# Full-Scale Implementation of Second-Stage Contactors for Manganese Removal

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The use of post-filtration contactors for the removal of manganese (Mn) in the dissolved, reduced form ($Mn^{2+}$ or Mn(II)) by sorption to manganese oxide–coated granular media and catalytic oxidation by free chlorine was implemented at the Lantern Hill Water Treatment Plant in Stonington, Conn., in order to lower disinfection by-product (DBP) formation while effectively controlling metals. The second-stage contactors (SSCs) successfully removed Mn at hydraulic loading rates of up to 10 gpm/ft$^2$ with little head loss accumulation and effluent Mn concentrations typically ≤0.01 mg/L. A mass balance showed similar masses of Mn removed from the water by the SSCs and in the backwash waste (total difference of <10%) during the study period. DBP concentrations were lower than historical concentrations for the plant, with average plant effluent total trihalomethane and five haloacetic acid concentrations of 30 µg/L each. Other treatment goals (e.g., turbidity, iron removal, free chlorine residual) were also successfully achieved.

**Keywords:** *adsorptive contactors, disinfection by-products, drinking water, manganese*

The presence of manganese (Mn) in distributed drinking water may lead to operational problems and consumer complaints related to aesthetic quality concerns (e.g., discolored water, staining of fixtures). The biochemical reduction of Mn-containing minerals in aquifers and reservoir sediments under anoxic conditions can result in elevated levels of dissolved manganese ($Mn^{2+}$ or Mn(II)) in source waters. The US Environmental Protection Agency (USEPA) set a secondary maximum contaminant level (SMCL) of 0.05 mg/L for Mn to control taste, odor, and color complaints by consumers (USEPA 1992) and a lifetime health advisory of 0.3 mg/L in water to address potential neurological effects (USEPA 2004). However, the recommended treatment goal to avoid operational and chronic problems such as water discoloration, turbidity, and scaling in pipes and valves is 0.01–0.02 mg/L Mn (Brandhuber et al. 2013, Kohl & Medlar 2007, Sly et al. 1990). The Canadian Federal-Provincial-Territorial Committee on Drinking Water recently published an updated drinking water guideline for manganese for public consultation. The guideline proposes a maximum acceptable concentration of 0.1 mg/L based on neurological effects observed in rodents and an aesthetic objective of 0.02 mg/L for total Mn in drinking water (Health Canada 2016).

The most commonly practiced Mn-control strategies include oxidation and precipitation by a strong oxidant (e.g., permanganate, chlorine dioxide, ozone) ahead of particle removal, and sorption of Mn(II) to manganese oxide–coated porous media in conjunction with catalytic oxidation by free chlorine. The latter method exhibits very rapid oxidation of surface-bound Mn(II) in the pH range of most waters and results in regeneration of the manganese oxide ($MnO_{x(s)}$) coating (Knocke et al. 1991). In contrast, homogenous oxidation of Mn(II) by free chlorine (HOCl, $OCl^-$) is slow at typical drinking water treatment pH, time, and temperature conditions (Knocke et al. 1987). The Mn(II) adsorption capacity of $MnO_{x(s)}$–coated media increases with increased surface $MnO_{x(s)}$ concentration, influent chlorine concentration, and solution pH (Tobiason et al. 2008, Knocke et al. 1991, Morgan & Stumm 1964). A measure of the Mn(II) uptake capacity of $MnO_{x(s)}$–coated filter media from several drinking water treatment plants (Islam et al. 2010) showed a general nonlinear increase in Mn(II) uptake with increasing $MnO_{x(s)}$ coating level (mg-Mn/g media). A continuously present free chlorine residual allows regeneration of surface sites and prevents Mn release at a pH of 6.5–7.1 (Gabelich et al. 2006, Knocke et al. 1991).

Halogenated disinfection by-products (DBPs) may form during treatment when chlorine or other disinfectants react with natural organic matter (NOM) in water. Some DBPs are known to be carcinogenic and genotoxic. Total trihalomethanes (TTHMs) and five haloacetic acids (HAA5s), all halogenated organic compounds, are regulated by the USEPA at maximum contaminant levels (MCLs) of 0.080 mg/L and 0.060 mg/L, respectively. Stage 2 of the Disinfectants and Disinfection Byproducts Rule (USEPA 2006) stipulates that locational running annual averages for each monitoring location in the distribution system meet these limits. The nine regulated compounds are only a small fraction of DBPs that have been identified to date, and studies show that other unregulated

DBPs may be more genotoxic than those currently regulated (Richardson et al. 2007). As the occurrence and toxicity of unregulated DBPs become better understood, there may be new regulation of these compounds.

While effective for Mn(II) removal, adding chlorine ahead of dual media filtration for catalytic oxidation can increase DBP concentrations as compared with chlorination after dual media filtration (Tobiason et al. 2008, Brown 2006, Corbin et al. 2003). Corbin et al. (2003) examined the effect of adding chlorine post-filtration instead of pre-filtration on DBP concentrations for three water treatment plants in Connecticut, USA. Samples were held for the average clearwell residence time plus 24 h for simulated distribution system (SDS) samples. SDS samples showed annual average decreases of up to 32 and 27% in HAA5 and TTHM concentrations, respectively, with the greatest decreases observed in the spring. However, the authors noted that post-filtration chlorination at plants with high seasonal iron (Fe) and Mn concentrations would be feasible only if metals removal was achieved by alternative methods (i.e., not preoxidation or sorption and catalytic oxidation across $MnO_{x(s)}$–coated granular media primarily designed for particle removal).

The use of second-stage contactors (SSCs) for Mn(II) removal by sorption and surface oxidation by free chlorine after particle removal by granular media filtration has been examined at laboratory and pilot scales (Chihoski 2012, Knocke et al. 2010, Tobiason et al. 2008). Having the sorption and catalytic oxidation process for Mn(II) removal after particle filtration minimizes DBP formation, probably by minimizing the contact of free chlorine with raw water and media associated NOM. The SSC configuration using $MnO_{x(s)}$–coated media coarser than traditional filter media (2.0–2.5 mm versus 0.5–1.0 mm diameter) successfully removed influent Mn(II) concentrations of 0.02–0.3 mg/L at high hydraulic loading rates (HLRs) of 16–24 gpm/ft$^2$, over a wide pH range. A free chlorine residual of at least 1.0 mg-$Cl_2$/L was necessary, and removal was greater at pH 7.0–8.0 than at pH 6.3–6.7 (Knocke et al. 2010).

