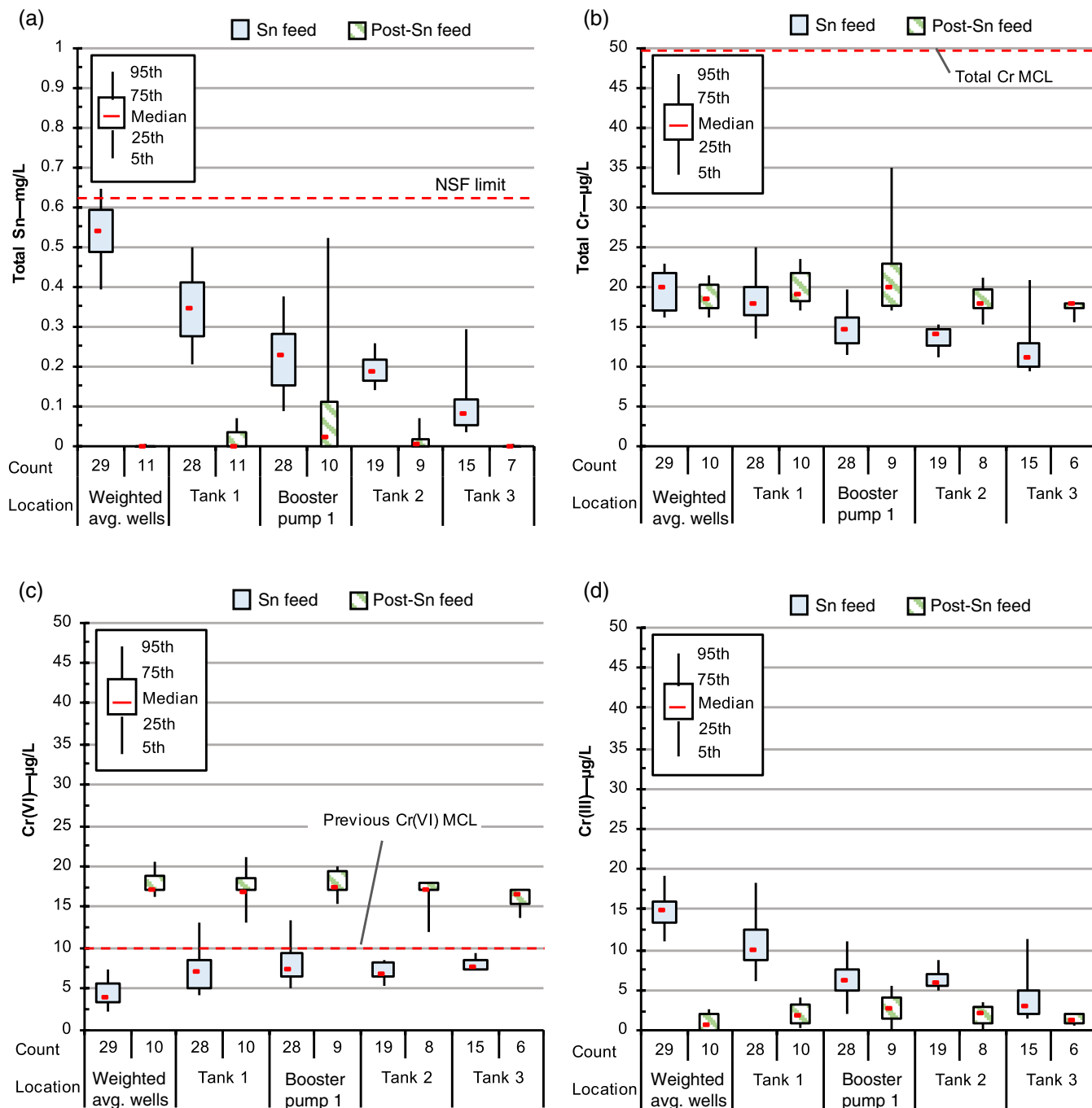


FIGURE 9 Total Sn, total Cr, Cr(VI), and Cr(III) boxplot by sampling location during and post-Sn feed. (a) Total Sn box plot. (b) Total Cr box plot. (c) Cr(VI) box plot. (d) Cr(III) box plot. Abbreviations: Cr, chromium; Cr(III), trivalent chromium; Cr(VI), hexavalent chromium; MCL, maximum contaminant level; Sn, tin

