Low-temperature effects on the removal of soluble manganese in MnO$_x$(s)-coated media systems

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ABSTRACT

The purpose of this study was to investigate the role of low-temperature conditions in potentially impacting soluble Mn^{2+} removal in MnO$_x$(s)-coated media systems. The study involved an extensive examination of water quality and process data for a 10-year period (2005–2014) from the Harwood's Mill Water Treatment Plant in Newport News, VA. Additionally, laboratory-scale shallow depth column studies were performed employing MnO$_x$(s)-coated media for soluble Mn^{2+} removal. Data were evaluated for the impacts of low temperature conditions, water pH, soluble Mn^{2+} concentration, and free chlorine concentration on the ability of MnO$_x$(s)-coated media to promote effective soluble Mn^{2+} removal. The results show that the uptake of soluble Mn^{2+} onto MnO$_x$(s)-coated filter media is significantly impacted by water temperatures below 15 °C, with impacts being very substantial under lower temperature (T < 10 °C) conditions. Also, the adverse effects of low temperature on MnO$_x$(s)-coated treatment processes can be at least partially mitigated by an increase in solution pH.

Key words | Mn control, pH impacts, temperature impacts

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INTRODUCTION AND RESEARCH OBJECTIVES

The removal of soluble manganese (Mn) in water treatment facilities is often necessary to minimize the potential for water discoloration and complaints by consumers. While aesthetic (discoloration) issues have been the primary motivation historically for practising Mn removal research, studies have documented potential health effects due to elevated Mn in drinking water (Liu 2005; Menezes-Filho et al. 2011). Such concerns have prompted Health Canada (2016) to propose a legally enforceable, health-based drinking water standard of 0.10 mg/L. The US Environmental Protection Agency likewise added Mn to its most recent promulgation of the EPA Critical Contaminants List (CCL4).

A common treatment process for soluble Mn^{2+} removal is the natural greensand effect (NGE) during granular media filtration, which has proven to be very effective over a wide range of raw water conditions (Griffin 1960; Knocke et al. 1988, 1991; Coffey et al. 1993; Hu et al. 2004; Brandhuber et al. 2013). During the NGE process, soluble Mn^{2+} ions are adsorbed to manganese oxide-coated (MnO$_x$(s)) media. The adsorbed Mn^{2+} is then oxidized by chlorine, forming more MnO$_x$(s) to become part of the coating structure. The MnO$_x$(s) coating level is increased over time through a continuous process of Mn^{2+} adsorption and oxidation, and the resulting media is available for the adsorption of additional soluble Mn^{2+} ions (Merkle et al. 1997a, 1997b). Studies have shown that the adsorptive uptake process for soluble Mn^{2+} on MnO$_x$(s)-coated media depends on: (1) the presence of a free chlorine residual in the filter-applied water, (2) a filter-applied pH of greater than 6.0, and (3) the presence of soluble Mn^{2+} for adsorptive uptake (Brandhuber et al. 2013). While such coatings typically develop naturally over time, researchers have demonstrated means by which MnO$_x$(s) coatings can be deposited on anthracite coal and sand media at significantly faster rates than occur

naturally in water treatment situations (Merkle *et al.* 1997b; Bazilio *et al.* 2016).

Anecdotal evidence has demonstrated that the removal of soluble Mn^{2+} by $MnO_x(s)$-coated media may be negatively impacted by low water temperatures. Charlton *et al.* (2002) found that low water temperature (<10 °C) hindered Mn control through $MnO_x(s)$-coated media filtration at a pilot plant in Philadelphia, even with a filter-applied free chlorine concentration of 1.0 mg/L. The authors found effective Mn control to be directly correlated with both pH and temperature, at least under low water temperature conditions. Kohl & Medlar (2006) looked at temperature effects on the NGE process and found that as the water temperature decreased, the ability of the NGE process to control Mn decreased (see Figure 1). As seen in Figure 1, Mn control was seemingly more variable at temperatures less than 10 °C. The authors pointed out that as the filter-applied water pH increased, the variability of Mn control started at a lower temperature. Additionally, as the pH increased, the variability of the effluent Mn concentration decreased.