The Lantern Hill Water Treatment Plant (LHWTP) in Stonington, Conn., treats a groundwater source with 1.5–2.5 mg-Fe/L, 0.15–0.25 mg-Mn/L, 3–4 mg/L of total organic carbon (TOC), and an average pH of 6.5. Prior to 2013, the plant employed a single stage of three parallel dual media filters (21 in. of anthracite over 24 in. of $MnO_{x(s)}$–coated glauconite) in a direct filtration treatment train. A high pre-filter chlorine dose was added for Fe oxidation and precipitation ahead of dual media filtration as well as maintenance of a significant free chlorine residual across the dual media for Mn removal and for plant effluent free chlorine residual; pre-filter permanganate addition was also practiced, which resulted in oxidation of some of the raw water Mn prior to the filter. The level of pre-filter chlorination resulted in elevated levels of DBPs due to the reaction of chlorine with the raw water NOM. A desire to pump the groundwater once only and the use of a single stage of direct filtration limited the treatment options. Lowering the pre-filter chlorine dose (and adding post-filter chlorination for the distribution residual target) resulted in lower DBP concentrations but was accompanied by increased effluent Mn concentrations after 45 days of operation (Russell 2008), most likely due to release of Mn from the filter media resulting from microbiological reduction (Islam 2010).

The addition of an SSC was considered in order to achieve Mn removal without forming high levels of DBPs. Pilot studies in the laboratory and onsite were conducted to test SSC performance for this system. Onsite studies using a two-stage pilot-scale filter system showed that an SSC with a 40-in. pyrolusite (an $MnO_2$ mineral) media bed, after iron and some TOC removal by dual media filtration, successfully removed Mn(II) and resulted in 60 and 80% decreases in TTHM and HAA5 concentrations, respectively, in effluent samples were held for 24 h (Pham 2010). Chihoski (2012) tested the performance of different types of SSC media including $MnO_{x(s)}$–coated anthracite, an $MnO_{x(s)}$–coated porous ceramic media[1] with an average grain density of 1.4 g/cm$^3$, and pyrolucite. The $MnO_{x(s)}$–coated porous ceramic media performed best at an HLR of up to 20 gpm/ft$^2$ and a free chlorine residual of approximately 1 mg/L, producing effluent Mn concentrations of 0.01 mg/L. Using carefully dosed pre-filter chlorine for dissolved iron ($Fe^{2+}$ or Fe(II)) oxidation only, and post-filter chlorine for oxidation of SSC-sorbed Mn(II) and system residual resulted in 59 and 58% decreases in the 24-h hold values for TTHMs and HAA5s, respectively, compared with the existing full-scale plant. In comparison, pre-permanganate oxidation of Fe(II) along with post-filter chlorine resulted in 63 and 61% decreases in TTHMs and HAA5s, respectively.

The Aquarion Water Co. (AWC) contracted with Tighe & Bond Engineers[2] to design an upgrade of the LHWTP based on results of the pilot studies. The new LHWTP with rebuilt dual media filters and added SSCs went on-line in July 2013.

The objective of this study is to document the performance of the full-scale plant with respect to Fe and Mn removal and control of DBPs, with special emphasis on the SSCs. The treatment approach taken is unusual and is perhaps the first application of this particular sequence and operation of treatment processes.

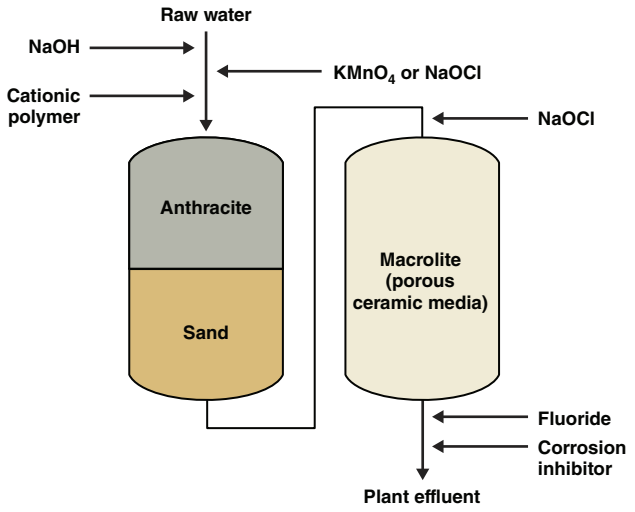
## MATERIALS AND METHODS

**The full-scale plant.** Figure 1 shows a schematic of the 700-gpm-capacity, updated LHWTP. Sodium hydroxide (NaOH) is added to the raw water to increase the pH from approximately 6.3 to 7.3. A sub-stoichiometric dose of sodium hypochlorite (NaOCl) is added to oxidize the dissolved iron for removal by the dual media filters. There is the option to use potassium permanganate ($KMnO_4$) as a preoxidant. Cationic polymer (C-572[3]) is also added to the raw water to increase TOC removal and aid particle retention by the dual media filters.

Steel vessels were reused for the three parallel dual media filters, each containing 25 in. of approximately 1 mm effective size (ES) anthracite (uniformity coefficient [UC] of 1.41) over 20 in. of approximately 0.5 mm ES silica sand (UC = 1.37). The filters have a design HLR of 3 gpm/ft$^2$, with backwash and air-scour capability.

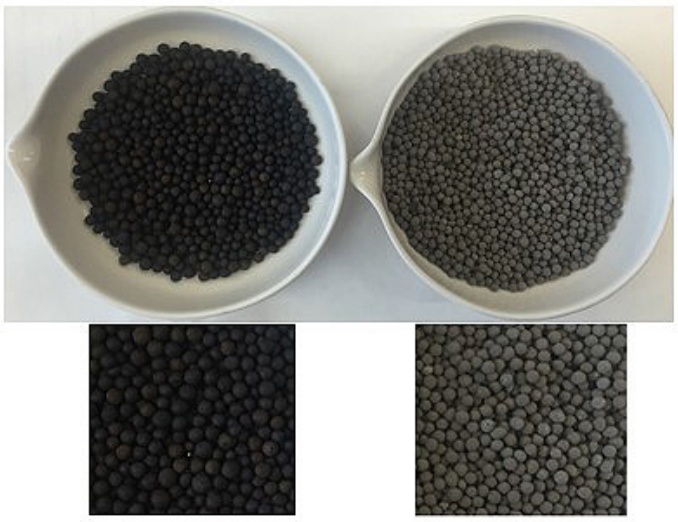
Dual media filter effluent is dosed with sufficient NaOCl to achieve catalytic manganese oxidation plus a plant effluent residual of approximately 1 mg-$Cl_2$/L, and then enters three parallel SSCs. Each SSC contains approximately a 40 in. depth of 2 mm ES porous ceramic media (UC = 1.2). The media was coated with $MnO_{x(s)}$ in the vessels prior to plant start-up using a procedure provided by a consultant.[4] Media were exposed to a 3% manganous sulfate ($MnSO_4$) solution followed by a 2% $KMnO_4$

**FIGURE 1** Schematic of reconstructed Lantern Hill Water Treatment Plant




$KMnO_4$—potassium permanganate, NaOCl—sodium hypochlorite, NaOH—sodium hydroxide

solution, with 30 min of air mixing followed by 30 min of soaking after the application of each solution, draining of the $MnSO_4$ prior to $KMnO_4$ soaking, and rinsing with two bed volumes of water after $KMnO_4$ application. The sequence of alternate solutions was performed three times. The coating procedure was evaluated in the laboratory prior to field implementation using uncoated porous ceramic media obtained from LHWTP to determine potential media $MnO_{x(s)}$ coating levels. Photographs of the uncoated media and the media coated at the plant by the described procedure are shown in the photograph on this page.



