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Evaluation of Second-Stage Contactor Media for Manganese Removal

A Master's Project Presented

By

Jonathan Chihoski

Submitted to the Department of Civil and Environmental Engineering of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

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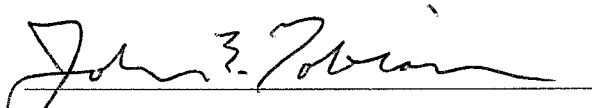
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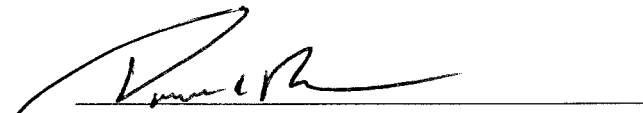
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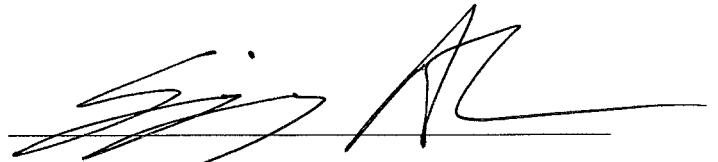
Approved as to style and content by:



Dr. John E. Tobiason, Chair



Dr. David A. Reckhow, Member



Dr. Sanjay R. Arwade, Graduate Program Director,
Civil and Environmental Engineering

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Abstract

The focus of this research was to determine the performance of different types of media for a post-filter second-stage contactor for the removal of manganese from a drinking water source. The Aquarion Water Company's Lantern Hill (LH) water treatment facility in Stonington, CT served as the motivation for this study. The groundwater at this site contains significant concentrations of manganese, averaging 0.2 mg/L, as well as iron, 2.3 mg/L, and total organic carbon (TOC), 3.5 mg/L. Currently, the Lantern Hill facility is using a combination of pH adjustment, potassium permanganate, chlorine, and cationic polymer addition prior to down flow through a dual media, anthracite over green sand, direct filtration process. Levels of pre-filter chlorine required to maintain a filter effluent manganese concentration of 0.02 mg/L or less result in unacceptable levels of disinfection byproducts (DBPs), specifically trihalomethanes (THMs) and haloacetic acids (HAAs). Prior UMass/AWC research has shown that a two-stage approach, with a first-stage dual media (DM) filter for the removal of particulate matter, including oxidized iron and some TOC, followed by a second-stage media contactor for manganese removal, is effective. Addition of chlorine after the first-stage filter results in much lower DBP levels compared to the addition of chlorine to the raw water at a level that yields effective manganese control. The design of a facility upgrade is in progress, which requires more information on media performance.

A laboratory study was conducted at the University of Massachusetts-Amherst to evaluate the performance of five different media types, including $\text{MnO}_{x(s)}$ coated anthracite and Macrolite, as well as pyrolusite, a naturally occurring form of MnO_x . The laboratory setup included a feed water tank from which water was pumped into the test line; dissolved manganese (Mn^{2+}) and chlorine (NaOCl) were then injected into the line prior to flowing down a column filled with the oxide coated media. Sampling ports were installed throughout the depth of the media. The experiment consisted of varying the hydraulic loading rate (10, 15, 20 GPM/ft²) and effluent chlorine residual (0.2, 1.0, 4.0 mg/L Cl_2) of the system and analysis of manganese levels in water samples from various depths throughout the media to evaluate performance.

In general, all media types performed best at the lowest hydraulic loading rate and highest chlorine residual. The full-scale operations at the Lantern Hill water treatment facility operate with a chlorine residual of approximately 1.0 mg/L. At this residual with hydraulic loading rates of 10 and 20 GPM/ft², the Macrolite removed the greatest fraction of Mn. However, with a chlorine residual of 1.0 mg/L and a hydraulic loading rate of 15 GPM/ft², the pyrolusite had the best performance. The average effluent Mn concentration of the permanganate conditioned anthracite column for a media depth of 27.5 inches at the above hydraulic loading rates and a chlorine residual of 1.0 mg/L ranged from 0.01 to 0.02 mg/L Mn. The average effluent Mn concentration for the Siemens conditioned anthracite column for a media depth of 40.5 inches at the above hydraulic loading rates and a chlorine residual of 1.0 mg/L was not detectable. The average effluent Mn concentration for the UMass conditioned Macrolite column for a media depth of 27.5 inches at the above conditions ranged from 0.02 to 0.03 mg/L Mn. The average effluent Mn concentration of the Macrolite column for a media depth of 40 inches at the above conditions ranged from not detectable to 0.01 mg/L Mn. The average effluent Mn concentration of the pyrolusite column for a media depth of 26.5 inches at the above conditions ranged from not detectable to 0.03 mg/L Mn. There were exponential decreases in the dissolved Mn concentration for all media types as the bed depth increased. For a 40 inch bed depth, both anthracites, Macrolite, and pyrolusite could achieve the desired finished water Mn levels of less than 0.02 mg/L at full-scale conditions.

Pilot plant experiments were conducted at the full-scale Lantern Hill plant, utilizing a two-stage approach, with the option of KMnO₄ or NaOCl as a pre-filter oxidant followed by post-filter chlorination. For the pre-KMnO₄ / NaOCl pilot, it was determined that an average sub-stoichiometric dose of 1.1 mg/L KMnO₄ ahead of the dual media filter could effectively oxidize all of the raw water iron. Also, for this system it was determined that an average C572 polymer dose of 6.9 mg/L could achieve a desired effluent turbidity of 0.1 NTU or less, as well as remove about 1 mg/L of TOC. An average post-filter chlorine dose of 4.0 mg/L was sufficient to continuously regenerate the oxide coated media and result in a desired finished water effluent chlorine residual of about 1.3 mg/L. For the pre-NaOCl / NaOCl pilot, it was determined that an average dose of 2.0 mg/L NaOCl ahead of the dual media filter could effectively oxidize all of

the raw water iron. Also, for this system it was determined that an average C572 polymer dose of 5.2 mg/L could achieve a desired effluent turbidity of 0.1 NTU or less, as well as remove about 1 mg/L of TOC. An average post-filter chlorine dose of 2.8 mg/L was sufficient to continuously regenerate the oxide coated media and result in a desired finished water effluent chlorine residual of about 1.3 mg/L. When the pre-NaOCl / NaOCl approach was used, a total chlorine dose of only 4.8 mg/L was required for successful pilot operation. This chlorine dose is not much more than the pre-KMnO₄ / NaOCl chlorine dosing requirements, however, it is much lower than the full-scale chlorine dosing at Lantern Hill of approximately 6.9 mg/L.

The performance of all media types tested during the pilot experiments was considered satisfactory, based on the desired finished water manganese concentration of 0.02 mg/L or less. This is a result of the conservative system design including a 40 inch media bed depth and a hydraulic loading rate of 10 GPM/ft². The Macrolite media performed best during the pilot experiments for both the pre-KMnO₄ / NaOCl and the pre-NaOCl / NaOCl systems; average effluent manganese concentrations were 0.01 mg/L.

Both pilot systems produced significantly less DBPs than the full-scale operations at Lantern Hill. The pre-KMnO₄ / NaOCl system produced 63 and 61 % decreases in the 24 hour hold values for THMs and HAAs, respectively. This system also produced 62 and 60 % decreases in the 48 hour hold values for THMs and HAAs, respectively. The pre-NaOCl / NaOCl system produced 59 and 58 % decreases in the 24 hour hold values for THMs and HAAs, respectively. This system also produced 58 and 52 % decreases in the 48 hour hold values for THMs and HAAs, respectively. The pre-KMnO₄ / NaOCl system produces slightly less DBPs than the pre-NaOCl / NaOCl system. However, the overall results show that the two-stage approach, with either KMnO₄ or NaOCl dosing ahead of the filter for iron oxidation, can meet effluent goals without exceeding regulated DBP values.