The primary purpose of this study was to further investigate the potential of low-temperature conditions to impact the removal of soluble Mn^{2+} in $MnO_x(s)$-coated media systems. The specific objectives of the study were as follows:

1. Evaluate the ability of $MnO_x(s)$-coated media to promote effective soluble Mn^{2+} removal as a function of water temperature, and to determine how observed Mn removal varies with pH conditions and free chlorine concentration.
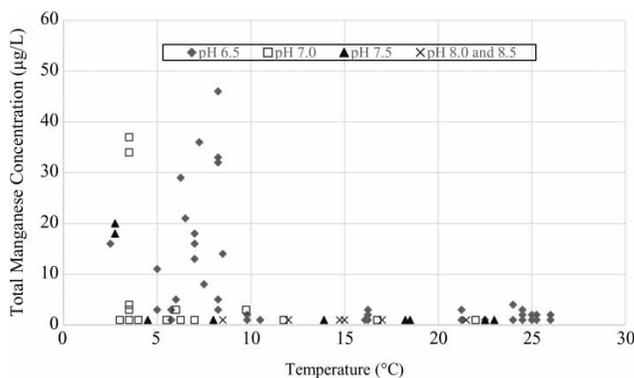

Figure 1 | Pilot plant total Mn effluent concentration as a function of temperature (Data from Kohl & Medlar 2006).

2. Identify a potential way to mitigate any potential negative temperature effects through process modifications. The primary process modification considered was pH adjustment of the water being applied to the $MnO_x(s)$-coated filter media.

To accomplish the stated objectives, water quality and process data for a 10-year period (2005 to 2014) were obtained from the Harwood's Mill Water Treatment Plant in Newport News, VA. Additionally, data were obtained from laboratory-scale column studies that employed shallow depths (up to 25 cm (10 inches)) of $MnO_x(s)$-coated filter media for soluble Mn^{2+} removal. Data were evaluated for the impacts of low temperature conditions, water pH, and free chlorine concentration on the ability of $MnO_x(s)$-coated media to promote effective soluble Mn^{2+} removal.

EXPERIMENTAL METHODS AND MATERIALS

This research effort was closely coordinated with the Newport News Water Authority in Newport News, Virginia. Harwood's Mill Water Treatment Plant is one of two major water treatment facilities operated by the Authority. The unit operations utilized at the Harwood's Mill plant include pre-oxidation/reaction (seasonal use), flash mixing/coagulation, ultra-high rate clarification, high rate filtration, pH adjustment and corrosion inhibitor chemical addition, and finished water storage. The filters consist of approximately 1 m of media, with approximately two thirds of the media depth being anthracite coal and the remaining depth in silica sand. The hydraulic loading rate (HLR) under normal operations is approximately 5 m/hr (2 gal/min-ft^2). Treatment at the Harwood's Mill plant includes the addition of free chlorine to the filter-applied water, resulting in the uptake of soluble Mn^{2+} across the filters and a substantial accumulation of $MnO_x(s)$ coating on the filter media. This coating helps promote very effective soluble Mn^{2+} removal (Brandhuber *et al.* 2013). While the US Environmental Protection Agency has promulgated a secondary (suggested; non-enforceable) maximum contaminant level for Mn in drinking water of 0.05 mg/L, the Authority has set its own operational goal for finished

water Mn concentration of 0.015 mg/L. This Mn goal was established to lower the total Mn loading released annually to the distribution system, with hopes to reduce the potential for chronic buildup of Mn in the system and minimize the potential for consumer complaints related to water discoloration. Such an operational goal is based upon the published work of Sly et al. (1990) and Kohl & Medlar (2006) who recommended water utilities keep finished water Mn concentrations at or below 0.02 mg/L to address water discoloration complaint potential.

