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Evaluate and Optimize Manganese Treatment

In light of increasing interest in water quality and health concerns related to manganese (Mn) at elevated levels, it's important for water utilities to optimize existing treatment processes to enhance Mn control.

BY ROGER ARNOLD, MARTIN R. EARLE, RONIT ERLITZKI, AND WILLIAM KNOCKE

EFFECTIVELY REMOVING manganese (Mn) at water treatment plants is critical to producing aesthetically pleasing drinking water, minimizing Mn accumulation in the distribution system, and avoiding health concerns. By optimizing treatment to proactively target lower Mn levels, water systems can further enhance consumer confidence in drinking water quality.

Mn treatment is often motivated by a goal to maintain drinking water aesthetics. Mn passing through a water treatment plant (WTP) can discolor water, undermining consumer confidence in drinking water. Prior studies support a treatment goal of 0.015 to 0.02 mg/L—well below the US Environmental Protection Agency's current secondary maximum contaminant level of 0.05 mg/L—to minimize consumers' aesthetic concerns and Mn accumulation in the distribution system. Effective treatment can assist water systems in producing finished-water Mn levels below this treatment goal.

MN SOURCE CHARACTERIZATION

Characterizing Mn levels in source water is critical for planning and optimizing treatment. Mn regularly occurs in surface water and groundwater sources in the following forms:

- Particulate—oxidized particles, MnOx(s)

- Dissolved—soluble reduced Mn(II) or soluble oxidized Mn(VII)

Dissolved Mn commonly occurs in groundwater sources, especially in anoxic conditions. Thermally stratified surface waters can also contain elevated levels of dissolved Mn as a result of dissolved Mn being released from sediments into lower levels of a reservoir (see sidebar, “Manage Manganese Levels at the Source”). River sources typically contain predominantly particulate Mn with low dissolved Mn levels due to the presence of dissolved oxygen, and elevated levels of

particulate Mn can co-occur with higher turbidity levels in a river.

Although Mn levels in groundwater sources are often more consistent than surface water sources, Mn levels can vary considerably between wells. Mn levels in source water can be managed through strategic placement of well locations and depths based on local hydrogeology and operating wells with lower Mn concentrations when possible.

Monitoring raw water as well as treated water at several key points in the

Table 1. Primary Manganese Treatment Strategies

Water professionals can consider several strategies to optimize Mn removal.

Control Strategy	Description
Oxidation and particulate separation	<ul style="list-style-type: none"> • Addition of a strong oxidant (chlorine dioxide or permanganate) to oxidize and precipitate dissolved Mn • Physical separation of particulate Mn by clarification and/or filtration
Sorption to filter media	<ul style="list-style-type: none"> • Sorption of dissolved Mn to oxide-coated filter media in the presence of free chlorine • Applied to conventional gravity filters or pressure filters for groundwater applications
Adsorptive contactor	<ul style="list-style-type: none"> • High-rate contactor for sorption of dissolved Mn to granular oxide-coated media • In surface water plants, best applied following a filtration step without an adsorptive media barrier (e.g., membranes) • Sorption to media in pressure filter vessels for groundwater treatment
Biological treatment	<ul style="list-style-type: none"> • Granular media filter operated without preoxidation for surface water • Mn adsorbs to biomass and is oxidized by microorganisms, resulting in the accumulation of Mn oxides • Effective for aerated groundwater; can be challenging for surface waters • Acclimation period can be long, but may be shortened using a layer of Mn oxide on top of filter



To provide safe, aesthetically pleasing drinking water to customers, it's important for water treatment plant operators to understand manganese sources and characterization, treatment strategies, and treatment considerations for surface water and groundwater systems.

treatment process can be used to assess Mn removal mechanisms and potential internal Mn sources. For example, WTP recycle flows can contain Mn previously removed from the treatment process—sometimes at higher levels than in raw water—and may influence treatment optimization. For source water and process monitoring, characterizing particulate and dissolved forms of Mn (Figure 1) is critical to effectively design and operate treatment systems. Filters with pore sizes of 0.22 or 0.45 micron are often used to separate particulate Mn from a sample; the difference between the unfiltered (total) and filtered Mn concentrations is the particulate Mn

concentration. In some cases, colloidal Mn may pass a 0.22 or 0.45 micron filter, and additional analysis can be conducted if necessary to determine the colloidal and truly dissolved Mn fractions.