**Manganese oxide–coated Macrolite M7 media (left) and Macrolite M7 media before it has been coated (right).**

The contactors were designed for an HLR of 10 gpm/ft$^2$. Water and air backwash options are included for the SSCs for fluidized backwash-based removal of accumulated $MnO_{x(s)}$ on the media. Fluoride and corrosion inhibitor (blended phosphates) are added to SSC effluent, and there is the option to add additional chlorine for the distribution system residual.

**Field sampling.** Samples were collected across the plant during SSC backwash events for onsite bench measurements or analyses at the University of Massachusetts, Amherst. Raw water, dual media filter influent and effluent, contactor influent, and plant effluent samples were collected for metals, turbidity, free chlorine residual, organic carbon, and DBP measurements. Samples were separated onsite into particulate, colloidal, and dissolved fractions for Fe and Mn measurements after Carlson et al. (1997). Samples were syringe-filtered with a 25-mm-diameter, 0.2-µm track-etched polycarbonate membrane filter,[5] and with a regenerated cellulose 30 kDa nominal molecular weight cutoff membrane ultrafilter (UF)[6] in a 200-mL UF cell[7] with stirring under nitrogen at 30 psi. The particulate fraction is that which does not pass through the 0.2-µm filter, the colloidal fraction passes through the 0.2-µm filter but not the 30 kDa UF, and the dissolved fraction passes through the 30 kDa UF.

Samples for instantaneous DBP measurement were quenched upon collection, and samples for 24- and 48-h SDS assessment were collected headspace free in biochemical oxygen demand (BOD) bottles, kept in the dark at 12°C, and quenched after 24 and 48 h, respectively. Ammonium chloride was used to quench samples for TTHM analysis, and sodium sulfite to quench samples for HAA5 analysis.

The SSCs underwent high-rate backwash approximately every six to eight weeks. Air scouring was employed periodically during backwash, as discussed in the Results section. Contactor backwash was initiated after dual media filter backwash and stabilization of plant effluent water quality. Composite backwash samples for each contactor were collected for Mn mass balance calculations. A 62-in. grain sampler[8] with 10 sample slots was used twice (February 2014 and September 2015) to obtain SSC media samples for $MnO_{x(s)}$ coating depth profile assessment.

Water quality data (e.g., water production, Mn and Fe levels across the plant, turbidity) were also provided by the utility. Three times weekly utility personnel made bench-top measurements of metals, free chlorine residual, pH, ultraviolet light absorbance at 254 nm ($UV_{254}$), and turbidity.

**Analytical methods.** ***Field measurements.*** Mn and Fe were measured using Hach method 8149 (low range with PAN indicator) and 8008, respectively, and the corresponding field spectrophotometers.[9] Free chlorine was measured by Hach method 8021 (DPD reagent). A turbidimeter[10] was used for bench-top turbidity measurements.

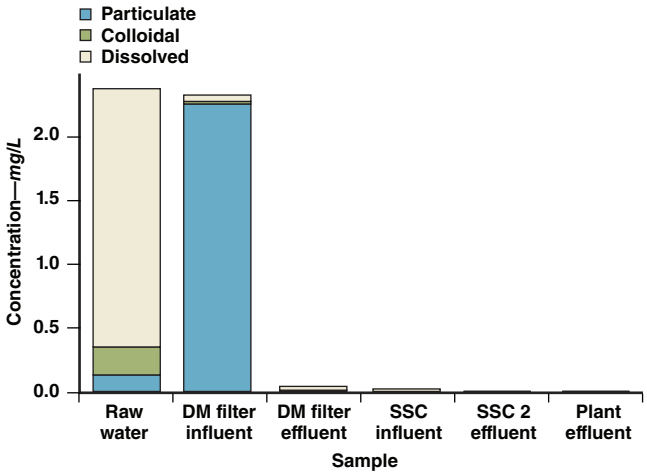
***Laboratory measurements.*** Metal measurements were made using an inductively coupled plasma mass spectrometer[11] (ICP-MS). Total and dissolved organic carbon were measured in accordance with Methods 5310 (*Standard Methods* 1998) using a total organic carbon analyzer.[12] TTHM concentration was determined using the USEPA 551.1 method (USEPA 1990), and HAA5 concentration using the USEPA 552.2 method (USEPA 1995) with

minor modifications. Gas chromatographs (GCs)[13] equipped with electron capture detectors were used. The temperature program used for HAA5 analysis was the same published by Brophy et al. (2000).

**Media and backwash particle characterization.** Contactor media $MnO_{x(s)}$ coating levels (mg-Mn/g media) were determined using the method published by Knocke et al. (1991). Approximately 1-g samples of dried media were subjected to reductive dissolution using hydroxylamine sulfate (HAS) and 250 mL of 2% by volume of trace metal grade nitric acid. Composite contactor backwash samples were similarly digested with approximately 1 g HAS/250 mL of backwash and 2% nitric acid. The resulting extract solution was diluted and analyzed by ICP-MS for Mn and other metals.

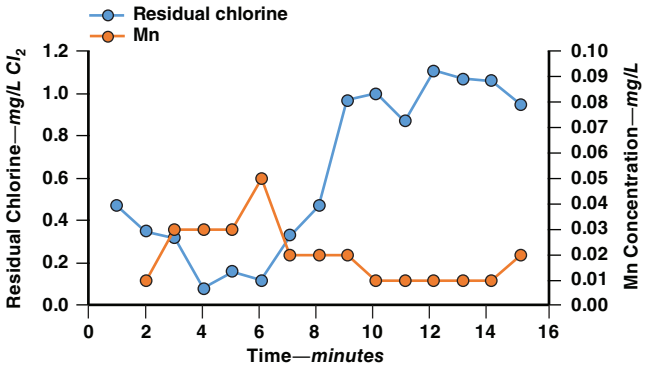
Scanning electron microcopy[14] (SEM) was performed on the $MnO_{x(s)}$–coated media and $MnO_{x(s)}$ particles of the composite contactor backwash sample. Samples were first dried for 48 h at 60°C, then mounted onto carbon tape and sputter coated[15] with platinum. The oxidation state of Mn in the backwash $MnO_{x(s)}$ was determined by X-ray photoelectron spectroscopy[16] (XPS) after Cerrato et al. (2010). X-ray diffraction[17] was performed on freeze-dried, as well as suspended, particles (in water) from contactor backwash.