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CHAPTER 1: INTRODUCTION

1.1 Problem Statement

Manganese is a naturally occurring element found in the earth's crust that is often found in groundwater; high manganese (Mn) concentrations are a common problem for water treatment facilities. Manganese presents aesthetic and possible health problems. Water containing higher levels of manganese can cause problems in distribution systems such as building up inside of pipes and restricting flows and can also accumulate in valves and cause operation and maintenance issues. In a similar manner, manganese can precipitate and cause brown staining of laundry as a result of use of detergents and bleaches. Higher manganese concentrations may also result in water discoloration and turbidity. In terms of potential health risks, a recent study (Bouchard et al. 2011) has shown that children exposed to water containing higher levels of manganese are at risk of developing lower IQs and development issues. To minimize the problems associated with manganese in drinking water the EPA has set a secondary maximum contaminant level (SMCL) of 0.05 mg/L. However, it is recommended that drinking water treatment facilities achieve a concentration of 0.02 mg/L or less to minimize problems associated with the distribution system and customer complaints, (Kohl & Medlar 2007).

Removal of manganese from drinking water can be accomplished by a number of methods depending on the capabilities and goals of a treatment facility. Two of the most common methods of removal are to oxidize and precipitate the manganese and then remove particles through clarification and filtration, or by adsorption of dissolved Mn to MnO_x coated media and surface oxidation. The first method of Mn removal is typically achieved by the introduction of a strong oxidant to oxidize the dissolved manganese to particulate form followed by particle removal. The oxidant dosing associated with this method can be challenging and have undesired results. For instance, if potassium permanganate (KMnO₄) is used as the oxidant, overdosing could lead to a pink colored water and raise the Mn concentration. In a similar manner, if chlorine dioxide (ClO₂) is used as the oxidant, high dosing can result in disinfection byproduct increases. The second method of Mn removal is achieved by flowing water through a

bed of MnO_x coated media with a continuous pre-media dosing of an oxidant, typically chlorine, for media regeneration. The dissolved manganese is first adsorbed onto the surface of the media and then it is catalytically oxidized by the oxidant, forming a MnO_x coating on the media. The use of MnO_x media for manganese removal was the focus of this research.

Aquarion Water Company's (AWC) Lantern Hill facility in Stonington, CT is a 1 MGD drinking water treatment plant that currently uses a direct filtration process with chemical oxidation and MnO_x coated media to achieve desired effluent water quality goals. The groundwater source for the Lantern Hill facility has significant concentrations of reduced manganese (Mn^{+2}) averaging approximately 0.2 mg/L, as well as approximately 2.3 mg/L of reduced iron (Fe^{+2}), and 3.5 mg/L of total organic carbon (TOC). Levels of pre-filter chlorine required to maintain a filter effluent manganese concentration of 0.02 mg/L or less result in unacceptable levels of regulated disinfection byproducts (DBPs). The facility is periodically shutdown by AWC to maintain regulatory compliance for the Mystic system. With the Stage II EPA DBP regulations taking effect in 2014 and focusing on the highest DBP locations in the distribution system, not the system average as for previous regulations, AWC determined that the LH facility needs to be upgraded for continued operation.

Prior UMass/AWC research has shown that a two-stage approach, with a first-stage dual media filter for the removal of particulate matter, including oxidized iron and some TOC, followed by chlorination and a second-stage media contactor for Mn removal by adsorption and catalytic oxidation, is effective for Mn control and drastically decreases filter effluent DBPs. The second-stage contactor media must have a Mn oxide ($\text{MnO}_{x(s)}$) surface. A pilot plant was constructed at the Lantern Hill facility to assess the effectiveness of this system and determine design parameters. This pilot system used the raw water at the facility and was operated for different treatment scenarios.

AWC has scheduled the renovation for the Lantern Hill facility to begin in the fall of 2012. The final design for this facility upgrade will utilize the two-stage approach. However, information is needed on the options and performance of MnO_x coated media before the media selection can be finalized. Additionally, there is a need for operational data for varying and optimizing

chemical dosing during performance evaluations. This operational data should also include DBP analysis.

1.2 Objective

The main objective of this research was to evaluate the performance of multiple types of MnO_x coated media for manganese removal by a second-stage contactor under various laboratory and pilot operational scenarios.

1.3 Scope of Work

This project involved operation and analysis of laboratory experiments conducted in the UMass laboratory and pilot experiments conducted at the Lantern Hill water treatment facility. The laboratory experiments involved monitoring the manganese removal performance of different second-stage contactor media types while varying the operational conditions, consisting of hydraulic loading rate and effluent chlorine residual. The pilot experiments included characterization of water quality across the pilot plant with a focus on manganese removal, effluent chlorine residual, and DBP analysis. The media types and chemical dosing were varied throughout the pilot experiments.

CHAPTER 2: BACKGROUND

This chapter provides background information on manganese and disinfection byproducts. General information as well as associated methods of treatment are discussed. The Aquarion Water Company's Lantern Hill water treatment facility and operations are described in detail. The challenges experienced at this facility are outlined and the motivation for research is discussed. Lastly, this chapter describes previous research conducted by the University of Massachusetts at Amherst at this facility.

2.1 Manganese

2.1.1 Sources and Exposure

Manganese is a naturally occurring metallic element found in the earth's crust. It exists in numerous compounds and the most common form is pyrolusite, a natural form of manganese oxide. Manganese is used in the production of numerous goods, including steel, batteries, electric coils, glass, and fertilizers (US EPA 2006). As a result of these manufacturing processes, manganese can be released to the environment. Manganese can be found in water, air, and food and has average values of 0.004 mg/L, 0.02 $\mu\text{g}/\text{m}^3$, and 1 to 5 mg/d, respectively (ATSDR 2008).

Human exposure to manganese is usually the result of consumption of food or drinking water containing manganese. Many foods, including nuts, legumes, and fruits, have been known to contain significant amounts of manganese. Depending on the source and level of treatment, many drinking waters can also contain considerable amounts of manganese. Households and water treatment facilities that use groundwater as a water source commonly encounter elevated manganese concentrations in their drinking water (US EPA 2006). Additionally, some surface water supplies are prone to seasonally higher manganese concentrations.

Manganese is an essential nutrient for human health. Processes, such as tissue and bone development, blood clotting, and absorption and utilization of minerals and vitamins, depend on manganese in the diet. Table 2-1 shows adequate manganese intake amounts for the human

population. Although manganese is necessary for the human diet, exposure to higher levels of manganese can have detrimental health effects. Inhalation of high levels of manganese can lead to adverse central nervous system effects. “Manganism” is a term associated with certain symptoms typically encountered by workers suffering from occupational exposure. These symptoms include muscle stiffness, lack of coordination, tremors, and problems with breathing and swallowing. Recent studies have shown that children exposed to higher levels of manganese are at risk of suffering from learning disabilities and neuromuscular problems (US EPA 2006). One study found that children exposed to manganese concentrations as low as 34 µg/L in drinking water could develop lower IQs than the general population (Bouchard et al. 2011).

Table 2-1: Adequate manganese intake amounts for the human population. (ASTDR 2008)

Life Stage	Age	Males (mg/day)	Females (mg/day)
Infants	0-6 Months	0.003	0.003
Infants	7-12 Months	0.6	0.6
Children	1-3 Years	1.2	1.2
Children	4-8 Years	1.5	1.5
Children	9-13 Years	1.9	1.6
Adolescents	14-18 Years	2.2	1.6
Adults	19 Years and older	2.3	1.8
Pregnancy	All ages	---	2
Lactation	All Ages	---	2.6

2.1.2 Problems with Manganese in Drinking Water

Elevated levels of manganese in drinking water can create problems for consumers and treatment facilities. Aside from the above mentioned possible health effects, higher Mn levels in drinking water commonly leads to aesthetic and distribution problems. In terms of aesthetics, water discoloration and elevated turbidity can occur. Also, staining of plumbing fixtures, such as toilets, sinks, and tubs can result. Laundry can become stained when detergents and bleach are added and manganese is oxidized and precipitates onto laundry. Additionally, higher levels of manganese in drinking water can give the water a metallic taste. The water distribution system can experience problems due to higher levels of Mn. Manganese

can accumulate inside of pipes and restrict flows. Also, manganese can accumulate inside of valves and other mechanical devices and cause seizing and other operation and maintenance issues.

2.1.3 Manganese Regulations

As a result of the problems associated with higher levels of manganese in drinking water, regulations and recommendations have been established to minimize issues for consumers and water treatment facilities. The US EPA has set a secondary maximum contaminant level (SMCL) of 0.05 mg/L for the manganese concentration in drinking water. However, it is recommended that water treatment facilities try to obtain a concentration of 0.02 mg/L or less, to minimize customer complaints and distribution issues (Kohl & Medlar 2007).