Water quality and process data for a 10-year period (2005–2014) were obtained from plant personnel at the Harwood's Mill Water Treatment Plant. Data were evaluated for the impacts of low temperature conditions, water pH, soluble Mn^{2+} concentration, and free chlorine concentration on the ability of $MnO_x(s)$-coated media to promote effective soluble Mn^{2+} removal. The data collected were stored in Microsoft Excel, which was used for data organization and comparison. JMP 12.1.0 statistical discovery software was used for statistical analysis (SAS Institute).

A statistical analysis (one-way analysis of variance) determined that differences in free chlorine residual (after water filtration) did not significantly impact the filter effluent soluble Mn^{2+} concentration as long as the free chlorine concentration was at least 0.5 mg/L. As such, the analysis for the Harwood's Mill treatment facility utilized only data wherein the free chlorine concentration was above 0.5 mg/L (which represented 98% of the overall values in the 10-year data set, since the Authority seeks to maintain a filtered water free chlorine concentration above 0.5 mg/L). Values for finished water soluble Mn^{2+} concentrations under conditions with a filtered water free chlorine residual less than 0.5 mg/L were not included in the data evaluation.

Laboratory-scale filter column experiments were also conducted as part of this research effort. Small-diameter (1.1 cm (7/16 inch) ID) glass columns were filled to a depth of 25 cm (10 in) with fully regenerated (using contact with free chlorine), $MnO_x(s)$-coated anthracite coal media from the Harwood's Mill Water Treatment Plant. The media had approximately 40 mg of extractable Mn present in the $MnO_x(s)$ coating per g of media (Mn extraction was performed using sample processing and analysis methods described by Tobiason et al. (2008)).

Two separate feed solutions were prepared and stored for feeding to the test columns. One contained the soluble Mn^{2+} feed and associated background ion concentrations. The second solution contained the same background ion concentrations and free chlorine at a concentration to produce the desire free chlorine dosage once the solutions were mixed just prior to addition to the column of media. The combined flowrate resulted in a HLR to the columns of approximately 10 m/hr (4 gpm/ft^2). This HLR yielded an empty bed contact time (EBCT) of 0.6 minutes in the 10-cm media depth column, and 1.6 minutes in the 25-cm media depth column. The columns were set up initially under room temperature (20–22 °C) for the first part of the experiment. An incubator and temperature control room were utilized to evaluate lower temperature conditions.

Column influent water quality characteristics were controlled to ensure that water applied to the $MnO_x(s)$-coated media was similar to filter-applied water for the Harwood's Mill facility. Influent soluble Mn^{2+} concentrations varied between 0.15–0.20 mg/L and involved addition of Mn from a stock solution prepared by dissolving manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) in high-purity distilled/deionized water. The alkalinity (from sodium bicarbonate addition) was targeted at 30–40 mg/L as $CaCO_3$. The desired range of free chlorine concentrations was 2.0–2.5 mg/L in order to achieve an effluent free chlorine concentration of approximately 1.0 mg/L. The pH values ranged from 5.7 to 7.9 and involved addition of dilute hydrochloric acid as needed to achieve the desired pH value in a given column experiment.

A HACH DR/2700 benchtop spectrophotometer was used to measure free chlorine concentration using the N, N-diethyl-p-phenylene-diamine method (HACH Method 8021) and reagents with a maximum detection limit of 2.0 mg/L as Cl_2. A Thermo Electron Corporation X-Series inductively coupled plasma mass spectrometer (ICP-MS) was used for soluble Mn^{2+} analysis. Ten mL of sample were collected in capped plastic ICP sample tubes and acidified to 2% nitric acid. Samples were analyzed using the laboratory method, which uses standard SM-1517-014. Limited testing of samples collected following passage through the column of media showed that it was not necessary to further process the samples by filtration prior to Mn analysis; instead, these tests demonstrated that it was

reasonable to assume that any Mn present in the column effluent was soluble Mn^{2+}.