**FIGURE 2** Iron fractionation across the Lantern Hill Water Treatment Plant on Aug. 27, 2013




DM—dual media, SSC—second stage contactor

**FIGURE 3** Contactor to waste Mn and residual chlorine concentrations post DM filter backwash on Nov. 11, 2013




DM—dual media, Mn—manganese

## RESULTS

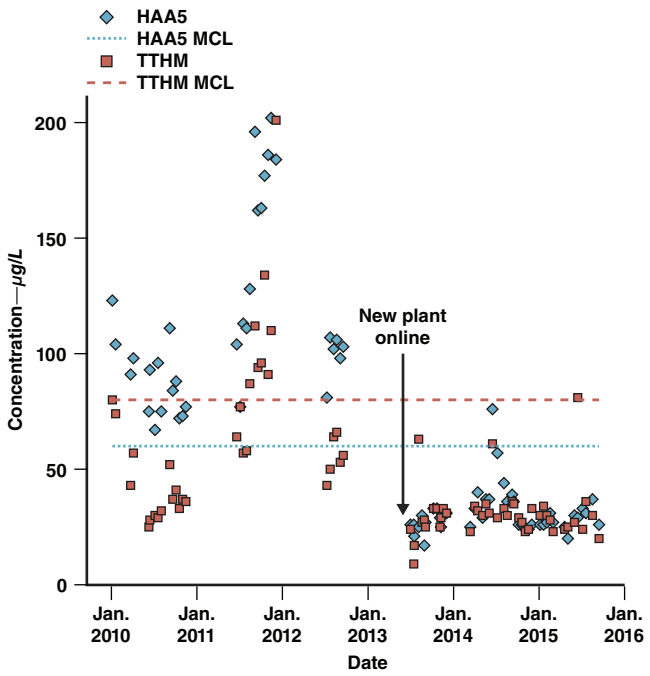
From its start-up in July 2013 to September 2015, the LHWTP flow rate ranged from 250 to 690 gpm, as determined by AWC personnel. The 1-mgd groundwater LHWTP is one of two treatment plants in Aquarion's Mystic System in Stonington, Conn., that produce potable water. The 2-mgd Deans Mill Surface Water Treatment Plant is the other facility in the Mystic System. AWC also has an interconnection with the neighboring town of Groton, Conn., which allows AWC to purchase water to meet demands. The LHWTP was off-line from Dec. 23, 2013, to Mar. 11, 2014, to complete construction. Overall, the new treatment train has performed very well. Metals and TOC removal were successful, and effluent DBP concentrations were low. Specifics of process performance are described herein.

**Dual media filtration: turbidity, iron, and NOM removal.** The filter influent chlorine-dosing objective is to achieve a dissolved iron concentration of less than about ~0.04 mg/L entering the dual media filters while leaving no free chlorine residual. Cationic polymer was also added to the influent for NOM precipitation ahead of the filters and to aid in controlling particle breakthrough. Dual media filter effluent turbidity was typically less than 0.1 ntu with turbidity breakthrough occurring earlier (<24 h) during periods of high flow. Fe removal was complete across the dual media filters (Figure 2) except in instances in which particle breakthrough occurred. Filter effluent Fe concentrations were less than 0.02 mg/L on average when breakthrough did not occur. When dual media filter breakthrough occurred, some Fe was removed by the SSCs (up to 0.3 mg-Fe/L), but not all because the SSCs are not designed for particle removal. Fe concentrations in the SSC backwash were elevated when these incidences occurred. As expected, very little Mn removal occurred across the dual media filters, at only 0.03–0.04 mg/L.

Decreases in TOC ranged from 1–2.5 mg/L across the dual media filters with no significant TOC removal observed across the SSCs. The $UV_{254}$ of the raw water was 0.16–0.18 $cm^{-1}$ and decreased to 0.04–0.06 $cm^{-1}$ in the filter effluent.

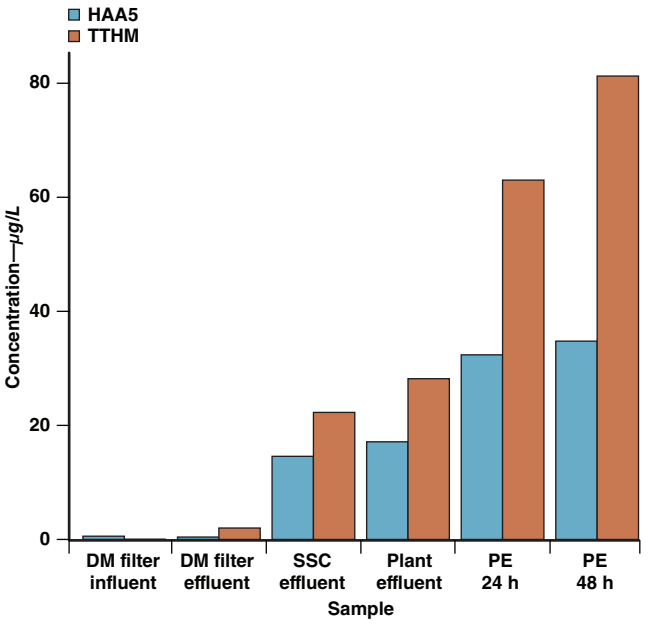
The dual media filters were backwashed approximately every 24 h using effluent from two filters to backwash the third, with a filter-to-waste period at the end of backwash. The entire filter backwash sequence duration was approximately 1.5 h, and there was no flow through the SSCs during this period. Initially after plant start-up, recurring drops in plant effluent free chlorine residual were observed after dual media filter backwash. This was attributed to chlorine demand exerted for oxidation of media-adsorbed Mn(II) in the contactors during the period of no flow; and thus no new influent chlorine. An increase in Mn with a decrease in $Cl_2$ residual in contactor-to-waste flow as seen in Figure 3 supports this hypothesis. To address the low effluent $Cl_2$ residual, the plant operation was changed to include

**FIGURE 4** Plant effluent DBP concentrations from 2010 to 2015




DBP—disinfection by-product, DM—dual media, HAA5—five haloacetic acids, MCL—maximum contaminant level, TTHM—total trihalomethanes

**FIGURE 5** Instantaneous across the Lantern Hill Water Treatment Plant, and 24- and 48-h SDS DBP concentrations on Aug. 29, 2013




DBP—disinfection by-product, DM—dual media, HAA5—five haloacetic acids, PE—plant effluent, SDS—simulated distribution system, SSC—second stage contactor, TTHM—total trihalomethanes

a contactor-to-waste period for about 10 min after completion of the dual media filter backwash.

**DBPs.** Effluent DBP concentrations for the redesigned LHWTP were significantly lower than for the original plant (Figure 4). The average HAA5 and TTHM effluent concentrations from July 2013 to September 2015 were 32.0 µg/L and 31.7 µg/L, respectively—well below their respective MCLs of 60 and 80 µg/L. The standard deviations were also low: 10 and 12 µg/L for HAA5s and TTHMs, respectively.