2.1.4 The Chemistry of Manganese in Water

Manganese can exist in 11 oxidation states, more than any other element. Table 2-2 shows the eight oxidation states of manganese found in natural waters. The most common forms of manganese are Mn^{2+} , Mn^{4+} , and Mn^{7+} . Mn^{2+} is the most reduced form of manganese and is quite soluble in water. In groundwater where reducing conditions typically exist, Mn^{2+} is dominant. In lakes and reservoirs, soluble manganese is usually found near the bottom, where anaerobic reducing conditions exist. Also, in general, in waters with a pH ranging from 7 to 8, Mn^{2+} is usually the predominant form of manganese. Mn^{4+} is the oxidized particulate form of manganese and is insoluble in water, occurring as $MnO_{2(s)}$. Near the top layer of lakes and reservoirs, particulate and colloidal forms of manganese are usually present, as a result of aerobic oxidizing conditions. Mn^{7+} is the highest oxidation state of manganese and is found in the soluble form as MnO_4^- , permanganate, a strong oxidizer (Divitre et al. 1988). Lastly, Morgan and Stumm (1964) concluded that manganese can exist as a mixed oxide, $MnO_{x(s)}$, where x ranges from 1.3 to 2.

Table 2-2: Oxidation states of manganese. (Tobiason et al. 2008)

Oxidation State	Mn Compound
0	Mn
2+	Mn ²⁺
2.67+	Mn ₃ O ₄
3+	Mn ₂ O _{3(s)}
4+	MnO _{2(s)}
5+	MnO ₄ ³⁻
6+	MnO ₄ ²⁻
7+	MnO ₄ ⁻

Manganese fractionation according to size was accomplished by Carlson et al. (1997) by use of an operational fractionation procedure. Particulate, colloidal, and dissolved forms of manganese were determined for a water sample by filtration and calculating the respective fractions. The amount of manganese retained by the 0.2 micron pore size filter was considered to be in the particulate form. The amount of manganese retained by the 30K molecular weight cutoff ultra-filtration membrane filter, but passing through the 0.2 µm filter, was considered to be in the colloidal form. The filtrate from the ultra-filtration membrane filter was considered to be dissolved manganese. This fractionation procedure is a useful diagnostic tool when trying to optimize the manganese treatment process.

2.1.5 Manganese Treatment Methods

There are several techniques for controlling the concentration of manganese in drinking water. The selection of the method of treatment can depend on the raw water quality. The most common approach is to remove the manganese from the drinking water. One approach for achieving this is to oxidize the dissolved manganese to the particulate form and then physically remove the particles. Another approach is to use manganese oxide coated media that removes dissolved manganese from the water by adsorption and surface oxidation.

2.1.5.1 Manganese Oxidation and Particle Removal

Manganese removal through oxidation and particle removal is one of the most common approaches for water treatment facilities. This method involves the use of a strong oxidant to oxidize the dissolved manganese to the particulate form. The manganese particles can then be removed through clarification and filtration. Dual media filters, as well as membrane filters, can accomplish particle removal. Typically, potassium permanganate, chlorine dioxide, or ozone is used to oxidize the dissolved manganese.

Potassium permanganate (KMnO_4) is a strong chemical oxidant that is effective at oxidizing dissolved manganese. Knocke et al. (1990) studied the kinetics of potassium permanganate for manganese oxidation, at significant initial manganese concentrations, for a wide range of temperatures and pH and found that complete oxidation occurred within one to two minutes of dosing. The rate of oxidation increased with temperature, as well as pH. It was also determined that increased levels of dissolved organic carbon (DOC), up to 10 mg/L, would inhibit the kinetics of the reaction, however, in most instances, complete oxidation occurred within two minutes. In another study, Gregory and Carlson (2003) found that the rate of Mn oxidation by potassium permanganate decreased as the initial dissolved manganese concentration decreased. When the initial manganese concentrations were as low as 0.06 mg/L, the time required for necessary oxidation ranged as high as 30 minutes or more. As a result of this, it is recommended that potassium permanganate should only be used for water sources with significant initial manganese concentrations. Another important thing to consider when using potassium permanganate as an oxidant is the stoichiometry of the dosing. If excessive permanganate dosing occurs, the finished water will have a pink color.

Chlorine dioxide (ClO_2) is an effective chemical oxidant used to oxidize dissolved manganese and it is also used as a disinfectant. Knocke et al. (1987 and 1991) and Gregory and Carlson (2003) found that dissolved manganese was rapidly oxidized by chlorine dioxide. The oxidation kinetics were not significantly affected by the initial manganese concentration for a pH less than 7. Knocke et al. (1990) found that stoichiometric dosing was not sufficient in water containing higher levels of organics. In fact, two to three times the stoichiometric dose was

sometimes required due to the oxidant demand of the organics. With these high dosing levels, considerable amounts of chlorite and chlorate were formed, two disinfection byproducts (DBPs) regulated by the US EPA. As a result of this, it is recommended that chlorine dioxide be used for manganese oxidation only for water with lower amounts of organics to minimize dosing requirements and subsequent DBPs.

Ozone (O_3) is a strong oxidant used to oxidize dissolved manganese and it is also used as a disinfectant. Knocke et al. (1990) found that ozone could rapidly oxidize dissolved manganese; however, if elevated levels of organics were present the oxidation was not as effective. Gregory and Carlson (2003) verified that ozone did rapidly oxidize dissolved manganese, however, unless the initial manganese concentrations were high, desired dissolved concentrations of 0.01 mg/L Mn could not be achieved. Also, the ozone demand based on the level of organics in the water can greatly affect dosing. It was determined that excessive ozone dosing could lead to the creation of permanganate, resulting in pink water. Use of ozone as an oxidant would be most effective for waters with higher initial manganese concentrations containing lower levels of organics.

2.1.5.2 Manganese Oxide Coated Media

Oxide coated media is a media, such as sand or anthracite coal, that has a manganese oxide coating on it. This coating can be applied to most materials, natural or synthetic, with a variety of methods. One procedure, as described by Knocke (1990), uses potassium permanganate as an oxidant to condition the media and develop this coating. When water containing dissolved manganese and free chlorine flows through a bed of Mn oxide coated media, the dissolved manganese is adsorbed to the manganese oxide coating. This dissolved manganese can then be oxidized by free chlorine, if present, and becomes more manganese oxide, and the coating on the media becomes more developed. This process has been extensively researched and quantified (Tobiason et al. 2008). The free chlorine addition is necessary to oxidize the adsorbed Mn^{2+} and regenerate the media, as well as prevent release of the manganese from the media (Islam et al. 2010). This manganese removal concept was referred to as the natural greensand effect by Merkle et al. (1997).

Media Performance

The pH of the water being treated has a significant effect on oxide coated media performance with respect to manganese removal. Morgan and Stumm (1964) and Knocke (1988) determined that at pH values of 8 and higher the media was extremely effective at removing manganese. When the pH was decreased to approximately 6, there was an 80 % decrease in manganese removal. Types of oxidants used ahead of the media were studied as well. It was determined that free chlorine was the most appropriate oxidant because other stronger oxidants caused the manganese to oxidize and manganese removal occurred through filtration of particles as opposed to adsorption to the media and surface oxidation.