The solution pH and temperature were measured with a portable HACH multi-parameter Model HQ40d meter and probe. The meter was calibrated before each use with buffers of pH 4, 7, and 10. For the low-temperature experiments, buffer solutions were stored at the same temperature as the corresponding column experiment, and the pH meter was calibrated at that temperature. Data from ICP-MS output as well as data collected in the laboratory were stored in a carbon copy notebook as well as in Microsoft Excel for organization and analysis.

EXPERIMENTAL RESULTS

Evaluation of Mn data from the full-scale Harwood's Mill water treatment facility

Data related to water temperature and filtered water Mn concentration for the full-scale Harwood's Mill treatment facility are presented in Figure 2. The data show an apparent relationship between the finished water soluble Mn^{2+} concentration (following filtration through $MnO_x(s)$-coated

filter media) and corresponding water temperature over the 10-year period of interest evaluated in this study. The data clearly indicate that temperature and finished water soluble Mn^{2+} concentration were inversely related, especially during the coldest water temperature conditions. As water temperature decreased during months with colder temperature conditions, soluble Mn^{2+} concentrations leaving the $MnO_x(s)$-coated media filters increased quite substantially, even when the filtered-water free chlorine concentrations were at or above 0.7–1.0 mg/L (which is normally recommended as being sufficient to keep the $MnO_x(s)$ coating on filter media in a well-regenerated state (Brandhuber et al. 2013)).

Data presented in Figures 3–5 identify an apparent relationship between water temperature and filtered water Mn concentration for certain specific pH ranges (the number of data points in the pH range below 6.0 was fairly small, so the data presentation focuses on these three pH conditions of interest). Evaluation of these data indicates a broader range of temperature conditions where it was difficult to achieve the desired 0.015 mg/L Mn concentration in the pH 6–6.3 range of operation (Figure 3). In comparison, the pH 6.3–6.6 range of operation (Figure 4) showed challenges in achieving this effluent Mn
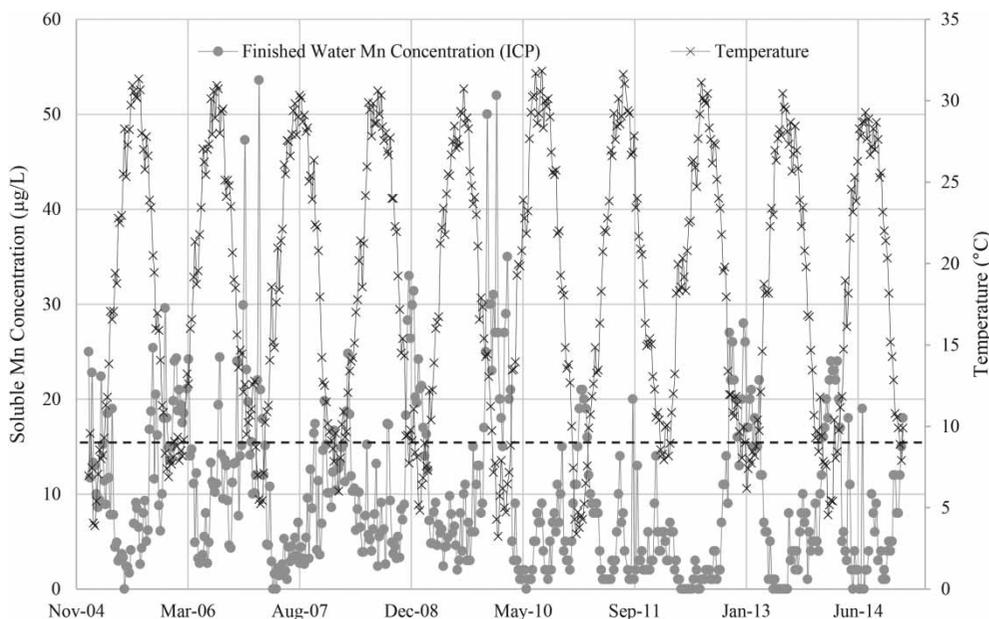