Measurement of DBPs concentrations across the plant showed an increase for Aug. 29, 2013 (Figure 5); the pre-filter chlorine dose was 3.01 mg/L and the contactor influent dose was 3.94 mg/L. Plant effluent SDS samples were held for 24 and 48 h and had relatively low DBP concentrations. Both 24- and 48-h HAA5 concentrations were below the HAA5 MCL; the 24-h sample TTHM concentration was below the TTHM MCL, and the 48-h sample was just above at 81.3 µg/L.

When the pre-filter chlorine dose was optimal, sufficient only for Fe(II) oxidation and leaving no residual, TTHM and HAA5 concentrations were typically lowest in the dual media influent. When the pre-filter chlorine dose was higher than the optimal dose, higher DBP concentrations resulted. For example, a pre-filter dose of 6.8 mg-$Cl_2$/L as compared with the average dose of 3.8 mg-$Cl_2$/L resulted in dual media influent HAA5 and TTHM concentrations of 19 and 22 µg/L, respectively, and plant effluent HAA5 and TTHM concentrations of 36 and 63 µg/L, respectively. Examination of available data showed no significant association between plant effluent DBP concentrations and dual media influent $UV_{254}$ absorbance, dual media effluent $UV_{254}$ absorbance, or plant effluent TOC concentration.

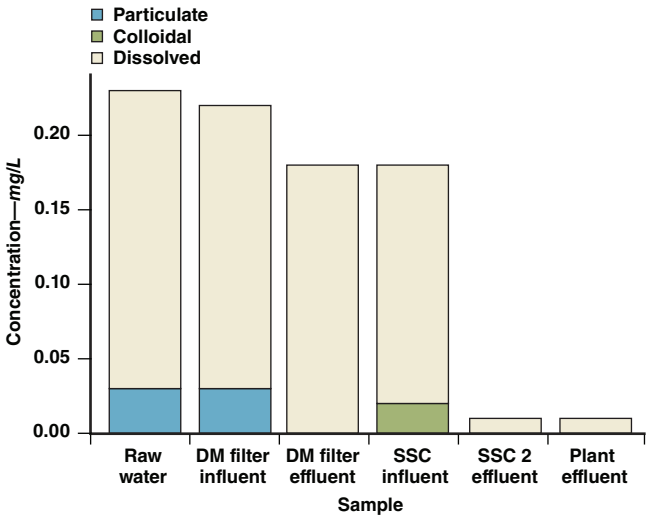
The plant is designed to employ pre-filter $KMnO_4$, which eliminates possible chlorine overdose and delays chlorine addition to post-filtration, potentially decreasing DBP formation, as observed by Corbin et al. (2003). However, practicing pre-filter Fe oxidation with $KMnO_4$ would add operational complexity of using a second oxidant, present the possibility of overdosing resulting in post-dual media filter permanganate that may create downstream concerns, and increase the overall amount of Mn in the treatment plant residuals.

**Second stage contactors.** ***Mn removal.*** Fractionation of Mn across the plant shows the forms of Mn and where removal occurs (Figure 6). Raw water Mn is nearly all dissolved, and dual media filter effluent Mn is all dissolved with about 10–20% removal across the filter, probably by association with precipitated Fe particles. This is expected on the basis of pre-filter oxidant dosing intended for Fe oxidation only and no free chlorine residual available for development of an $MnO_{x(s)}$ coating on the dual media filters. As designed, 80–90% of the Mn removal occurred across the SSCs. The Mn concentration entering the SSCs was approximately 0.14 mg/L, and effluent Mn concentrations were typically at or below the field method detection limit of 0.01 mg/L. The average contactor influent chlorine dose was 3.8 mg-$Cl_2$/L, and the pH ranged from 7.2 to 7.4. The average free chlorine residuals entering and leaving the SSCs were 1.5 and 0.9 mg-$Cl_2$/L, respectively.

***Contactor backwash.*** Because of the large size of the media in the contactors, the low influent turbidity, and lack of particle

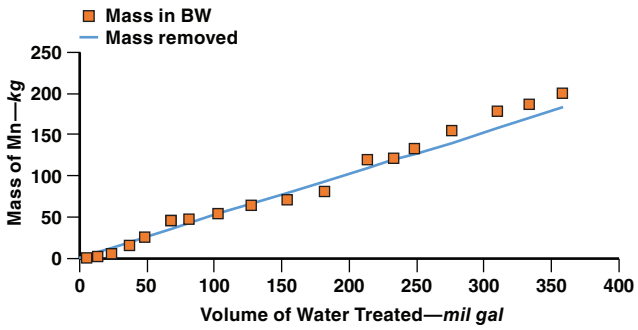
removal, as designed, the increase in head loss across the SSCs between backwashes was negligible. At lower plant flow rates (~350 gpm), SSC head loss was around 1.5 psi; at higher flows (~695 gpm), head loss was around 6 psi. Backwash was initially scheduled for every two weeks but changed to every six weeks because there was no noticeable increase in head loss and continued effective Mn removal. An SSC backwash schedule of every six to eight weeks with air scouring was adapted when it was determined from the mass balance (as described further within this study) that this did not adversely affect the oxide coating on the media. Similar to the dual media filters, the three SSCs were backwashed sequentially, with down flow through two contactors used to backwash the third contactor at an HLR of 14 gpm/ft$^2$ achieving ~15% bed expansion. After backwashing of the SSCs is complete, a 10-min contactor-to-waste period occurs to achieve stable Mn and chlorine levels prior to flow being directed to the distribution system.

**FIGURE 6** Manganese fractionation across the Lantern Hill Water Treatment Plant on Aug. 27, 2013




BW—backwash, DM—dual media, SSC—second stage contactor

**FIGURE 7** Cumulative mass of Mn removed and in backwash from July 2013 to September 2015




BW—backwash, Mn—manganese

After the initial few weeks of operation, recurring brief spikes in plant effluent turbidity but not in dual media filter effluent turbidity were observed after the approximately daily dual media filter backwash events. Investigations revealed that $MnO_{x(s)}$ particles were released from the contactor media when valves were operated to switch flow from contactor to waste (at atmospheric pressure for discharge) to the distribution system (at ~65 psi). System data have shown that the raw water pump flow briefly drops to zero, then increases rapidly to the production set point (or beyond) as the variable speed pump drive responds to the change in discharge pressure. It is likely that the SSC media were slightly agitated during this rapid flow change, leading to release of $MnO_{x(s)}$ particles. The impact was greater the longer the period of contactor operation without backwash. Operational changes have been made to minimize or eliminate the SSC effluent turbidity spike following the dual media filter backwash and contactor-to-waste sequence.