2.2 Disinfection Byproducts (DBPs)

Typically, raw water sources used by drinking water treatment facilities contain natural organic matter (NOM). Depending on the source, the level of NOM can be quite high. Total organic carbon (TOC) and ultraviolet absorbance at 254 nm (UV_{254}) are two parameters used to assess the amount of NOM in a water source. TOC is a measure of the carbon in water that is of organic origin. UV_{254} is the absorbance of ultraviolet light at a 254 nm wavelength. During the water treatment process, if and when chlorine is used, typically for disinfection, and if the water contains NOM, the formation of chlorinated organic compounds can occur. These chlorinated organic compounds are known as disinfection byproducts (DBPs) and have been linked to serious health risks, such as cancer (US EPA 2012). Trihalomethanes, haloacetic acids, bromate, and chlorite are DBPs regulated by the US EPA. Table 2-3 shows a list of EPA regulated DBPs as well as how they are formed and the associated health effects. (US EPA 2012)

Table 2-3: EPA regulated disinfection byproducts, how they are formed, and the associated health effects. (US EPA 2012)

Disinfection Byproduct (Chemical Abstract Service Registry Number)	How is it formed?	Health Effects
Total Trihalomethanes:		
<i>Bromodichloromethane (75-27-4)</i>	Trihalomethanes occur when naturally-occurring organic and inorganic materials in the water react with the disinfectants, chlorine and chloramine.	Some people who drink water containing total trihalomethanes in excess of the MCL over many years could experience liver, kidney, or central nervous system problems and increased risk of cancer.
<i>Bromoform (75-25-2)</i>		
<i>Dibromochloromethane (124-48-1)</i>		
<i>Chloroform (67-66-3)</i>		
Haloacetic acids:		
<i>Dichloroacetic acid (79-43-6)</i>	Haloacetic acids occur when naturally-occurring organic and inorganic materials in the water react with the disinfectants, chlorine and chloramine.	Some people who drink water containing haloacetic acids in excess of the MCL over many years may have an increased risk of getting cancer.
<i>Trichloroacetic acid (76-03-9)</i>		
<i>Chloroacetic acid (79-11-8)</i>		
<i>Bromoacetic acid(79-08-3)</i>		
<i>Dibromoacetic acid (631-64-1)</i>		
Bromate (15541-45-4)	Bromate occurs when bromide in the water reacts with the disinfectant, ozone.	Some people who drink water containing bromate in excess of the MCL over many years may have an increased risk of getting cancer.
Chlorite (7758-19-2)	Chlorite occurs when chlorine dioxide breaks down.	Some infants and young children who drink water containing chlorite in excess of the MCL could experience nervous system effects. Similar effects may occur in fetuses of pregnant women who drink water containing chlorite in excess of the MCL. Some people may experience anemia.

DBPs are regulated by the US EPA Stage I and II DBP rules which assess DBP concentrations throughout the distribution system. Table 2-4 shows the associated regulatory limits for the Stage I and II regulations (US EPA 2012). Bromate is only regulated for treatment plants that use ozone in the treatment process. Also, chlorite is only regulated for plants that use chlorine dioxide in the treatment process. The EPA Stage I DBP regulations set maximum contaminant levels (MCLs) for DBPs and disinfectant residuals, in addition to a preliminary monitoring plan. The EPA Stage II DBP regulations, use the same concentration limits, however, the monitoring plan is more conservative, focusing on location running annual averages as opposed to system wide annual averages. Additionally, monitoring is focused on the locations in the distribution system where the DBP concentrations are greatest.

2.2.1 DBP Control Methods

There are a few common approaches used by water treatment facilities to decrease the amount of DBPs formed during the treatment process. Increased removal of NOM prior to disinfection would result in less DBP precursors and ultimately lower DBP levels. The use of alternative disinfectants and oxidants to minimize DBP formation potential could be employed. The dosing sequencing and quantities could be altered to decrease chemical reactions with organic compounds. Residence time in the distribution system can be reduced by optimizing system performance. This would result in less time for the disinfectants and organics to react, ultimately decreasing DBP values. Lastly, the pH throughout the distribution system should be monitored and efforts should be made to maintain the pH between 7 and 8 to minimize increases in DBP concentrations.

Table 2-4: EPA Stage I and II DBP regulations. (US EPA 2010)

Table 2. Regulated Contaminants and Disinfectants				
	Stage 1 DBPR		Stage 2 DBPR	
Regulated Contaminants	MCL (mg/L)	MCLG (mg/L)	MCL (mg/L)	MCLG (mg/L)
TTHM	0.080		Unchanged ²	
Chloroform		-		0.07
Bromodichloromethane		Zero		Unchanged ²
Dibromochloromethane		0.06		Unchanged ²
Bromoform		Zero		Unchanged ²
HAA5	0.060		Unchanged ²	
Monochloroacetic acid		-		0.07
Dichloroacetic acid		Zero		Unchanged ²
Trichloroacetic acid		0.3		0.2
Bromoacetic acid		-		-
Dibromoacetic acid		-		-
Bromate (plants that use ozone) ¹	0.010	Zero	Unchanged ²	Unchanged ²
Chlorite (plants that use chlorine dioxide)	1.0	0.8	Unchanged ²	Unchanged ²
Regulated Disinfectants	MRDL ³ (mg/L)	MRDLG ³ (mg/L)	MRDL (mg/L)	MRDLG (mg/L)
Chlorine	4.0 as Cl ₂	4	Unchanged ²	Unchanged ²
Chloramines	4.0 as Cl ₂	4	Unchanged ²	Unchanged ²
Chlorine Dioxide	0.8	0.8	Unchanged ²	Unchanged ²
¹ A new analytical method for bromated was established with the Stage 2 DBPR.				
² Stage 2 DBPR did not revise the MCL or MRDL for this contaminant/disinfectant.				
³ Stage 1 DBPR included MRDLs and MRDLGs for disinfectants, which are similar to MCLs and MCLGs.				

2.3 Lantern Hill Drinking Water Treatment Facility

The Lantern Hill (LH) Drinking Water Treatment Plant (DWTP) located in Stonington, CT supplies drinking water to parts of Mystic, CT. This facility is owned and operated by Aquarion Water Company of CT (AWC), a private water supply company. The LH DWTP can produce approximately 1 million gallons per day (MGD) of drinking water. This facility utilizes a groundwater source for its raw water supply. Table 2-5 shows the average water quality at Lantern Hill during pilot experiments conducted between July 2011 and August 2012.

Table 2-5: Average Lantern Hill raw water quality during pilot testing.

	Total Mn (mg/L)	Dissolved Mn (mg/L)	Total Fe (mg/L)	Dissolved Fe (mg/L)	pH	UV ₂₅₄ (cm ⁻¹)	TOC (mg/L)
Average	0.17	0.17	1.85	1.69	6.51	0.153	3.48
Range	0.14-0.22	0.12-0.22	1.16-2.39	1.03-2.34	6.35-6.67	0.128-0.165	3.03-4.30

2.3.1 Full-Scale Lantern Hill Treatment Description

The full-scale operations at this facility include a single-stage direct filtration process. Figure 2-1 shows a schematic of the full-scale treatment process. Sodium hydroxide (NaOH) is added to adjust the pH to approximately 7.3. Next, potassium permanganate (KMnO₄) and chlorine (NaOCl) are added ahead of the filters for complete iron oxidation and oxide coated media regeneration. C572, a cationic polymer, is also added ahead of the filters to improve removal of organic matter and particles to control effluent turbidity. The dual media filters consist of 20 inches of anthracite over 24 inches of greensand. These filters remove iron and some TOC particles and dissolved manganese. Post-filter chlorine dosing occurs for the purposes of disinfection and a distribution system chlorine residual. NaOH is added again to adjust the pH. Fluoride is dosed to obtain the desired residual and phosphate (PO₄) is added for corrosion control.

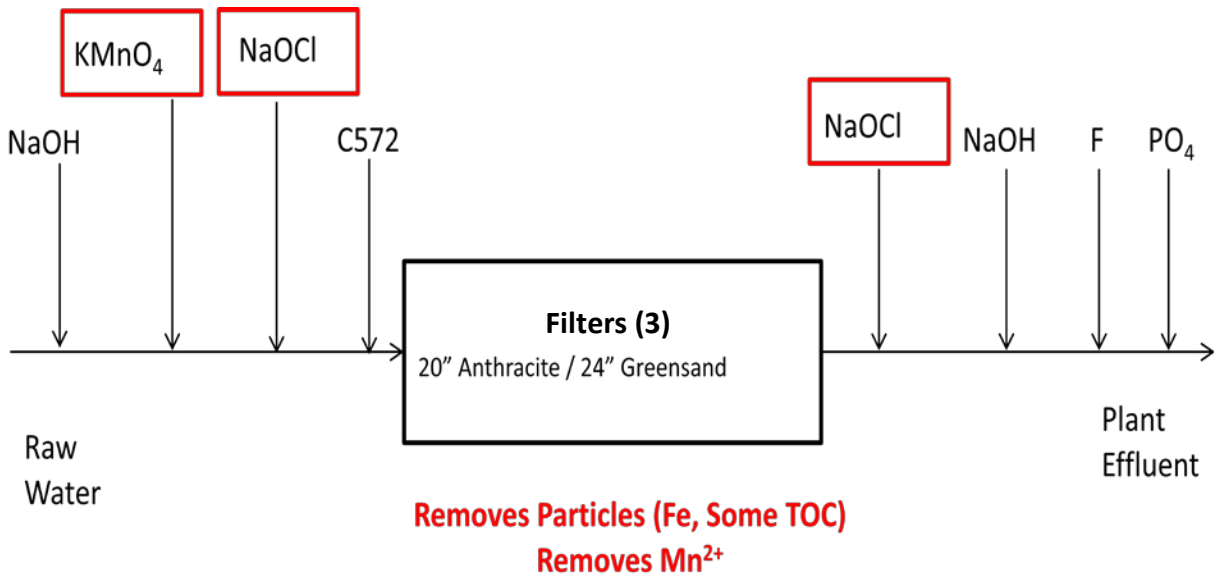


Figure 2-1: Schematic of full-scale operations at the Lantern Hill water treatment facility.