5.4 | Flushing experiment

To evaluate if Sn and Cr particles settled in the distribution system and/or if scales formed that could be resuspended and released during hydraulic changes, flushing experiments were conducted before and at the end of Sn addition. The distribution system was flushed in this location approximately 4 months before Sn addition. The flush location is in a low-

flow area of the distribution system where iron accumulation occurs and is released during flush events. Iron concentrations measured at the end of stannous addition (stannous flush) are provided in Figure S2 and show that iron was as high as 0.2 mg/L initially, and then concentrations declined quickly after 3 min. Most of the iron was in a particulate size range between 1 and 0.45 µm. These results could indicate that iron scales were fractured or that settled iron particles

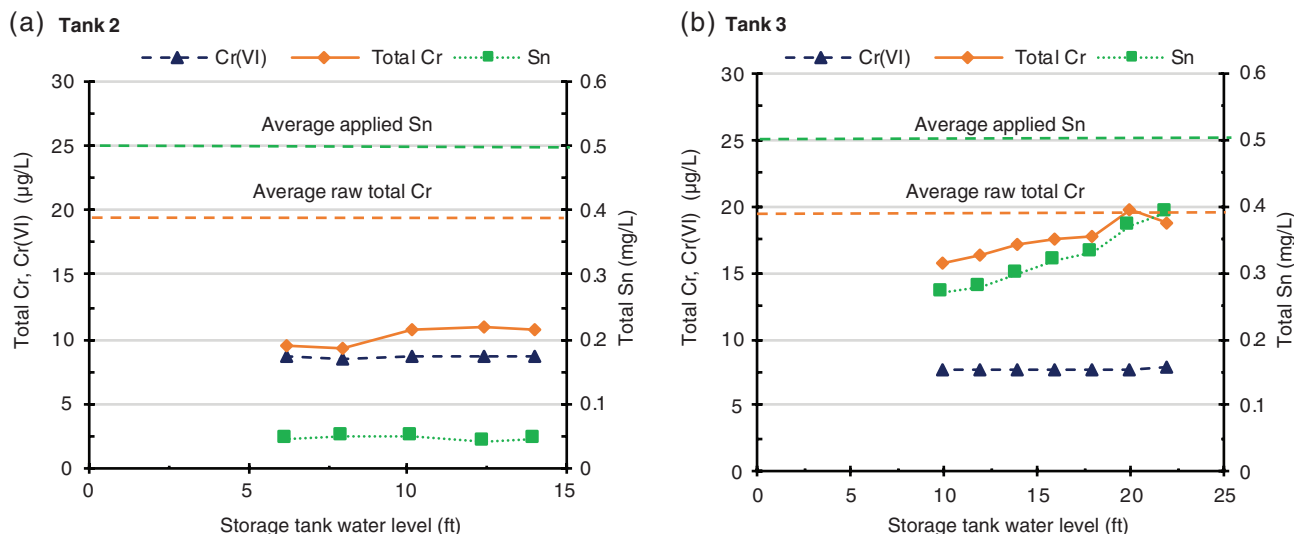


FIGURE 10 Tank draining tests conducted with Tanks 2 and 3. Abbreviations: Cr(VI), hexavalent chromium; Sn, tin