Figure 2 | Historical data for finished water manganese concentration and corresponding water temperature for the Harwood's Mill water treatment facility (dashed horizontal line at 15 μg/L denotes Newport News Water Authority operational goal for finished water Mn concentration).
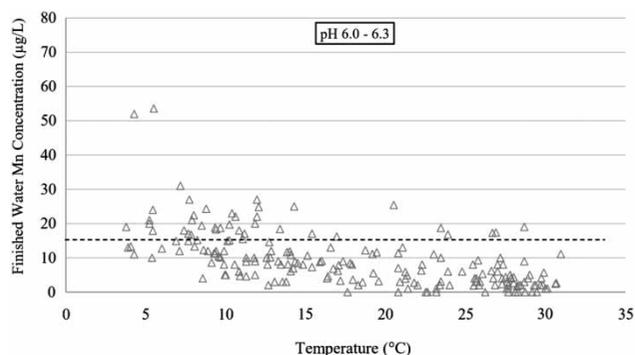
Figure 3 │ Finished water soluble Mn concentration as a function of solution temperature for pH 6.0–6.3.
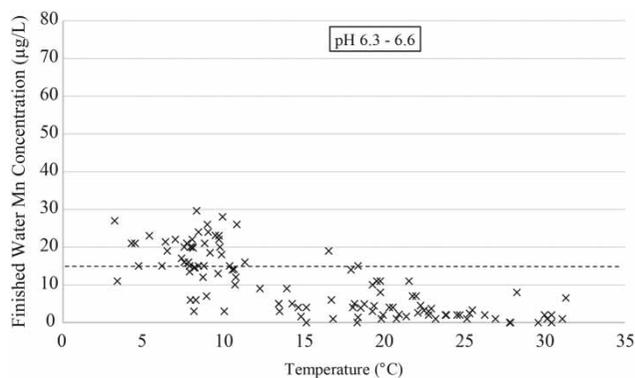

Figure 4 │ Finished water soluble Mn concentration as a function of solution temperature for pH 6.3–6.6.
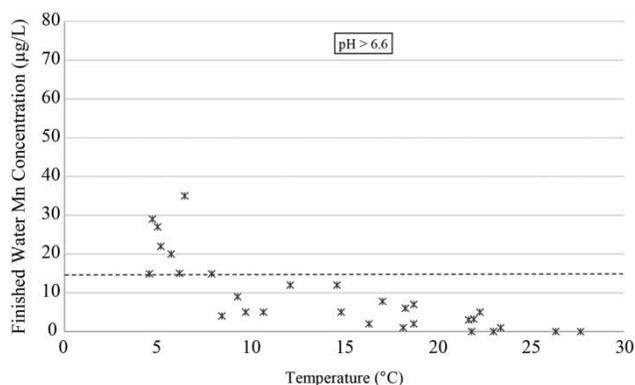

Figure 5 │ Finished water soluble Mn concentration as a function of solution temperature for pH > 6.6.

concentration only when the temperature was at or below 10 °C; likewise, for the pH > 6.6 operating range (Figure 5) the effluent Mn concentration exceeded 0.015 mg/L only under very low (4–7 °C) temperature conditions.

Information presented in Figure 6 shows mean soluble Mn^{2+} concentration as a function of the filter-applied water pH and water temperature. The interactions between different pH and temperature groups were compared statistically via a two-way analysis of variance with Tukey's Honest Significant Difference (Tukey's HSD). The analysis of variance showed a significant statistical difference between soluble Mn^{2+} concentrations for different levels of pH and temperature interaction. According to Tukey's HSD, average soluble Mn^{2+} concentrations were statistically different for interactions between high and low temperature conditions and high and low pH conditions.