2.3.2 Lantern Hill Treatment Challenges

The current full-scale operations at Lantern Hill are able to achieve the desired effluent goals for metal concentrations of 0.02 mg/L or less Mn and approximately 0.01 mg/L Fe, as well as maintain a low turbidity (< 0.1 NTU) for a 20 to 24 hour cycle. However, high pre-filter chlorine dosing (~8 mg/L NaOCl) is required to remove dissolved manganese and prevent Mn release. This high chlorine dosing combined with the high level of NOM present in the raw water result in DBP values that frequently exceed regulated values for THMs and HAAs. As a result of these exceedances, this facility has to periodically shutdown during the year to maintain system compliance. With the EPA Stage II DBP regulations coming into effect, which focus on the highest DBP values in the system, this facility would experience significant closure. AWC realized this problem and conducted pilot-scale research in conjunction with the University of Massachusetts – Amherst, Civil and Environmental Engineering Department to evaluate treatment alternatives. AWC wanted to utilize the existing pressure driven system, without the addition of pumps or reservoir tanks, and to start the construction of a facility upgrade in the fall of 2012.

2.3.3 Previous AWC/UMass Research

Initially, to decrease the impacts of high pre-filter chlorine dosing, a pre- and post-filter chlorination approach was used. In addition to 0.6 mg/L of KMnO_4 , a chlorine dose of about 2 mg/L was used ahead of the filter for manganese removal and oxide coated media regeneration. A post-filter chlorine dose of about 1.5 mg/L was used to obtain the desired distribution system residual. This approach greatly decreased the amount of DBPs being produced during the treatment process. However, after about two months of full-scale operation, manganese levels in the filter effluent increased considerably, most likely the result of manganese releasing from the surface of the oxide coated media (Russell 2008). The pre-filter chlorine dose was raised to about 6 mg/L, effectively controlling Mn removal, but the DBPs increased significantly.

Next, various chemical dosing and sequencing options were evaluated. Filter effluent iron, manganese, and DBP concentrations were used as indicators of performance. The turbidity and UV_{254} were also studied. Eventually, a post-filter, second-stage contactor containing manganese oxide coated media (pyrolusite) for dissolved manganese removal, was implemented into the pilot study. It was determined that a two-stage approach, as shown in Figure 2-2, could effectively meet effluent metal concentration and turbidity goals, while greatly decreasing the amount of DBPs created. The average 24 hour hold THM and HAA concentrations were decreased by approximately 60 and 80 %, respectively (Pham 2010). The pilot system included NaOH addition to adjust the pH of the raw water. Next, the iron was oxidized ahead of the dual media filter by addition of either KMnO_4 or a low dose of NaOCl. Then C572 polymer was added ahead of the dual media filter to improve particle removal. The dual media filter consisted of 20 inches of anthracite over 18 inches of sand and removed particles, including all iron and some TOC. Next, NaOCl was dosed ahead of the second-stage contactor for the purposes of media regeneration and a desired distribution system chlorine residual. The second-stage contactor removed dissolved manganese from the water through adsorption and surface oxidation on the media. Pyrolusite was studied at hydraulic loading rates ranging from 2 to 20 GPM/ft². Manganese removal modeling showed that a bed depth of approximately 40 inches would be

sufficient for expected conditions (Pham 2010). With the design for the facility upgrade underway, additional data on the second-stage oxide coated media performance was needed. Hence, the current study focused on the performance of different media types for the second-stage contactor.

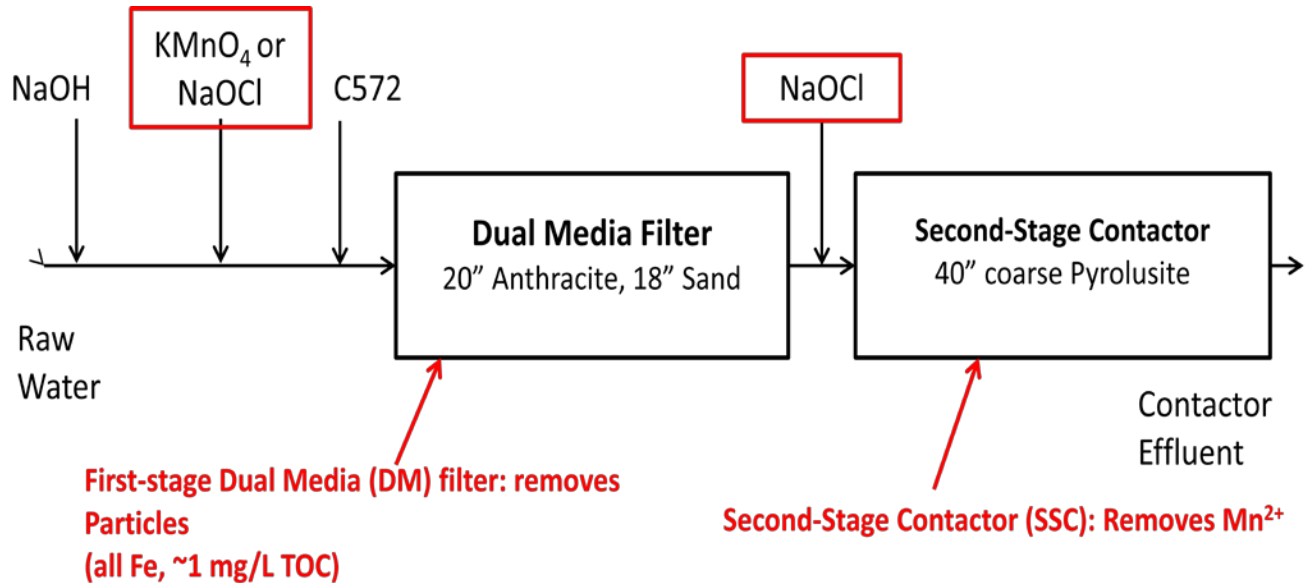


Figure 2-2: Schematic of the two-stage treatment system used for pilot experiments at Lantern Hill in 2010.

CHAPTER 3: MATERIALS AND METHODS

This chapter provides detailed information about second-stage contactor media experiments conducted at the University of Massachusetts – Amherst water treatment laboratory and pilot plant experiments conducted at the Lantern Hill water treatment facility. Parameters analyzed as well as the associated analytical methods are discussed.

3.1 University of Massachusetts - Amherst Laboratory Contactor Media Experiments

Second-stage contactor media experiments were conducted in the UMass laboratory to compare media performance and the impacts of operational variables.

3.1.1 Second-Stage Contactor Media Column System Description

The second-stage contactor experimental system included columns filled with MnO_x coated media that were operated in the water treatment research laboratory at the University of Massachusetts-Amherst. Figure 3-1 shows a diagram of the experimental setup for the contactor media testing. The media columns consisted of 3-in internal diameter clear PVC tubes, about 58 inches in height, with PVC flanges installed on the top and bottom. A filter underdrain nozzle was installed at the bottom of the column to retain media during operation. Influent and effluent lines, consisting of 0.5-in PVC pipe, were installed on the top and bottom, respectively. Numerous sampling ports, consisting of 0.5-in x 0.125-in hose barbs were installed throughout the depth of the tube with increments ranging from 1.5 to 6 inches. The total media bed depths tested ranged from 26.5 to 40.5 inches and were based on available media and a desired full-scale depth of 40 inches. The values for sampling port spacing and the associated media bed depth can be seen in Table 3-1. The system utilized a tap water feed that flowed through a granular activated carbon filter (General Electric Smartwater GAC Filter) to a reserve tank. Water was pumped from the reserve tank and manganese and chlorine solutions were injected into the water line by pumps (Cole Parmer gear pump drive assemblies) prior to entering the media column. $\text{MnO}_{x(s)}$ coated anthracite (conditioned using two different processes), Macrolite (conditioned in the UMass lab and commercially supplied), and pyrolusite

media types were studied. One anthracite sample (anthracite # 1) was conditioned using potassium permanganate (KMnO_4), according to the procedure from Knocke (1990). Another anthracite sample (anthracite # 2) was conditioned using potassium permanganate and manganous sulfate, according to Siemens. One sample of Macrolite (UMass Macrolite) was conditioned using potassium permanganate (KMnO_4), according to the procedure from Knocke (1990) with modifications to increase the Mn coating. Another sample of Macrolite (Macrolite) was commercially available with a $\text{MnO}_{x(s)}$ coating. The pyrolusite, a naturally occurring form of MnO_x , was supplied by Layne Christianson Co.