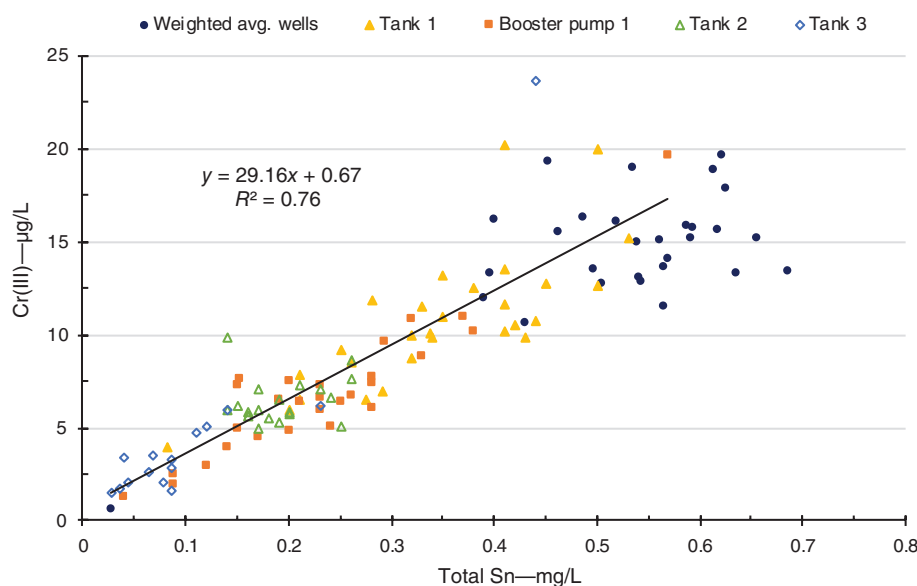


FIGURE 11 Cr(III) concentration plotted versus total Sn concentrations measured at distribution system locations when Sn was fed to the distribution system, and Cr(VI) was $\leq 10 \mu\text{g/L}$. Abbreviations: Cr, chromium; Cr(III), trivalent chromium; Cr(VI), hexavalent chromium; Sn, tin

were resuspended. Total Sn, Cr(VI), total Cr, and Cr(III) concentrations measured before Sn addition (prestannous) and in the stannous flush are provided in Figure 12. As shown in Figure 12a, the first sample collected after 1 min of flushing during the prestannous flush had low ($<0.06 \text{ mg-Sn/L}$) but there was detectable Sn in the unfiltered, $0.35 \mu\text{m}$ -, and $1 \mu\text{m}$ -filtered water. Both Cr(VI) and total Cr concentrations were lower in filtered than unfiltered samples. These findings were likely a result of residual Sn in the filtration system from previous pilot efforts that used both stannous and ferrous as reductants. Figure 12g shows that, in the 1-min sample, Cr(III) was the highest in the $0.35 \mu\text{m}$ filtrate, which was not expected and may be a result of Cr(III) in the filtration system from the previous pilot effort. After the first prestannous flush sample, all Sn results

were nondetect with consistent Cr(VI), total Cr, and Cr(III) concentrations through the end of the flush as anticipated (Figure 12).

During the stannous flush event, Cr(VI) concentrations were not affected by filtration and remained between 6 and 7 $\mu\text{g/L}$, which confirmed that Cr(VI) stayed dissolved (Figure 12d). These Cr(VI) levels are similar to the average Cr(VI) concentration measured in Tank 2 (Table 3), which is near the hydrant used for the flushing experiment, and suggests there was a similar level of Cr(VI) reduction and Cr(III) reoxidation at these locations. During the first 5 min of the stannous flush, Sn concentrations in unfiltered and $1 \mu\text{m}$ -filtered water were between 0.35 and 0.6 mg-Sn/L , and total Cr concentrations varied between 17 and 23 $\mu\text{g/L}$. Because Sn and total Cr concentrations in the flush