***Mn mass balance.*** Measurements of total Mn in digested composite contactor backwash samples were made to estimate the mass of Mn removed from the media during each backwash event. The mass of Mn removed by the contactors between backwash events was calculated using plant water production and average contactor influent and effluent Mn concentrations measured three times per week by utility personnel. Figure 7 compares the cumulative mass of Mn removed across the contactors and the estimated Mn mass in the contactor backwash for the cumulative volume of water treated from July 2013 to September 2015. Air scour was employed on Dec. 23, 2013 (68 mil gal treated), before taking the plant off-line to complete construction and again one year later on Dec.17, 2014 (213 mil gal treated). One contactor (1) was air scoured for approximately 1 min in March 2015 (249 mil gal treated) when the air scour was mistakenly left on. Air scouring was performed for all contactor backwash events starting on July 15, 2015 (310 mil gal treated).

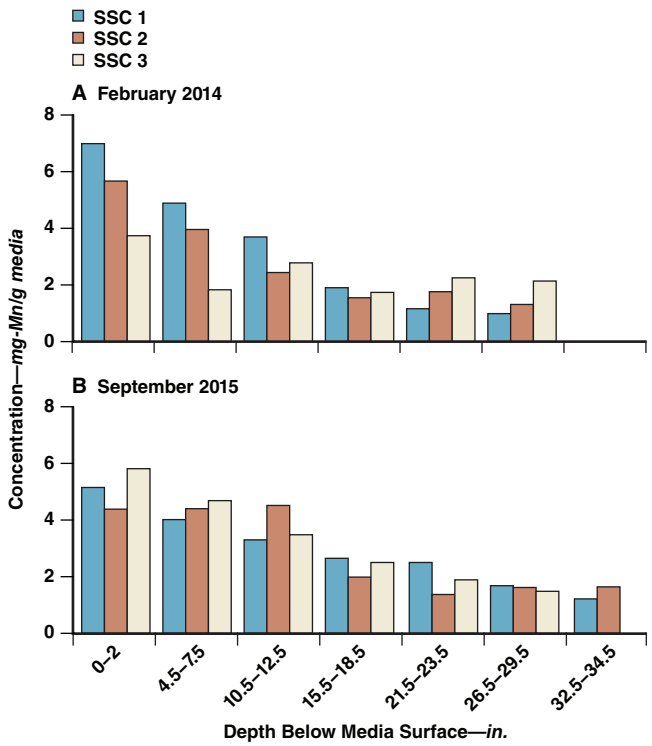
The total amount of Mn in the waste contactor backwash for the period (201 kg) is similar to the total amount of Mn removed by the contactors (183 kg). The 10% difference in the Mn removed by the contactors and the Mn in the backwash may be because of the underestimation of contactor Mn removal and/or overestimation of the Mn mass in the backwash. The mass of Mn removed by the contactors was calculated using the plant water production and the decrease in Mn concentration across the contactors. This does not take into account Mn removed by the contactors during periods of plant operation when the flow is wasted (e.g., during contactor to waste) and does not enter the distribution system.

***Media and backwash $MnO_{x(s)}$ characterization.*** Contactor media $MnO_{x(s)}$ coating levels were measured at the top of the media bed before plant start-up in June 2013. Depth $MnO_{x(s)}$ profiles were measured in February 2014 and September 2015 (Figure 8). Prior to start-up, the $MnO_{x(s)}$ coating levels at the top of the three contactors were 3.7, 3.4, and 2.5 mg-Mn/g media; in February 2014 the coating levels 0–4 in. from the media surface were 7.0, 5.7, and 3.7 mg-Mn/g media for contactors 1–3, respectively. In September 2015, the coating levels of the top 2 in. of the media beds were 5.2, 4.4, and 5.8 mg-Mn/g media, respectively, for the three contactors. The oxide coating levels at the top of the media increased significantly from the initial coating before

start-up to the February 2014 sampling, while the levels in September 2015 were similar to or higher than the levels in February 2014. Contactor backwash, with and without air scouring, clearly did not remove all the $MnO_{x(s)}$ coating, leaving levels sufficient for needed Mn(II) adsorption.

Depth profiles showed greater $MnO_{x(s)}$ coating levels at the top of the media beds in all three contactors, at approximately 5.3 mg-Mn/g media, which generally decreased with increasing depth to about 1.5 mg-Mn/g media at depths below ~30 in. Profile measurements made in September 2015 indicated levels from 5.1 to 3.8 mg-Mn/g media for the first 13 in., and lower levels of approximately 2.4–1.5 mg-Mn/g media for the remainder of the bed. Similarly, measurements made in February 2014 ranged from 5.5 to 3.0 mg-Mn/g media for the first 13 in., and 1.7 to 1.5 mg-Mn/g media for the remainder of the bed. This profile is similar to data showing that the majority of Mn removal occurs toward the top of a fixed media bed in general (Islam et al. 2010, Knocke et al. 1991) and in the LHWTP lab and pilot studies conducted prior to full-scale design (Chihoski 2012). The contactor media profile for the mono media bed of porous ceramic media indicates that the media are not completely mixed by backwashing. This could reflect differences in media size and/or density such that some bed stratification is maintained after backwashing. In addition, available water depth above the media limits the extent of expansion and thus likely decreases the likelihood of full depth media mixing.

**FIGURE 8** SSC media $MnO_{x(s)}$ coating depth profiles for February 2014 (A) and September 2015 (B)




$MnO_{x(s)}$—manganese oxide, SSC—second stage contactor

SEM images of the $MnO_{x(s)}$–coated porous ceramic media and $MnO_{x(s)}$ particles in waste contactor backwash samples are shown in Figure 9. As expected, images of the waste backwash particles show clusters of particles similar to those observed on the surface of the $MnO_{x(s)}$–coated media.

XPS analysis of the contactor backwash particles indicated that Mn in the $MnO_{x(s)}$ was in the +4 oxidation sate. This is in agreement with Cerrato et al. (2011) who showed that Mn removal by sorption and catalytic oxidation in the presence of chlorine resulted in $MnO_{2(s)}$. X-ray diffraction analysis of the LHWTP backwash particles showed one small peak at a diffraction angle (2θ) of approximately 36.5 degrees (2.43 Å). The diffraction pattern with a low degree of crystallinity is similar to the amorphous δ-$MnO_2$ characterized by Morgan and Stumm (1964) and Murray (1974).