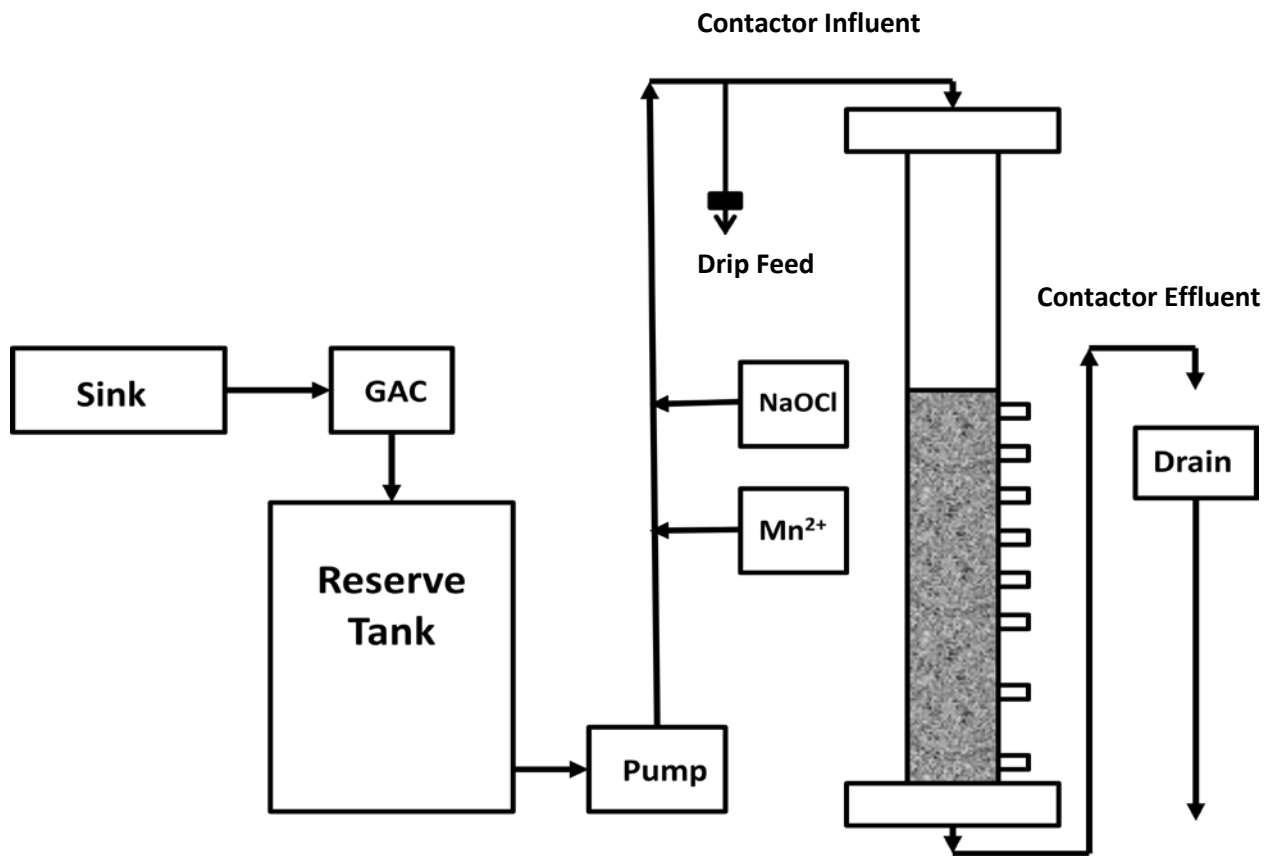


Figure 3-1: Diagram of the UMass laboratory setup for the second-stage contactor media experiments.

Table 3-1: Sample port labels and locations relative to media depth for each media column for laboratory experiments.

Anthracite # 1	depth of media (in.)	Anthracite # 2	depth of media (in.)	UMass Macrolite	Depth of media (in.)	Macrolite	depth of media (in.)	Pyrolusite	depth of media (in.)
Influent	0	Influent	0	Influent	0	Influent	0	Influent	0
port 0	1.5	port 1	2.5	port 0	1.5	port 0	4	port 0	1.5
port 1	4.5	port 2	8.5	port 1	4.5	port 1	10	port 1	4.5
port 2	7.5	port 3	14.5	port 2	7.5	port 2	16	port 2	7.5
port 3	10.5	port 4	17.5	port 3	10.5	port 3	22	port 3	10.5
port 4	13.5	port 5	20.5	port 4	13.5	port 4	28	port 4	13.5
port 5	19.5	port 6	23.5	port 5	19.5	port 5	34	port 5	19.5
port 6	24.5	port 7	26.5	port 6	24.5	Effluent	40	port 6	24.5
Effluent	27.5	port 8	32.5	Effluent	27.5			Effluent	26.5
		port 9	37.5						
		Effluent	40.5						

3.1.1.1 Media Descriptions

The media types tested were natural and synthetic and included a range of physical properties. A coarse media size of approximately 2 mm was selected to minimize head losses for water flowing through the contactor. The conditioning process required for each media type ranged from nothing required for the pyrolusite to a Siemens proprietary process for the anthracite. After conditioning, the media were backwashed with GAC filtered tap water containing a chlorine residual of about 1.0 mg/L. This water was then run through the media bed in a downflow manner until the chlorine demand from the influent to the effluent had stabilized. Once the chlorine demand stabilized, preliminary testing was conducted in which the influent and effluent Mn concentrations were measured to verify Mn removal. Between runs, all media were stored in water containing a chlorine residual of approximately 1.0 mg/L.

Anthracite

Anthracite is a naturally occurring form of coal that is found in abundant quantities across the world. It has a black color and its finish has a luster. The grain density of this media is approximately 1.5 g/cm³. This anthracite was passed through a # 8 sieve and retained on a # 10 sieve, yielding an effective size of about 2.2 mm. It was then backwashed with de-ionized water in a column with about 25 % expansion for approximately an hour, until all fines were removed and the water was clear.

Permanganate Conditioned Anthracite (Anthracite #1)

To create a MnO_x coating on the media, the anthracite was conditioned with potassium permanganate according to the procedure of Knocke (1990). This procedure required preparation of a solution containing de-ionized water and 100 mg/L potassium permanganate. This solution was pumped through the media for a period of about 24 hrs. The solution was flushed and the media was rinsed with GAC filtered tap water with a chlorine residual of about 1.0 mg/L and then backwashed prior to experimentation. For the laboratory experiments, the media bed depth in the column was 27.5 inches. For pilot plant experiments, the media bed depth was 40.0 inches, however, at one point media was lost and the bed depth was

temporarily decreased to 34 inches prior to addition of more media to bring the bed depth back to 40 inches.

Siemens Conditioned Anthracite (Anthracite # 2)

With a Siemens representative in the UMass Laboratory, this anthracite was conditioned with potassium permanganate and manganous sulfate according to a proprietary Siemens process. This procedure required preparation of a solution containing de-ionized water and chemicals. The media were then conditioned in this solution for a predetermined amount of time. The solution was flushed and the media were rinsed with GAC filtered tap water with a chlorine residual of about 1.0 mg/L and then backwashed prior to experimentation. For the laboratory and pilot plant experiments, the media bed depth in the column was 40.5 inches.