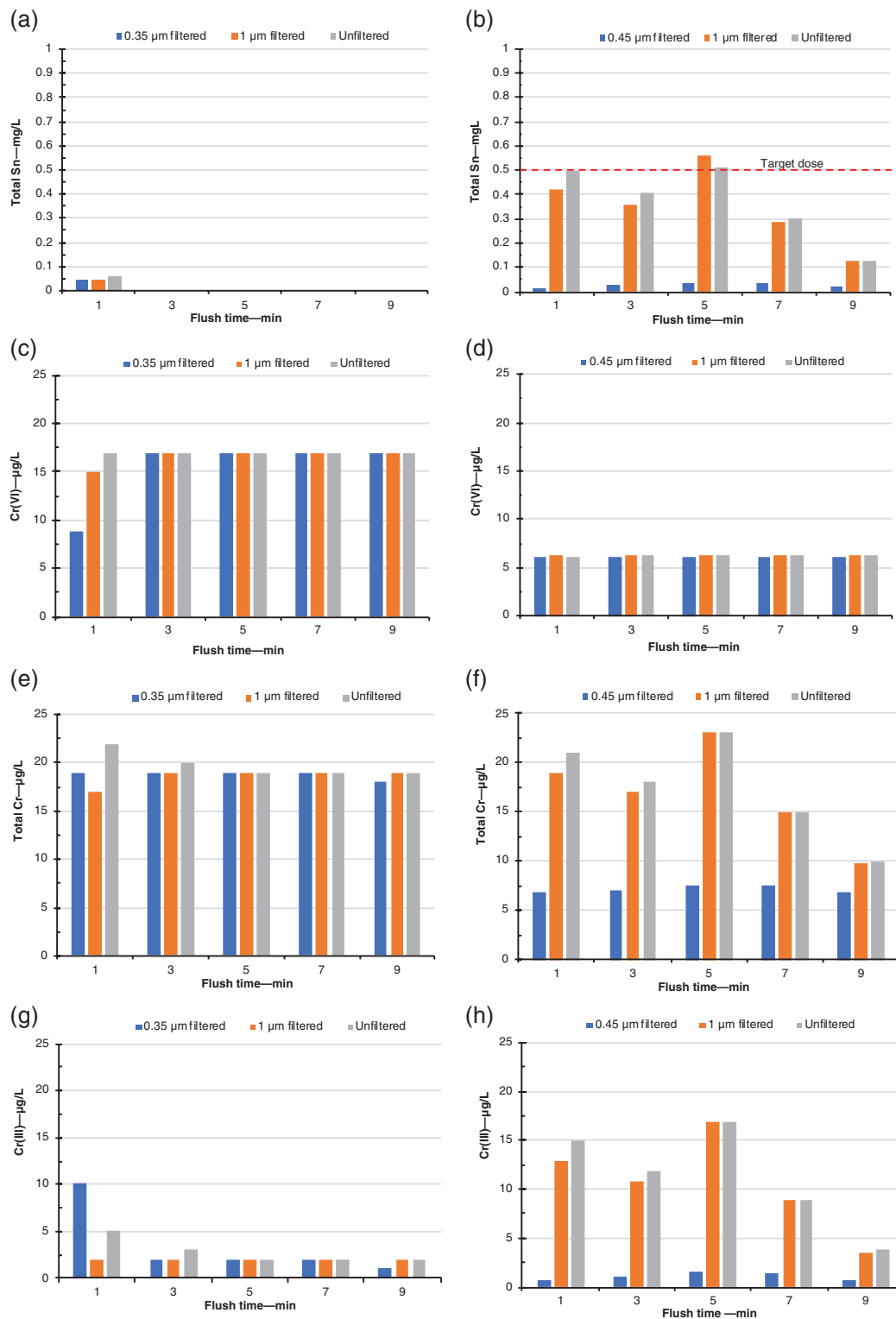


FIGURE 12 Total Sn, Cr(VI), total Cr, and Cr(III) concentrations for prestannous and stannous flush experiments. (a) Prestannous flush, Sn. (b) Stannous flush, Sn. (c) Prestannous flush, Cr(VI). (d) Stannous flush, Cr(VI). (e) Prestannous flush, total Cr. (f) Stannous flush, total Cr. (g) Prestannous flush, Cr(III). (h) Stannous flush, Cr(III). Abbreviations: Cr, chromium; Cr(III), trivalent chromium; Cr(VI), hexavalent chromium; ID-8, Improvement District No. 8; Mn, manganese; Sn, tin

water were greater than what was measured in Tank 2 around this period (Sn and total Cr concentrations were ≤ 0.2 mg-Sn/L and < 15 $\mu\text{g/L}$, respectively, on the day of and the week

before the stannous flushing test), these results suggest that accumulated Sn and Cr were released into the flush water. However, the maximum Sn and total Cr concentrations in