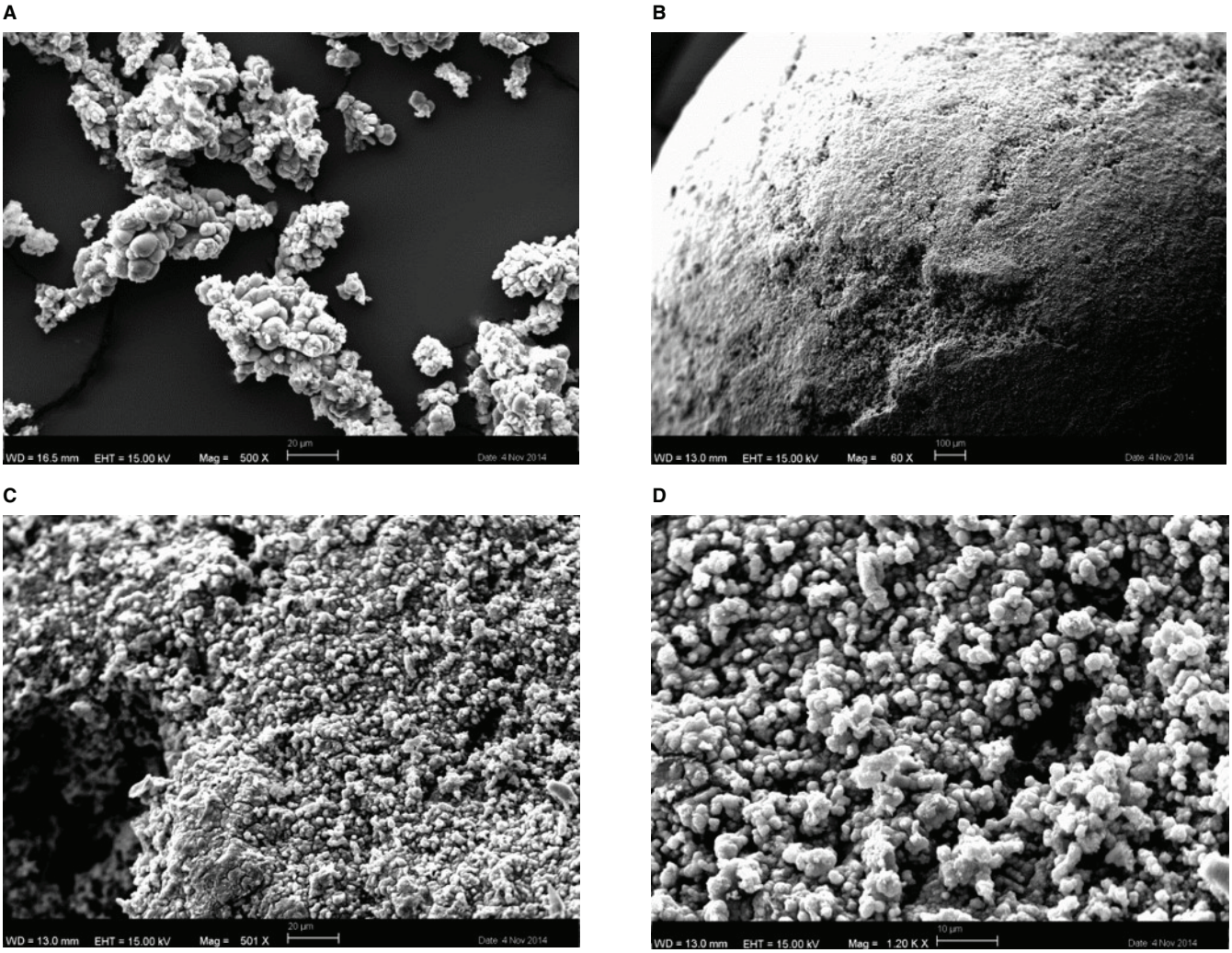
## BROADER TREATMENT APPLICATIONS

The SSCs for the LHWTP groundwater source were implemented specifically for the removal of Mn(II) following removal of particles by upstream treatment processes. There are a number of situations in which high HLR, coarse media, contactors for robust control of dissolved Mn in plant effluent may be an effective and optimal treatment alternative. For surface waters with seasonally elevated raw water Mn, use of SSCs with free chlorine allows for upstream biologically active media filtration, with decreased or eliminated raw water strong oxidant addition as the contactors function effectively for variable levels of Mn(II). Free chlorine use can achieve both Mn control and primary disinfection, as well as provide a distribution system disinfectant residual. For groundwaters with multiple contaminants, and especially NOM, separation of processes for particle removal and Mn(II) removal can provide a more effective and reliable treatment process as compared with single-stage approaches. Increasing health-based attention to control of Mn in finished water may lead to the need for Mn removal from sources that have relatively low levels of Mn. These sources may be amenable to removal by high-rate coarse media contactors with lower energy demand as compared with traditional "greensand" type approaches using finer media.

## CONCLUSIONS

Implementation of SSCs for removal of Mn(II) after first-stage dual media filtration for particle removal was successful at the full scale for a groundwater source. The use of this approach was driven by the desire to use a single pumping step from well to distribution system (necessitating direct filtration) and also to achieve both metals removal and DBP control. Delaying the addition of chlorine for catalytic Mn(II) oxidation until after particle and some NOM removal (by dual media filtration) resulted in a drastic decrease in plant effluent DBP concentrations compared with levels from the original plant design. Effluent Mn concentrations of <0.01 mg/L were consistently achieved while maintaining low DBP concentrations. A mass balance showed that the Mn removed by the SSCs was reflected in the Mn present in the infrequent waste contactor backwash.

**FIGURE 9** SEM images of contactor backwash $MnO_{x(s)}$ particles (magnification 500×) (A) and $MnO_{x(s)}$–coated Macrolite (porous ceramic media) at magnifications of 60× (B), 500× (C), and 1,200× (D)




**$MnO_{x(s)}$—manganese oxide, SEM—scanning electron microscope**

This study shows that SSCs can be implemented for Mn(II) removal at full scale. Use of SSCs would allow plants to practice post-filter chlorination (e.g., to enable use of biofiltration or to control DBP formation) even if they experience seasonal elevated Mn(II) concentrations in the raw water.

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## ENDNOTES

[1]Macrolite M7, Fairmount Water Solutions, Chardon, Ohio
[2]Tighe & Bond, Westfield, Mass.
[3]Superfloc C-500 series, Kemira, Atlanta, Ga.
[4]Derek French, Wateropolis Inc., Toronto, Ont.
[5]Nuclepore, Whatman, Clifton, N.J.
[6]Millipore, Billerica, Mass. Amicon, Beverly, Mass.
[7]Millipore Ultracel, Millipore, Billerica, Mass.
[8]Best Harvest Farm and Home Testing Equipment, Largo, Fla.
[9]Hach Pocket Colorimeter IITM Manganese, Iron (FerroVer®), and free chlorine kits, Hach, Loveland, Colo.
[10]Hach 2100 N Turbidimeter, Hach, Loveland, Colo.
[11]Elan 9000, Perkin Elmer, Waltham, Mass.
[12]Shimadzu TOC-VCPH, Shimadzu, Kyoto, Japan
[13]Agilent Technologies 6890 Network, Santa Clara, Calif.
[14]Zeiss EVO 50 SEM, Zeiss, Jena, Germany
[15]Edwards Xenosput XE200, Edwards, Inc., Tewksbury, Mass.
[16]Phi Quantum 2000 spectrometer, Physical Electronics Inc. (a division of ULVAC-Phi), Chanhassen, Mn.
[17]PANalytical X'Pert PRO X-ray diffraction system, PANalytical Inc., Westborough Mass.