Laboratory-scale column results

A series of experiments was conducted in small-scale filter columns that contained samples of $MnO_x(s)$-coated anthracite coal that was obtained from a full-scale filter at the Harwood's Mill Water Treatment Plant. The media was initially exposed to a high-strength (at least 10 mg/L as Cl_2) free chlorine solution to regenerate the $MnO_x(s)$ coating present; likewise, the media was maintained with approximately 1 mg/L free chlorine residual in the filtrate water during all experiments as this free chlorine concentration helps to ensure effective $MnO_x(s)$ surface regeneration (Brandhuber et al. 2013). Samples were collected for analysis at both 10-cm and 25-cm media depths during these column experiments. These media depths were well below the standard media depths used in full-scale, dual-media water filters (typically from 0.7 to 1 m (24 to 36 inches) of media); however, they were selected to help ensure the presence of significant residual Mn concentrations after exposure to the $MnO_x(s)$-coated media in the columns so that the effect of various parameters on soluble Mn^{2+} removal could be better evaluated.

Data from the laboratory-scale column studies (shown in Figures 7 and 8) show pH-sorted soluble Mn^{2+} concentrations as a function of temperature for the 10-cm media depth and the 25-cm media depth, respectively. As was seen in the full-scale Harwood's Mill data evaluation, a decrease in water temperature yielded a decreased ability of the $MnO_x(s)$-coated media to remove soluble Mn^{2+} at either media depth. In general, as both the temperature
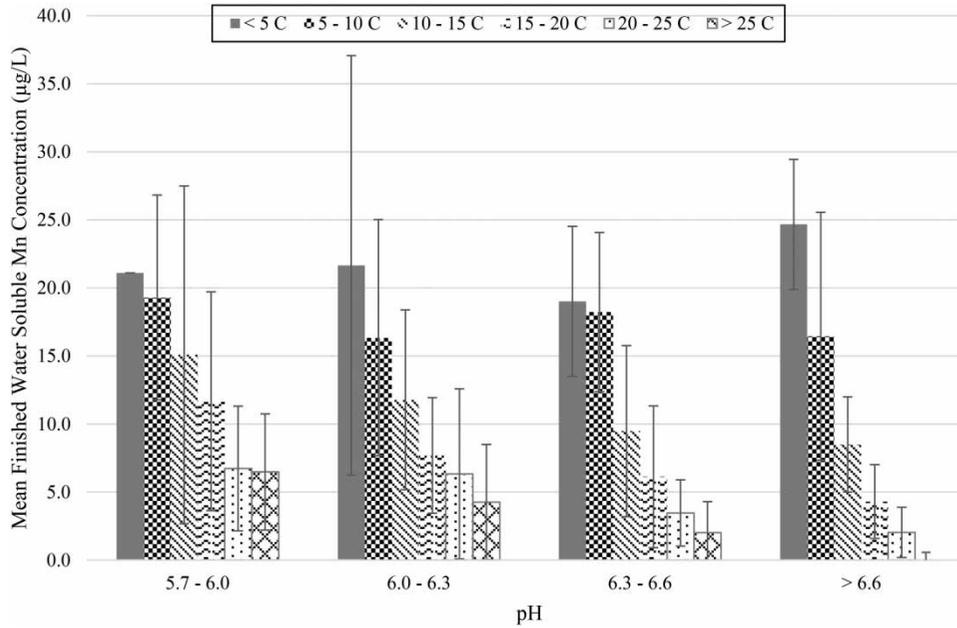
Figure 6 │ Mean filter effluent soluble Mn concentration as a function of pH and temperature.
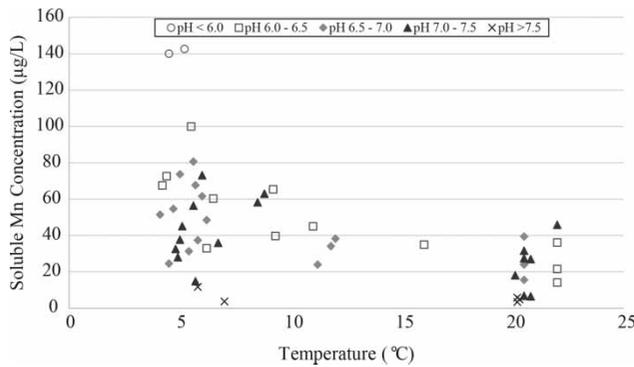