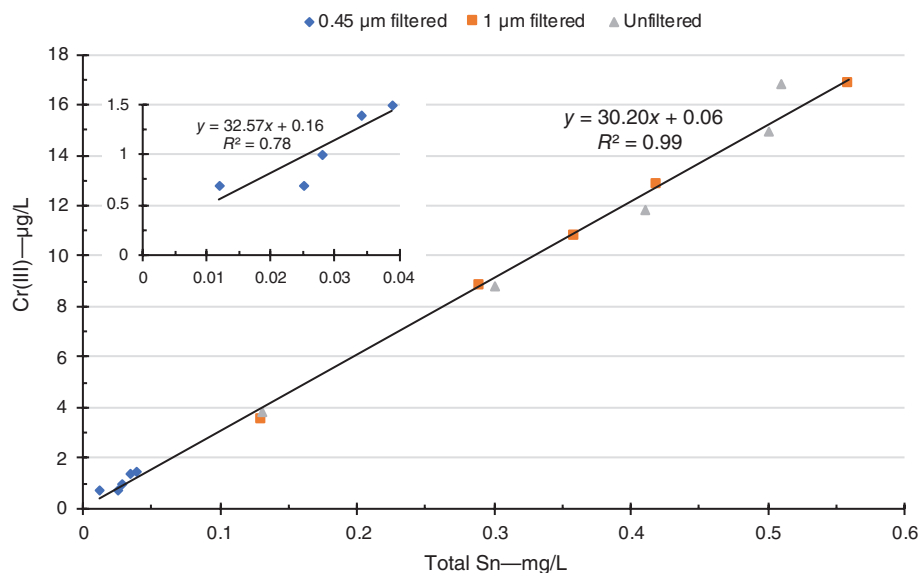


FIGURE 13 Cr(III) concentration plotted versus total Sn concentrations measured in stannous flush water
Abbreviations: Cr(III), trivalent chromium; Sn, tin

the flush water were similar to that measured in the POE to the distribution system (Table 3). In addition, Sn and total Cr concentrations decreased substantially after 7 min of flushing; after 9 min, concentrations were within the range of concentrations measured nearby at Tank 2 (Figures 6 and 8). The 9-min sample could have been representative of distribution system water quality under normal operating conditions, and these filtration results show that Sn was mainly present in a size range between 0.45 and 1 µm by the time it reached the flush location near Tank 2. Thus, the accumulated Sn released during the flush was likely similar in size to the Sn present under normal operating conditions, which could suggest that the accumulated Sn released was not dislodged from scales that might be associated with larger particles.

These results show it is possible that the release of accumulated Sn and Cr may not be an issue when a hydraulic disruption occurs. However, there is the potential for a longer period of Sn addition and more aggressive flushing conditions to release more Sn and Cr. In addition, because of the lack of data on the flows out of the main portions of the distribution system, a mass balance cannot be performed, and the amount of accumulated Sn and total Cr that was resuspended/released cannot be quantified.

Figure 12 shows that Sn and Cr(III) concentrations were similar in the unfiltered and 1-µm filtrate and decreased to <0.04 mg-Sn/L and ≤1.5 µg/L, respectively, in the 0.45 µm filtrate. Therefore, the majority of Sn and Cr(III) particles have nominal diameters between 0.45 and 1 µm. As particles in this size range are often classified as nonsettling, fairly low levels of Sn and total Cr may have been measured in the stannous flush water because most Sn and Cr particles stayed suspended in the distribution system and did not settle.

Cr(III) and Sn concentrations measured in unfiltered, 1 µm-, and 0.45 µm-filtered water during the “stannous

flush” are plotted against each other in Figure 13. There is a strong linear relationship between the two metals. In Figure 13, Cr(III) and total Sn concentrations are provided in units of µg/L and mg/L, respectively; the regression slope was ~30, and the intercept was near zero, which was also observed for the regression in Figure 11. The insert in Figure 13 illustrates that a small fraction of Sn and Cr(III) was able to pass through the 0.45-µm filter and that the regression slope was also near 30. The fact that the ratio between Cr(III) and Sn stayed constant in filtered and unfiltered water, which suggests Cr(III) and Sn are associated with particles of a similar size distribution, provides further evidence that Cr(III) and Sn were complexed in the distribution system.

5.5 | Main pipeline analysis

Sn and Cr were observed in both outer and inner corrosion layers of a tubercle in a pipe harvested from the ID-8 system near Booster Pump 1 after the 10-week stannous application (Figure 14). Control experiments were performed to determine the presence of select metals originating in the pipe not exposed to Sn treatment. Two 3" × 3" pipe coupons were cut and sanded to expose fresh metal on all sides and were then electrochemically corroded in treated groundwater from the ID-8 system by connecting the two pipe coupons as anode and cathode and applying a constant current of 500 mA for 12 h to simulate cumulatively 5 years of corrosion process (Smart et al., 2001). Corrosion scales were collected and analyzed via ICP-MS, confirming that both Sn and Cr were not originally present in the manufactured pipe, and little Cr likely integrated into the scale in the absence of Sn. Compared with its natural abundance in the earth's crust, both Sn and Cr were much higher in the corrosion scales harvested from the distribution system.