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## REFERENCES

Brandhuber, P.; Clark, S.; Knocke, W.; & Tobiason, J., 2013. *Guidance for the Treatment of Manganese*. Water Research Foundation, Denver.

Brophy, K.S.; Weinberg, H.S.; & Singer, P.C., 2000. Quantification of Nine Haloacetic Acids Using Gas Chromatography With Electron Capture Detection. *Natural Organic Matter and Disinfection By-Products: Characterization and Control in Drinking Water, ACS Symposium Series 761* (S.E. Barrett; S.W. Krasner; & G.L. Amy, editors). American Chemical Society, Washington.

Brown, M., 2006. The Relationship Between Pre-filter Chlorine Addition and Enhanced Disinfection Byproduct Formation. Master's thesis, Department of Civil and Environmental Engineering, University of Massachusetts, Amherst, Mass.

Carlson, K.H.; Knocke, W.R.; & Gertig, K.R., 1997. Optimizing Treatment Through Fe and Mn Fractionation. *Journal AWWA,* 89:4:162.

Cerrato, J. M.; Knocke, W.R.; Hochella, M.F. Jr.; Dietrich, A.M.; Jones, A.; & Cromer, T.F., 2011. Application of XPS and Solution Chemistry Analyses to Investigate Soluble Manganese Removal by $MnO_{x(s)}$-Coated Media. *Environmental Science & Technology,* 45:23:10068. http://dx.doi.org/10.1021/es203262n.

Cerrato, J.M.; Hochella, M.F. Jr.; Knocke, W.R.; Dietrich, A.M.; & Cromer, T.F., 2010. Use of XPS to Identify the Oxidation State of Mn in Solid Surfaces of Filtration Media Oxide Samples From Drinking Water Treatment Plants. *Environmental Science & Technology*, 44:15:5881. http://dx.doi.org/10.1021/es100547q.

Chihoski, J., 2012. Evaluation of Second-Stage Contactor Media for Manganese Removal. Master's thesis, Department of Civil and Environmental Engineering, University of Massachusetts, Amherst, Mass.

Corbin, M.J.; Reckhow, D.A.; Tobiason, J.E.; Dunn, H.J.; & Kaminski, G.S., 2003. Controlling DBPs by Delaying Chlorine Addition Until After Filtration. *Journal of the New England Water Works Association,* 117:4:243.

Gabelich, C.J.; Gerringer, F.W.; Knocke, W.R.; & Lee, C.C., 2006. Sequential Manganese Desorption and Sequestration in Anthracite Coal and Silica Sand Filter Media. *Journal AWWA*, 98:5:116.

Health Canada, 2016. Manganese in Drinking Water: Document for Public Consultation. Federal-Provincial-Territorial Committee on Drinking Water, Water and Air Quality Bureau, Ottawa, Ont.

Islam, A.A.; Goodwill, J.E.; Bouchard, R.; Tobiason, J.E.; & Knocke, W.R., 2010. Characterization of Filter Media MnOx(s) Surfaces and Mn Removal Capability. *Journal AWWA,* 102:9:71.

Islam, A.A., 2010. Manganese Removal by Media Filtration: Release and Complexation. Doctoral dissertation, Department of Civil and Environmental Engineering, University of Massachusetts, Amherst, Mass.

Knocke, W.R.; Zuravnsky, L.; Little, J.C.; & Tobiason, J.E., 2010. Adsorptive Contactors for Removal of Soluble Manganese During Drinking Water Treatment. *Journal AWWA*, 102:8:64.

Knocke, W.R.; Occiano, S.C.; & Hungate, R., 1991. Removal of Soluble Manganese by Oxide-Coated Filter Media: Sorption Rate and Removal Mechanism Issues. *Journal AWWA*, 83:8:64.

Knocke, W.R.; Hoehn, R.C.; & Sinsabaugh, R.L., 1987. Using Alternative Oxidants to Remove Dissolved Manganese From Waters Laden With Organics. *Journal AWWA*, 79:3:75.

Kohl, P.M.; & Medlar, S.J., 2007. Occurrence of Manganese in Drinking Water and Manganese Control. Water Research Foundation, Denver.

Morgan, J.J.; & Stumm, W., 1964. Colloid-Chemical Properties of Manganese Dioxide. *Journal of Colloid Science*, 19:4:347. http://dx.doi.org/10.1016/0095-8522(64)90036-4.

Murray, J.W., 1974. The Surface Chemistry of Hydrous Manganese Dioxide. *Journal of Colloid and Interface Science*, 46:3:357. http://dx.doi.org/10.1016/0021-9797(74)90045-9.

Pham, M., 2010. Two-Stage Filtration to Control Manganese and DBPs at the Lantern Hill Water Treatment Plant. Master's thesis, Department of Civil and Environmental Engineering, University of Massachusetts, Amherst, Mass.

Richardson, S.D.; Plewa, M.J.; Wagner, E.D.; Schoeny, R.; & DeMarini, D.M., 2007. Occurrence, Genotoxicity, and Carcinogenicity of Regulated and Emerging Disinfection By-Products in Drinking Water: A Review and Roadmap for Research. *Mutation Research/Reviews in Mutation Research*, 636:1–3:178.

Russell, J., 2008. Control of Manganese, Iron, and Disinfection By-Products for the Mystic Connecticut Water System. Master's thesis, Department of Civil and Environmental Engineering, University of Massachusetts, Amherst, Mass.

Sly, L.I.; Hodgkinson, M.C.; & Arunpairojana, V., 1990. Deposition of Manganese in a Drinking Water Distribution System. *Applied and Environmental Microbiology*, 56:3:628.

*Standard Methods for the Examination of Water and Wastewater*, 1998 (20th ed.). APHA, AWWA, and WEF, Washington.

Tobiason, J.E.; Islam, A.A.; Knocke, W.A.; Goodwill, J.E.; Hargette, P.H.; Bouchard, R.; & Zuravnsky, L., 2008. Characterization and Performance of Filter Media for Manganese Control. AWWA Research Foundation, Denver.

USEPA (US Environmental Protection Agency), 2006. *National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule*. EPA 71 FR 387, Washington.

USEPA, 2004. *Drinking Water Health Advisory for Manganese*. USEPA Health and Ecological Criteria Division, Office of Water, Washington.

USEPA, 1995. *Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatization and Gas Chromatography With Electron Capture Detection, Method 552.2*, USEPA, Cincinnati, Ohio.

USEPA, 1992. *Secondary Drinking Water Regulations: Guidance for Nuisance Chemicals*. EPA-810/K-92-001, USEPA, Washington.

USEPA, 1990. *Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron-Capture Detection, Method 551.1*, USEPA, Cincinnati, Ohio.