TREATMENT STRATEGIES

Selecting a Mn treatment strategy depends on source water quality, Mn concentrations, form of Mn (i.e., particulate or dissolved), holistic treatment objectives, and compliance requirements. Table 1 summarizes the primary Mn treatment strategies described in this article. Several of these strategies involve maintaining a stable Mn oxide-coated filter

media surface in the treatment process as the primary barrier for Mn removal.

Separating Oxidized Mn Particles. For raw water containing primarily particulate Mn (e.g., many river sources), substantial Mn removal can occur through coagulation and clarification, without the addition of a raw water oxidant. Mn particles are enmeshed in floc and removed via clarification or filtration.

For raw water containing primarily dissolved Mn, the dissolved Mn must be oxidized to form particulate Mn to facilitate physical separation during treatment. Strong oxidants such as chlorine dioxide, permanganate, or ozone are typically used to oxidize Mn because of their rapid reaction rates. In surface WTPs, strong oxidants are usually applied in a pipe or tank before coagulation to allow Mn particles to form and be subsequently enmeshed in floc. Following oxidation and coagulation, particulate Mn can be separated by clarification and/or filtration. For source waters where coagulation isn't needed—often a groundwater with low organic carbon—effective removal of oxidized Mn requires use of microfiltration or ultrafiltration membranes rather than media filters. Settled residuals held in the sedimentation basins

Figure 1. Manganese Fractionation Approach

Characterizing particulate and dissolved forms of Mn is critical for source water and process monitoring.

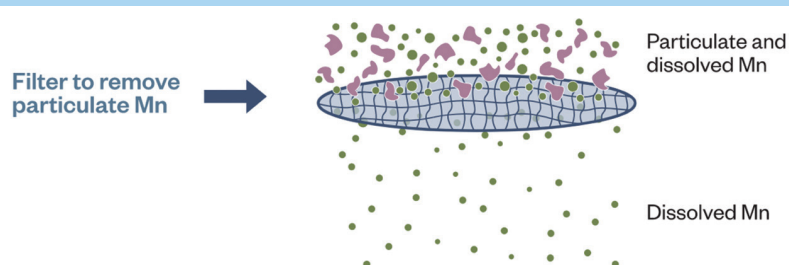
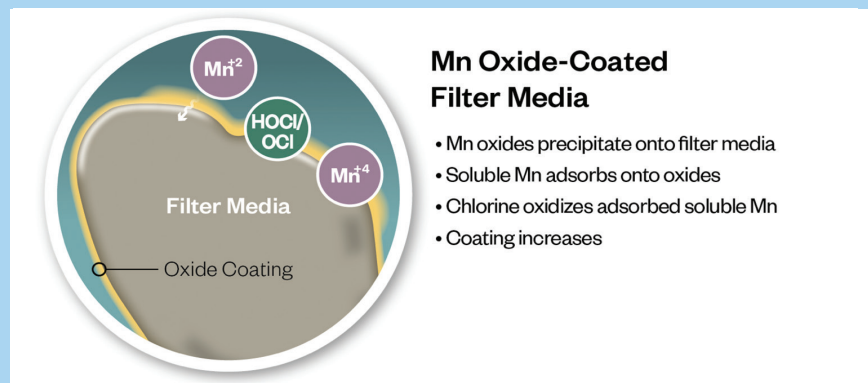


Figure 2. Manganese Sorption to Oxide-Coated Filter Media

Sorbed Mn is quickly oxidized by free chlorine, creating a continuously regenerated adsorptive surface when chlorine is dosed before the filter.



must be managed to minimize release of Mn within the WTP.

Free chlorine isn't an effective oxidant for dissolved Mn in bulk water at typical pH levels (e.g., pH 6–9), because the oxidation reaction kinetics are too slow to provide sufficient Mn oxidation within typical WTP time scales. Many conventional surface treatment facilities have successfully removed free chlorine application to raw water to minimize disinfection byproduct formation without sacrificing Mn removal by clarification and filtration. However, an alternate strong preoxidant may be needed based on the source water Mn characteristics and other treatment processes.

Optimizing oxidant doses can pose operational challenges, and operators must consider dissolved Mn concentrations and competing oxidation reactions. Although oxidant doses can be approximated on the basis of stoichiometric relationships, competing reactions with organics and iron can significantly affect optimal dosing. A portion of the total Mn is often in particulate form (Mn oxide) and doesn't require oxidation before solid-liquid separation processes. Quantification of the dissolved Mn fraction of the total Mn is needed to accurately set oxidant doses.