Figure 7 │ pH sorted laboratory-scale filter effluent soluble Mn concentration as a function of solution temperature for a 10-cm media depth.
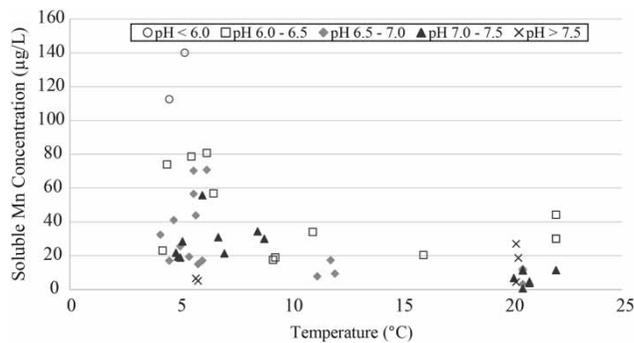

Figure 8 │ pH sorted laboratory-scale filter effluent soluble Mn concentration as a function of temperature for a 25-cm media depth.

and pH decreased, the soluble Mn^{2+} concentration in the column increased. For example, soluble Mn^{2+} concentrations at 5 °C were higher for data in the pH range of 6.0–6.5 than data in the pH range of 6.5–7.0. It should be noted that soluble Mn^{2+} concentrations were below the recommended target of 0.015 mg/L at temperatures below 10 °C for pH conditions greater than 7.5. Data presented in Table 1 show mean soluble Mn^{2+} concentration as a function of pH under low water temperature conditions (4–7 °C) for the laboratory-scale data. As shown in Table 1, soluble Mn^{2+} concentration decreased with an increase in solution pH.

Table 1 │ Mean soluble Mn concentration as a function of pH for temperatures between 4 and 7 °C

	Soluble Mn concentration (µg/L)	
pH range	10-cm media depth	25-cm media depth
<6.0	141	126
6.0–6.5	67	63
6.5–7.0	53	39
7.0–7.5	38	25
>7.5	8	6

ENGINEERING SIGNIFICANCE OF RESEARCH FINDINGS

A primary goal of this study was to provide useful guidance to water process engineers and water treatment plant personnel on the conditions that will allow $MnO_x(s)$-coated treatment systems to operate effectively for soluble Mn^{2+} control even under low temperature conditions. For example, one process control parameter in the NGE is the concentration of free chlorine present in the water applied to $MnO_x(s)$-coated filter media. Conceivably a response to colder water temperature conditions could be to increase the free chlorine dosage prior to the coated media. However, analysis of the 10 years of Harwood's Mill Water Treatment Plant operational data showed that for the same pH condition the filter effluent Mn concentrations for residual free chlorine concentrations between 0.5 and 1.0 mg/L were not statistically different to those with a free chlorine residual greater than 1.0 mg/L. Hence, as long as the filter free chlorine residual was maintained at or above 0.5 mg/L there was no discernible impact on Mn removal within the filter media.

In comparison, experimental results showed that both solution pH and temperature were significant for defining soluble Mn^{2+} removal using the $MnO_x(s)$-coated media process; further, the impacts of pH on soluble Mn^{2+} removal were magnified under low temperature ($<10\ ^\circ$C) conditions. Information presented in Table 2 shows the percentage of finished water soluble Mn^{2+} concentration values that exceeded the recommended Newport News Water

Table 2 | Percentage of finished water soluble Mn concentration values exceeding the target of 0.015 mg/L as a function of water temperature and solution pH (data analyzed from Newport News Water Authority full-scale water plant operations)

Temperature	Solution pH value			
	5.7–6.0	6.0–6.3	6.3–6.6	> 6.6
<5 °C	100	60	80	66
5–10 °C	65	54	61	56
10–15 °C	45	30	19	0
15–20 °C	25	8	10	0
20–25 °C	11	8	0	0
>25 °C	6	5	0	0

Authority goal of 0.015 mg/L when sorted by pH and temperature for the full-scale Harwood's Mill plant data. As shown in Table 2, the percentage of finished water soluble Mn^{2+} concentration values exceeding the goal generally decreased as the solution temperature increased. Likewise, the percentage of finished water soluble Mn^{2+} concentration values exceeding the goal of 0.015 mg/L decreased as the pH increased within each temperature range. Finally, results presented in Table 2 also demonstrate that an increase in solution pH may at least partially mitigate the negative effects of low water temperature on Mn removal using $MnO_x(s)$-coated filter media treatment systems.