Macrolite

Macrolite media is a synthetic ceramic media manufactured by Fairmount Water Solutions. It has a dull gray appearance and a porous surface. The high surface area makes it effective in terms of adsorbing contaminants. The M7 media size was selected for experiments. This media has an effective size of approximately 1.7 mm and a grain density of about 1.4 g/cm³. It was backwashed with de-ionized water in a column with about 25 % expansion, for approximately an hour, until all fines were removed and the water was clear. Also, floating pieces of media were removed at the end of this backwash.

Permanganate Conditioned Macrolite (UMass Macrolite)

Uncoated M7 Macrolite was supplied by Fairmount Water Solutions. In an attempt to create a MnO_x coating, this media was conditioned with potassium permanganate according to the procedure of Knocke (1990). After initial testing, the media was not effectively removing Mn from water. It was concluded that this media had not developed a significant MnO_x coating. Another attempt was made to condition the media. This attempt involved increasing the potassium permanganate concentration to 250 mg/L and allowing the media to soak for approximately one week. The media were rinsed and backwashed prior to preliminary testing.

The media were then evaluated with respect to Mn removal and showed promising results. GAC filtered tap water was chlorinated and run through the column containing the media until the chlorine demand from the influent to the effluent had stabilized. The column media bed depth was 40.5 inches for laboratory experiments. Due to time constraints, this media was not tested in the pilot plant because other media types had better and more consistent performance.

Factory Conditioned Macrolite

MnO_x coated M7 Macrolite was supplied by Fairmount Water Solutions. GAC filtered tap water was chlorinated and run through the column containing the media until the chlorine demand from the influent to the effluent had stabilized. Initial testing consisted of Mn analysis for the influent and effluent to determine if Mn was being removed by the media prior to the start of testing. The column media bed depth was 40 inches for laboratory experiments and for the pilot experiments.

Pyrolusite

Pyrolusite is a natural form of manganese oxide that is found in the earth's crust. The surface of the media has a reflective smooth black finish. The grain density of this media is approximately 5.1 g/cm³. The pyrolusite used for this experiment was supplied by Layne Christianson. This media was passed through a # 8 sieve and retained on a # 10 sieve, yielding an effective size of about 2.2 mm. It was then backwashed with de-ionized water in a column with about 25 % expansion, for approximately an hour, until all fines were removed and the water was clear. Since pyrolusite is MnO₂, an oxidant conditioning process to develop an MnO_x coating was not necessary. GAC filtered tap water was chlorinated and run through the column containing the media until the chlorine demand from the influent to the effluent had stabilized. Initial testing consisted of Mn analysis for the influent and effluent to determine if Mn was being removed by the media prior to the start of testing. The column media bed depth was 26.5 inches for laboratory experiments. For the pilot experiments, the column media bed depth was 42 inches.

3.1.2 Second-Stage Contactor Media Column System Operation

The second-stage contactor media system utilized a tap water feed that flowed through a granular activated carbon filter (General Electric Smartwater GAC Filter) to a reserve tank. Water was pumped from the reserve tank and the manganese and chlorine solutions were injected into the water line prior to entering the column containing the MnO_x media. A manganese solution was prepared by adding manganous sulfate ($MnSO_4$) to de-ionized water. The manganese influent concentration was kept constant at approximately 0.2 mg/L. A chlorine solution was prepared by adding sodium hypochlorite ($NaOCl$) to de-ionized water. The effluent chlorine residual was varied from 0.2 to 4.0 mg/L. The hydraulic loading rate was varied from 10 to 20 GPM/ft².

3.1.3 Laboratory Contactor Media Experimental Methods

A column was filled with 27 to 40 inches of oxide coated media and was backwashed with water with about a 25 % bed expansion until the effluent was clear. The column was examined for any trapped air; if air was identified it was vented through the top of the column. The depth of the media was measured and recorded. The hydraulic loading rate was set by determining the cross sectional area of the column and then applying the required flow rate necessary to obtain a hydraulic loading rate of 10, 15, or 20 GPM/ft². The flow rate of the effluent was measured and adjusted by throttling the pump motor speed until the desired values were achieved. The influent manganese concentration was adjusted to 0.2 mg/L and kept constant at this value for the duration of each experiment. The chlorine solution was injected into the water line to achieve a desired effluent chlorine residual. The influent and effluent chlorine concentrations were monitored until there was a stabilized chlorine demand across the media. Once this occurred, chlorine dosing was adjusted until the effluent chlorine residual was set at one of the desired effluent residual values of 0.2, 1.0, or 4.0 mg/L.

Once the test parameters were set at the desired levels, water samples were taken from the influent, effluent, and across the depth of the media column. For a given hydraulic loading rate and effluent chlorine residual, samples were taken and analyzed at one hour sampling intervals

for a total of four sets of samples. The influent manganese concentration, the hydraulic loading rate, and effluent chlorine residual were checked immediately prior to sampling, as well as periodically in between samples to assess operating conditions. The influent line had a tee and a 0.5-in. ball valve with tubing attached and was operated in a constant drip mode. The sampling ports installed throughout the depth of the column consisted of 0.5-in. hose barbs with 0.25-in. tubing with pinch tubing clamps installed. These sampling ports were closed until it was time to take samples. During sampling, the pinch clamp was removed and the tubing was allowed to purge approximately three tubing volumes of water prior to sample collection. The effluent line was open and continuously flowed into a small funnel setup. Effluent samples were collected from the open effluent stream.

For each set of samples, the chlorine and manganese concentrations were measured and recorded. The chlorine concentration was measured for the influent and effluent. The manganese concentration was measured for the influent, effluent, and throughout the depth of the media bed. The fraction of initial manganese remaining in a sample was used as a measure of media performance. Profile plots of the fraction of initial manganese, as a function of bed depth, were used to compare the media types at the various operating scenarios.

3.2 Lantern Hill Two-Stage Pilot Plant Contactor Media Experiments

The two-stage pilot plant contactor media experiments conducted at the Lantern Hill water treatment facility in Stonington, CT occurred after most of the laboratory experiments and were a significant portion of the overall research project.

3.2.1 Two-Stage Pilot Plant Contactor Media Column System Description

A two-stage pilot-scale system was constructed at the Lantern Hill water treatment facility for evaluation of the different $\text{MnO}_{x(s)}$ coated media types at full-scale conditions utilizing the raw water source. Figure 3-2 shows a schematic diagram of the pilot plant system. The pilot system was fed by raw water and consisted of a primary dual media (DM) filter and two second-stage contactors (SSC) in parallel. The DM filter consisted of a 7.5 inch diameter clear PVC tube filled with 20 inches of anthracite over 18 inches of sand on top of 3 inches of gravel with a filter

nozzle installed on the bottom. The effective sizes of the anthracite and the sand were 0.9 and 0.5 mm, respectively. The chemically pre-treated water entered the top of the DM filter through an influent line and exited the bottom through an effluent line. Valves were installed in multiple locations to allow for filter isolation as well as backwashing with finished plant water. The second-stage contactors consisted of 3 inch diameter clear PVC tube filled with approximately 40 inches of MnO_x coated media. Sampling ports were installed throughout the depth of the contactors in order to obtain profiles of Mn removal as a function of media bed depth; see Table 3-2 for locations and port spacing. Two contactors were installed in parallel in order to simultaneously evaluate two different media types under identical water conditions.