To optimize strong oxidant doses, operators can perform jar tests to replicate oxidation of reduced Mn and remove particulate Mn by coagulation and clarification. Mn remaining in filtered samples of clarified water approximates dissolved Mn that may require additional oxidant dosing.

Sorption to Oxide-Coated Filter Media.

Dissolved Mn can rapidly adsorb to Mn oxide surfaces such as oxide-coated filter media and can be oxidized on the surface; the mechanism is known as sorption and

catalytic oxidation. Although free chlorine is typically an ineffective (too slow) oxidant for Mn treatment in bulk water (e.g., pipe or tank), sorbed Mn is quickly oxidized by free chlorine, creating a continuously regenerated adsorptive surface when chlorine is dosed before the filter (Figure 2).

Mn removal by sorption and catalytic oxidation typically requires a filter-effluent free chlorine residual of at least 0.5–1.0 mg/L and a pH >6.0. Operating at applied pH values <6.0 will negatively affect Mn sorption to the media, and these conditions may occur for facilities operating at lower pH values for enhanced coagulation for organics removal. Also, extended operation with reduced-effluent free chlorine residual can result in increased finished-water Mn concentrations from desorption of dissolved Mn or reduction of Mn oxides.

In practice, this strategy can effectively treat moderate concentrations of dissolved Mn (i.e., up to approximately 0.2 mg/L). Even for WTPs practicing upstream oxidation and separation of particulate Mn before filtration, maintaining an adsorptive barrier in the filters can enhance dissolved Mn removal to produce consistently low concentrations (i.e., <0.02 mg/L).

CASE STUDY

CHLORINE FEED UPGRADES OPTIMIZE SURFACE WATER TREATMENT

Hanover County, Va., implemented chlorine feed upgrades at the 4-mgd Doswell Water Treatment Plant (WTP) to simultaneously optimize manganese (Mn) removal and control disinfection byproducts. To evaluate Mn removal, full-scale process monitoring was conducted to characterize Mn levels in the plant's river source and primary removal mechanisms. Mn in the river was primarily in the particulate form, indicating that oxidation of Mn prior to coagulation (e.g., permanganate) wasn't necessary for effective treatment.

Bench-scale coagulation testing confirmed that most of the Mn in raw water was removed through coagulation and sedimentation without oxidation. The county implemented upgrades to feed chlorine before each filter, allowing the WTP to maintain filter-effluent chlorine residuals of approximately 0.5 mg/L to form an oxide coating on filter media. Although most of the Mn removal occurred in the sedimentation basins, sorption of Mn to oxide-coated filter media provided filter-effluent Mn levels consistently below 0.02 mg/L. This project demonstrates the effectiveness of sorption to oxide-coated filter media as a primary barrier for Mn control.

Selecting the most cost-effective Mn treatment approach requires detailed analysis of the specific water chemistry and Mn concentrations.

Some treatment processes may not provide an adsorptive filter media barrier. Although membranes can provide separation of particulate Mn, microfiltration/ultrafiltration membranes don't remove dissolved Mn. Treatment facilities with granular activated carbon (e.g., biologically active filtration) wouldn't maintain a free chlorine residual across the media to form an adsorptive barrier.

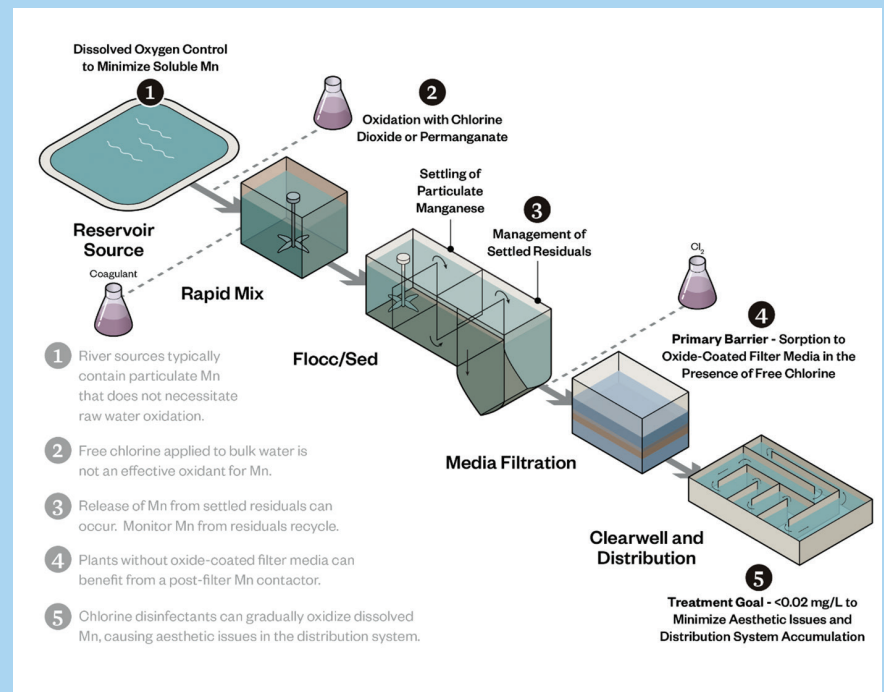
Effective removal of dissolved Mn by sorption and surface oxidation can also be achieved without continuous pre-filter chlorine dosing by using media with a Mn oxide surface for sorption (e.g., a “green-sand” media) with periodic, or intermittent, regeneration with permanganate.