The water treatment significance of these findings is of specific importance to a limited number of treatment situations. The reality is that elevated soluble Mn concentrations in surface water treatment situations are typically seen during the warmer months of the year (e.g., summer and early to mid-fall, prior to overturn and subsequent mixing in a stratified lake or reservoir). At these times of the year, water temperatures are typically at or above 15 to 20 °C, a temperature condition that would predict highly effective soluble Mn^{2+} removal by the $MnO_x(s)$-coated media. For example, at the Harwood's Mill treatment facility the filtered water Mn concentration in the non-winter months is typically below 0.010 mg/L, and sometimes below the analytical detection limit for Mn. However, on occasion during the winter months (when water temperatures are typically well below 12–15 °C) there will be upsets in the Harwood's Mill Reservoir (e.g., storm events) that result in a limited-duration episode of elevated soluble Mn^{2+} entering the treatment plant. The full-scale data as well as the laboratory-scale column studies demonstrate that, under low water temperature conditions, this Mn removal process is less effective and can yield finished water Mn concentrations that significantly exceed the Authority's 0.015 mg/L target concentration. The data also indicate that, under these treatment conditions, in the future the Authority could consider pH adjustment in the filter-applied water to improve soluble Mn^{2+} removal across their filters.

This research effort was not designed to evaluate the specific mechanisms by which low temperature conditions negatively impact soluble Mn^{2+} removal on $MnO_x(s)$-coated filter media; instead, the primary focus was on

documenting that such an impact does exist. However, it is possible to at least speculate on how temperature could affect the process. Soluble Mn^{2+} removal on MnO_x(s)-coated media is known to be a two-step process involving initial soluble Mn adsorption onto the MnO_x(s) surface followed by subsequent surface-catalyzed oxidation of the Mn by free chlorine (Knocke *et al.* 1991; Coffey *et al.* 1993; Merkle *et al.* 1997b). Prior research (Tobiason *et al.* 2008) showed that the Mn adsorptive capacity of MnO_x(s)-coated media from the Harwood's Mill Water Treatment Plant was quite substantial, owing to the large amount of MnO_x(s) surface coating present on the media at the facility. This large capacity typically resulted in almost complete soluble Mn uptake within the first 6–12 inches of media depth in the filter. Thus, even if lower temperature conditions reduced the Mn adsorptive capacity of the media to some degree, the overall depth of coated media (typically 30 to 36 inches) should have been sufficient to still achieve the 0.015 mg/L Mn level in the treated water. Instead, it may be more likely that lower temperature conditions negatively impact the surface-catalyzed Mn oxidation step. If this regeneration step is slowed, then the adsorptive capacity of the MnO_x(s)-coated media would in fact decline over time and could lead to increased Mn levels in the filtered water. Again, these thoughts are purely speculative as an evaluation of the direct effect of temperatures on the mechanisms of the removal process was beyond the scope of this research.

CONCLUSIONS

The following conclusions were formulated based upon the results obtained in this research effort:

- The uptake of soluble Mn^{2+} onto MnO_x(s)-coated filter media is negatively impacted by water temperature conditions below 12–15 °C, with the most extreme impacts observed under very low water temperature conditions (4–7 °C).
- The adverse effects of low water temperature on soluble Mn^{2+} removal within MnO_x(s)-coated media systems may be at least partially mitigated by increasing the pH of the water applied to the MnO_x(s)-coated media.

- Finished water soluble Mn concentration is not significantly affected by free chlorine residual concentration as long as it is greater than 0.5 mg/L.

ACKNOWLEDGMENTS

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