SEM of the corrosion scale harvested from the distribution system indicates the predominance of iron oxide particles (Figure 15a). The size of spherical and rod-like particles varied from 0.25 to 2.5 μm . EDS mapping of the sample confirmed that Sn and Cr were detected in the corrosion scale (Figure 15b). Fitting of the EDS spectra indicated concentrations of 250 ± 30 mg/kg Sn and 20 ± 8 mg/kg Cr in the outer layer of the corrosion scales. The same analysis was conducted on the inner-layer corrosion scale and yielded results of 320 ± 20 mg/kg Sn and 160 ± 10 mg/kg Cr. These values are similar to those obtained by ICP-MS, further confirming the presence of Sn and Cr in the corrosion scales.

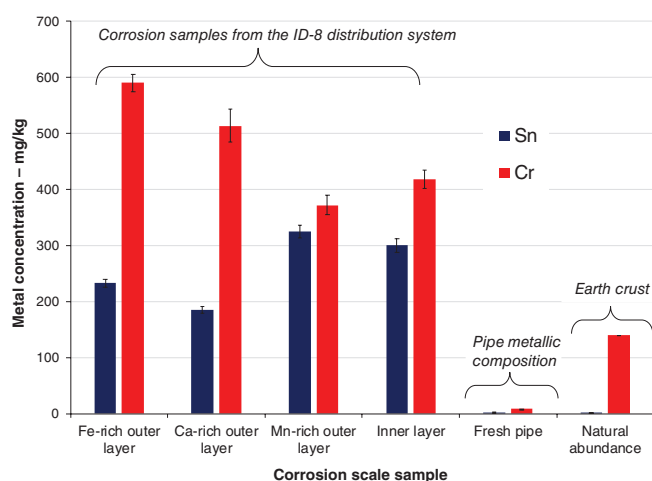


FIGURE 14 Total Sn and Cr concentrations found in various sections of the pipe via ICP-MS. Abbreviations: Ca, calcium; Cr, chromium; Fe, iron; ICP-MS, inductively coupled plasma mass spectrometry; ID-8, Improvement District No. 8; Mn, manganese; Sn, tin

While a pipe sample before Sn addition was not collected and analyzed, the artificially corroded sample served as a representative substitute. Although it is difficult to quantify the exact fraction of the Cr-containing tubercles that developed before Sn addition, as the age and history of the pipe are unknown, these results unambiguously confirmed that Sn coated pipe walls. Considering that the ratio between Sn and Cr(III) remained constant throughout the distribution system, Cr(III) likely accumulated along with Sn on pipe walls. The accumulation of Cr(III) can take place with the deposition of $\text{Cr(OH)}_{(s)}$ on the pipe walls and the integration into Cr(III)–Fe(III) hydroxides or Cr(III)/Sn(IV)-mixed oxide phase. Such Cr accumulation could be less susceptible to release back into the distribution system relative to the resuspension of settled particles during a hydraulic disruption, which may be why relatively little Sn and Cr was released during the flushing test. However, the possibility for more substantial Cr and Sn particle settlement and resuspension and/or fracturing and dissolution of scales than what were observed here cannot be ruled out under more severe hydraulic and/or water quality fluctuations.

6 | SUMMARY

At the bench scale, SnCl_2 doses ≥ 0.3 mg-Sn/L (i.e., ≥ 4.4 times the stoichiometric dose ratio to reduce Cr(VI)) were effective in decreasing Cr(VI) concentrations from 20 to < 2 $\mu\text{g/L}$. Less than 8 $\mu\text{g/L}$ of Cr(III) was reoxidized even with target chlorine doses as high as 1.5 mg- Cl_2 /L. An evaluation of water quality through the ID-8 distribution system demonstrated consistent Cr(VI) concentrations < 10 $\mu\text{g/L}$ at all sample locations for over 30 days of stannous feed. While some Cr(VI) reoxidation likely occurred downstream