Post-Filter Adsorptive Contactor. The beneficial aspects of soluble Mn removal via sorption and continuous oxidation by chlorine on an oxide-coated media have been incorporated into the concept of what's called a “Mn contactor.” Given the fast kinetics of soluble Mn sorption, contactors can be designed with relatively high (e.g., 12–18 gpm/ft²) hydraulic loading rates. Likewise, contactors typically employ media of relatively large effective size (e.g., 1.3–2.0 mm), which allows high hydraulic loading rates without generating large amounts of clean-bed head loss. Typical contactor media bed depths would be 24–36 inches, but pilot testing where possible would help define media requirements.

A Mn contactor would typically be placed at the end of the overall treatment train, downstream of particle filtration systems.

Figure 3. Manganese Treatment Optimization Strategies for Surface Water

Mn can be optimized at key points in a conventional surface water treatment plant.



The contactor should be operated with a free chlorine residual of 0.5–1.0 mg/L to maintain continuous Mn sorption by regeneration of sorption sites on the media. In addition, utilities that increase the finished-water pH for corrosion control should consider adjusting pH upstream of the post-filter contactor because higher pH improves Mn removal effectiveness.

Because the media surface generates some amount of head loss over time, the contactor needs to be backwashed every several weeks, with the contactor run time depending on the total Mn mass loading over time. A well-operated Mn contactor can effectively produce finished-water Mn concentrations ≤ 0.01 mg/L.

Biological Filtration. Mn can also be removed from water using biological treatment technologies such as biofiltration. Operating granular media filters with little to no oxidant (e.g., chlorine) applied upstream allows bacteria and other microorganisms to grow within the filter to remove Mn; sufficient influent dissolved oxygen is important. Once biologically oxidized, Mn accumulates on filter media as active Mn oxides, which may increase Mn removal across the biofilter via catalytic oxidation.

BEST PRACTICES

MANAGE MANGANESE LEVELS AT THE SOURCE

Managing manganese (Mn) levels in source water can simplify treatment processes and operation. Thermal stratification of reservoirs can lead to oxygen depletion and release of dissolved Mn from sediments into the hypolimnion, the lower layer of water in a stratified reservoir. When possible, strategically selecting the intake withdrawal depth can help decrease Mn levels in raw water. Reservoir hypolimnetic oxygenation systems or artificial destratification systems can control the release of dissolved Mn into the water column by minimizing anoxic conditions at the bottom of a reservoir.

Biofiltration has been used successfully to control Mn from groundwater sources, and it has recently seen increased use in surface WTPs. For groundwater treatment, biofiltration is simple, inexpensive, reliable, and sustainable. As Mn removal across biofilters is affected by a variety of factors such as pH, ammonia concentration, and temperature, it can be more difficult to use Mn biofilters for surface waters, which have more variable quality than groundwater. Therefore, utilities considering building new biofilters or converting to biofiltration should consider performing treatment studies to determine optimal filter design and pretreatments.

Additionally, WTPs using biofiltration for other treatment objectives, such as organic carbon removal, must still consider potential biological accumulation of Mn onto filter media. If significant chemical or biological changes are made to the water applied to the filters (e.g., depletion of dissolved oxygen), a biofilter may begin to release Mn into the finished water.

OPTIMIZING SURFACE WATER TREATMENT

Water professionals can consider a suite of strategies to optimize Mn removal at conventional surface WTPs. In some cases, Mn removal can occur unintentionally as an outcome of other surface water treatment processes. These strategies can help water professionals investigate and optimize Mn removal while meeting simultaneous treatment objectives.

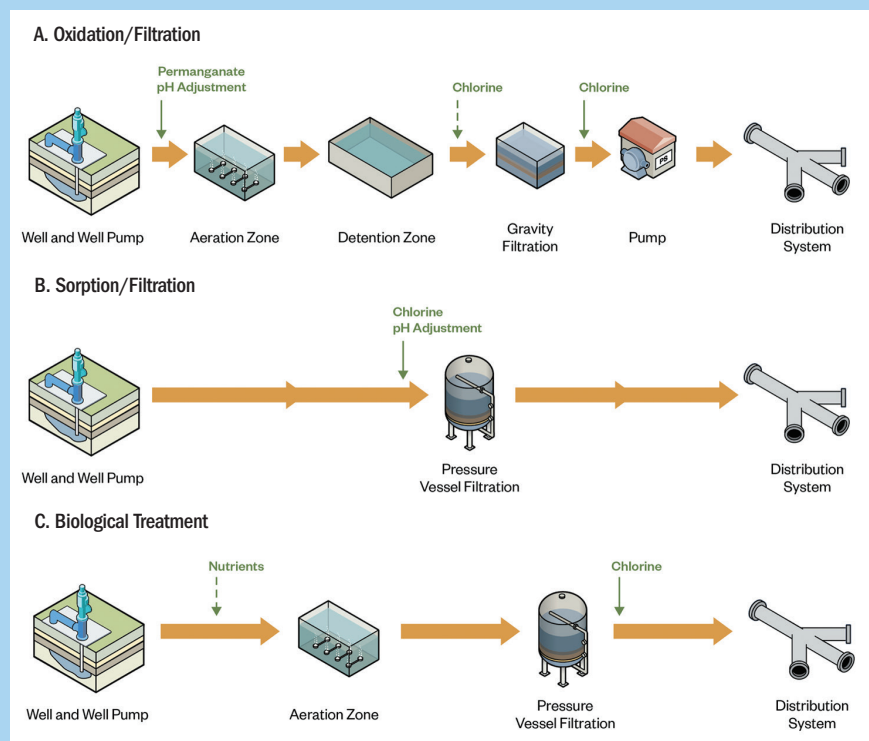
For many WTPs, the single greatest barrier for Mn removal is maintaining an adsorptive surface on the filter media—or a post-filter contactor—with consistent concentrations of free chlorine. This technique can provide finished-water Mn concentrations meeting a treatment goal of <0.02 mg/L.

Figure 3 illustrates key points for optimizing Mn control in a conventional surface water treatment plant:

- Mn control begins with understanding and managing the source water. For WTPs with a reservoir source, control of dissolved oxygen levels in the

Figure 4. Manganese Treatment Options for Groundwater

The sorption/filtration process is becoming more common because of its simplicity and cost-effectiveness.



A—Oxidation/Filtration: The traditional oxidation/filtration treatment system has several treatment stages and a larger footprint. Depending on the raw water quality, chemical feed for pH adjustment and a strong oxidant (e.g., permanganate) may be needed as well as an aeration zone and detention time. Disinfection with chlorine is typically applied downstream of the filter, and an additional pump is required to distribute the treated water.

B—Sorption/Filtration: A sorption/filtration treatment system provides a reduced footprint and lower equipment cost. The combination of chlorine with the catalytic media eliminates the need for permanganate, aeration, and the extended contact time. Chlorine is dosed just enough to sustain the oxide-coated media surface and provide residual chlorine for disinfection. The direct pressure filtration system eliminates the need for an additional pump.

C—Biological Treatment: A biofiltration system can provide operational benefits, requiring only aeration, granular media filtration, and post-filter disinfection in some cases. In these systems, Mn is removed by a combination of biological and chemical sorption and oxidation. Biofilters may take several weeks to acclimate, and some systems may require nutrient enhancement (typically phosphate). Biofilters may be operated by gravity or direct pressure.

reservoir can help reduce dissolved Mn levels in the raw water.

- For WTPs receiving raw water with moderate to high levels of dissolved Mn, a strong oxidant can be added before coagulation to form particulate

Mn. Competing constituents, including iron and organic matter, can consume the strong oxidant. Monitoring dissolved Mn and iron concentrations and other constituents is critical for optimizing oxidant dose.