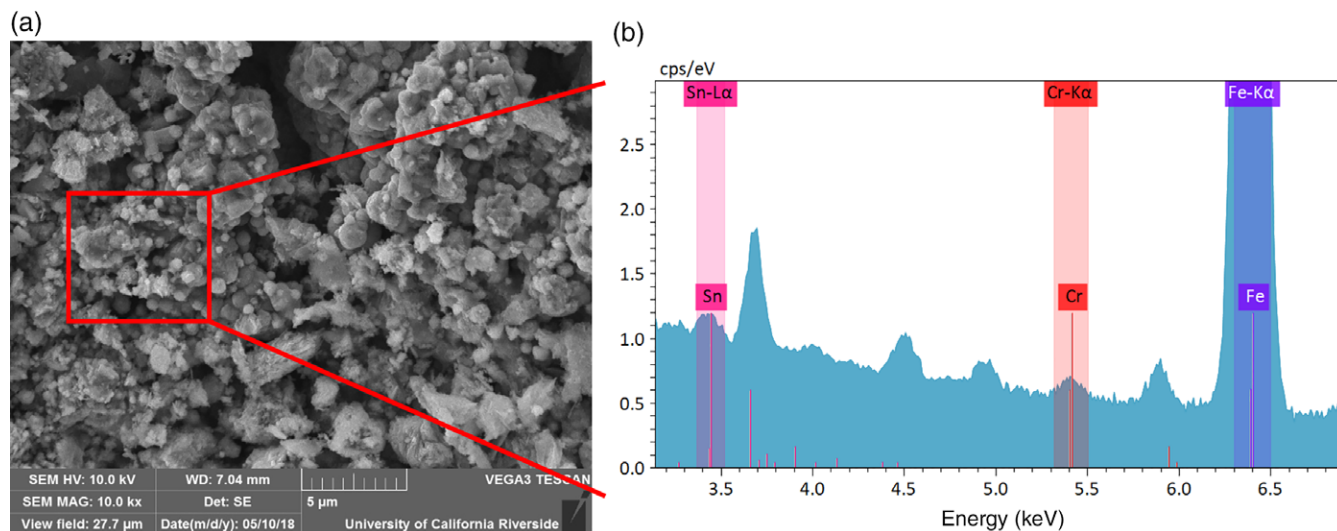


FIGURE 15 SEM and EDS mapping of outer-layer scale from ID-8 pipe sample. Abbreviations: EDS, energy-dispersive X-ray spectroscopy; ID-8, Improvement District No. 8; SEM, scanning electron microscope

of the POEs on the basis of bench-scale reoxidation rate experiments, most of the reoxidation likely occurred by the first sample location in the distribution system, Tank 1, as Cr(VI) concentrations were similar at each sampling location a little more than a week after tank exercising began. The water quality goal for turbidity and the total Cr MCL were also satisfied for the entire duration of testing, and pH and temperature stayed fairly constant (Table 3).

Sn concentrations decreased with increased distance from the POE to the distribution system, which was anticipated because Sn is a corrosion inhibitor intended to coat pipe walls (Hozalski et al., 2005, 2010). Pipe section analysis confirmed that Sn was deposited onto the inner pipe walls and incorporated into the corrosion products together with Cr. Cr(III) concentrations exhibited a similar decrease as Sn with distance from the POE to the distribution system. Because the ratio between Cr(III) and Sn concentrations remained nearly constant throughout the distribution system and in filtered and unfiltered flush water, Cr(III) was likely associated with Sn-containing scales. It is also possible that Cr and Sn were associated in particles that accumulated by settling out of water in the distribution system. It is not anticipated that substantial Cr and Sn settlement would occur in this distribution system given that Cr(VI) remained dissolved, and most Cr(III) and Sn particle diameters were <1 μm and should remain suspended. Accumulated Sn and Cr that coated pipe walls could be less susceptible to release relative to settled particles during hydraulic disruptions. If a substantial amount of accumulation occurred by scale formation, this could explain why main flushing at the end of the demonstration resulted in a relatively small increase in Sn and Cr concentrations. For other systems considering Sn application, the fate of Sn and Cr should also be evaluated to determine the potential for Cr and Sn particle settlement, resuspension, and release.

Upon establishment of a new Cr(VI) MCL, CVWD intends to pursue full-scale stannous addition permitting with DDW to reduce Cr(VI) levels in any wells impacted by the new MCL. Concurrent with any implementation of stannous addition, monitoring of the potential accumulation and release of Cr in the distribution system under different operational scenarios should be conducted. Special monitoring performed during any interruptions in Sn and chlorine addition and during scour flow events can assist with full-scale implementation. This monitoring may help answer outstanding research questions and provide additional operating information.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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