Although the chemical principles are the same, there are different considerations affecting Mn treatment strategies for surface water and groundwater systems.

- Iron coagulants (e.g., ferric sulfate and ferric chloride) may contain dissolved Mn. Dissolved Mn introduced by coagulants may not be oxidized by pre-oxidants applied before coagulation. Accounting for dissolved Mn added during coagulation can be important for optimizing treatment.
- Particulate Mn, either present in raw water or formed via oxidation, can effectively settle in sedimentation basins. Managing settled residuals is important to minimize the potential for Mn release in sedimentation basins (e.g., by continuous withdrawal of settled solids from the basins).
- By maintaining a filter-effluent chlorine residual of at least 0.5–1.0 mg/L and a pH >6.0, granular media filters can provide a robust barrier for Mn removal through sorption to oxide-coated filter media and catalytic oxidation by free chlorine.
- For WTPs without an oxide-coated filter media barrier (e.g., membranes or granular activated carbon filters), a post-filter contactor with continuous chlorine dosing can enhance dissolved Mn removal and reliably produce low finished-water Mn levels.

OPTIMIZING GROUNDWATER TREATMENT


Although the fundamental treatment chemistry is the same, Mn treatment in groundwater poses a different set of considerations. Dissolved Mn in groundwater can be treated by oxidation and filtration, sorption to oxide-coated filter media, or other techniques. Traditionally, oxidation of dissolved Mn followed by filtration was a common treatment technique. However, the sorption/filtration process is becoming more common because of its simplicity and cost-effectiveness, as shown in Figure 4. Sorption/filtration systems can be designed with higher hydraulic loading rates (e.g., 4–10 gpm/ft²), which results in significant footprint reduction. For specific raw water qualities (e.g., when ammonia is also present

in the water in addition to Mn), biological filtration presents an environmentally friendly and high-recovery approach to Mn removal from water.

Additional contaminants present in groundwater can influence the selection of a Mn treatment strategy. Selecting the most cost-effective Mn treatment approach requires detailed analysis of the specific water chemistry and Mn concentrations. Often, Mn co-occurs with iron, arsenic, hydrogen sulfide, ammonia, and/or organic matter in groundwater. Consequently, treatment technologies that remove multiple contaminants at the same time are preferred. Depending on simultaneous treatment objectives, other treatment processes such as cation exchange or nanofiltration/reverse osmosis membranes can be used to remove Mn.

BETTER AESTHETICS, MORE CONFIDENCE

Optimizing Mn treatment can enhance drinking water aesthetics and minimize Mn accumulation in the distribution system, improving customers' confidence in their drinking water. Characterizing raw water Mn levels, including fractionation of dissolved and particulate Mn, is critical for optimizing Mn treatment. Source water Mn control measures can simplify treatment needs.

Although the chemical principles are the same, there are different considerations affecting Mn treatment strategies for surface water and groundwater systems. Maintaining a stable Mn oxide-coated filter media surface in the treatment process—using a post-filter contactor if necessary—can provide robust and reliable Mn removal, producing consistently low Mn levels. These treatment strategies can help systems achieve lower Mn levels at the point of entry below approximately 0.02 mg/L to optimize drinking water aesthetics. 

Editor's Note: This article is the second in a series produced by the Manganese Subcommittee of the AWWA Inorganics Committee. The first article, "Know the Benefits of Effective Manganese Management Strategies" (<https://doi.org/10.1002/opfl.1587>), appeared in Opflow's October issue. The next article in the series will appear in Opflow's January/February 2022 issue and describe strategies to control legacy Mn in the distribution system.

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CASE STUDY

SORPTION/FILTRATION SYSTEM OPTIMIZES GROUNDWATER TREATMENT

Upchurch Place is a community in North Carolina with a water system owned and operated by Aqua North Carolina. The groundwater supply contains approximately 1.43 mg/L of iron and 0.23 mg/L of manganese, which created aesthetic challenges that were difficult to manage through operational methods such as periodic flushing, tank cleaning, and even sequestration.

The persistent aesthetic issues, and recognition that sequestration didn't effectively address the high contaminant levels, led Aqua North Carolina to install a sorption/filtration system to remove these secondary contaminants below aesthetic targets. The site has no access to sewer for backwash waste disposal, so the treatment system also included a backwash recycle system to provide >99% overall water recovery. Following the system's start-up in 2019, Aqua North Carolina and the community held an open house to educate consumers about the new treatment system's ability to achieve their drinking water quality goals.