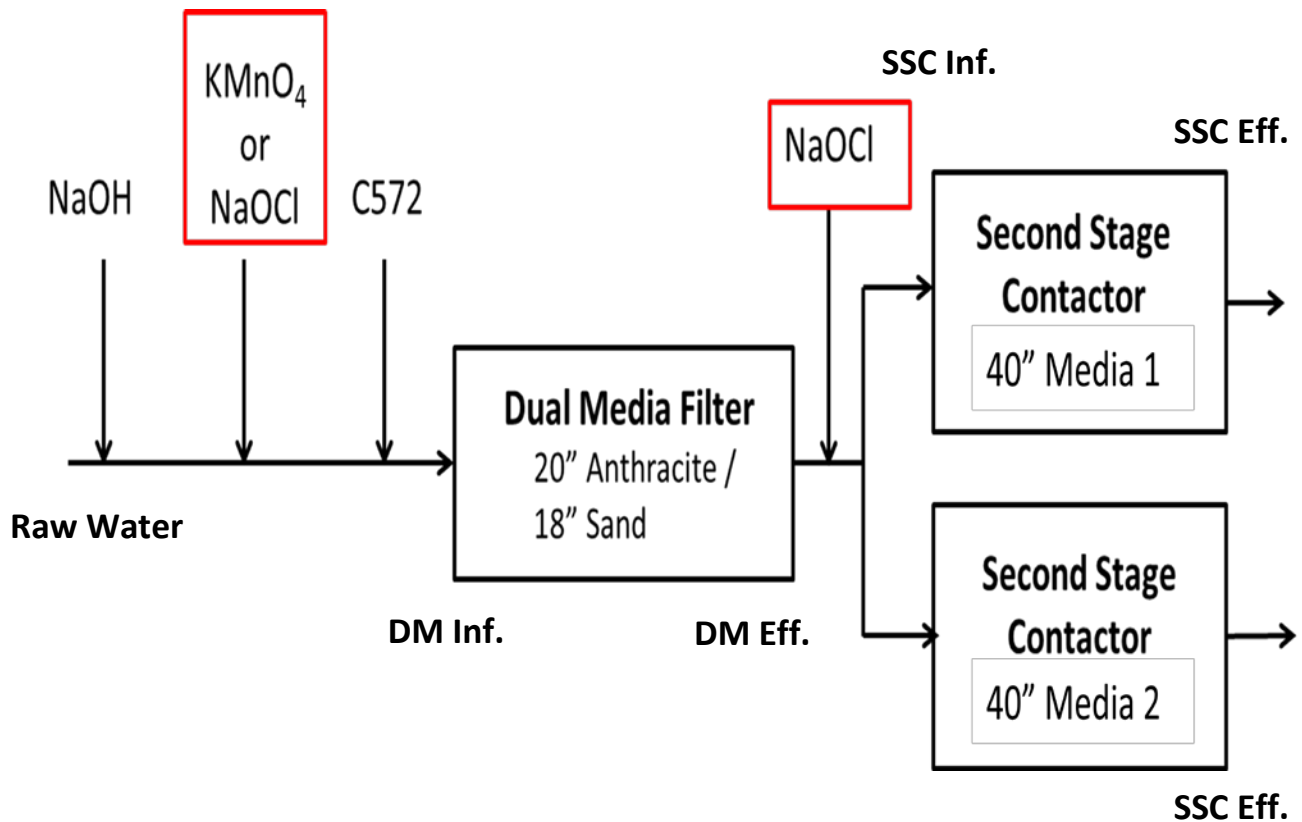


Figure 3-2: The Lantern Hill pilot plant diagram with pre-filter oxidation and post-filter chlorination with the second-stage contactors in parallel.

Table 3-2: Sample port labels and locations relative to media depth for each pilot media column.

Anthracite # 1*	depth of media (in.)	Anthracite # 2	depth of media (in.)	Macrolite	depth of media (in.)	Pyrolusite	depth of media (in.)
Influent	0	Influent	0	Influent	0	Influent	0
port 0	13.5	port 1	2.5	port 0	4	port 0	17.0
port 1	16.5	port 2	8.5	port 1	10	port 1	20.0
port 2	19.5	port 3	14.5	port 2	16	port 2	23.0
port 3	22.5	port 4	17.5	port 3	22	port 3	26.0
port 4	25.5	port 5	20.5	port 4	28	port 4	29.0
port 5	31.5	port 6	23.5	port 5	34	port 5	35.0
port 6	36.5	port 7	26.5	Effluent	40	port 6	40.0
Effluent	40.0	port 8	32.5			Effluent	42.0
		port 9	37.5				
		Effluent	40.5				

* Anthracite media depth changed 3 times, this was the final depth. Media was lost during backwash and added at a later date.

3.2.2 Two-Stage Pilot Plant Contactor Media Column System Operation

Chemical Dosing and Operation

First, the pH was adjusted by adding NaOH to achieve a pH of approximately 7.3 ahead of the filter. Next, raw water was dosed with either KMnO_4 or NaOCl for the primary purpose of iron oxidation. The minimal oxidant amounts necessary to oxidize all of the iron prior to entering the DM filter were used. A one minute contact loop was installed to mimic the reaction time associated with KMnO_4 dosing at the full-scale. Also, SuperFloc C572, a cationic polymer, was injected ahead of the filter to improve removal of organic matter and particles. The DM filter

effluent turbidity was used as an indicator of optimal polymer dosing. The DM filter effluent was dosed with NaOCl prior to entering the two second-stage contactors. This post-filter chlorine addition achieved a second-stage contactor effluent chlorine residual of about 1.3 mg/L, desired for media regeneration and distribution system chlorine residual. The hydraulic loading rate for each contactor was 10 GPM/ft² and the flow was frequently verified using a graduated cylinder and stopwatch. The Mn removal profiles were determined by measuring the fraction of the initial Mn concentration, as a function of bed depth, for each media type. These profiles were used to directly compare the performance of each media type.

Pre-Contactor Conditions

During each pilot experiment at Lantern Hill, the raw water quality was analyzed to determine chemical dosing requirements. The total and dissolved manganese and iron concentrations were measured. The UV₂₅₄, turbidity, and pH were also measured. After dosing the raw water, the dual media filter influent was characterized to determine the intermediate water quality of the system. The particulate and dissolved iron and manganese concentrations were determined. The chlorine residual was measured when chlorine was added as a pre-filter oxidant. The pH of the dual media filter influent was also measured.

After passing through the DM filter, the effluent water quality was determined. The particulate and dissolved iron and manganese concentrations were measured. The turbidity was also measured. The DM filter effluent turbidity was measured to assess particle removal. Polymer coagulant dosing was adjusted to achieve turbidity values of less than 0.1 NTU. Lastly, the pH of the dual media filter effluent was measured to verify acceptable pH adjustment.

Head loss across the DM filter was monitored for each pilot system. The DM filter was backwashed every 24 hours of operation, in a similar manner to full-scale conditions.

Contactor Conditions

The water quality for the second-stage contactors was analyzed. The chlorine residual and manganese concentration of the influent to the contactors were measured. Next, the

manganese concentration at each sampling port was determined to assess media performance. The turbidity, chlorine residual, and manganese concentration were measured for the effluent of the contactors. The second-stage contactors were periodically backwashed, and they had finished plant water with a chlorine residual of approximately 1.3 mg/L flowing through them went not in use.

3.3 Analytical Methods

3.3.1 Fractionation

Water samples were periodically fractionated to determine the particulate, colloidal, and dissolved iron and manganese concentrations. This was accomplished by filtering samples through a 0.2 micron pore size Millipore membrane filter using a 60 ml syringe setup, as well as an Amicon 8200 200 ml ultra-filter cell with a Millipore YM30 ultra-filter membrane pressurized by nitrogen gas. Particulate metals were retained by the 0.2 micron membrane filter; colloidal metals passed through the 0.2 micron filter but were retained by the 30K UF setup, and the UF filtrate was considered dissolved. The majority of the raw water colloidal and dissolved fractions were in the dissolved form; as a result, a syringe filter was most often used to distinguish between the particulate and dissolved forms of the metals. The dissolved metal concentrations were used to determine dosing requirements for the oxidants.

3.3.2 Disinfection Byproduct Analysis

After sufficient media performance and operational data had been gathered for the pre-KMnO₄ / NaOCl and pre-NaOCl / NaOCl systems, DBP analyses were conducted for each system. Instantaneous and 24 and 48 hour hold samples were analyzed for THM and HAA concentrations. The instantaneous samples were quenched immediately with ammonium chloride or sodium sulfate to stop the reaction between the chlorine and organics in the samples. This is representative of the DBP concentrations in the finished water as it leaves the water treatment facility. The 24 and 48 hour hold samples were held at the temperature of the distribution system for the respective time periods and then quenched with ammonium chloride or sodium sulfate. This is representative of the DBP concentration after the reaction

time in the distribution system prior to reaching a household and is known as a simulated distribution system DBP analysis. For both pilot systems, instantaneous, 24 hr hold, and 48 hr hold DBP samples were analyzed for the contactor effluents. Additionally, for the pre-NaOCl / NaOCl system, instantaneous DBP samples were analyzed for the DM filter influent and effluent. Instantaneous, 24 hr, and 48 hr hold analyses were also conducted across the full-scale treatment facility.

THM and HAA measurements were conducted at the University of Massachusetts-Amherst Laboratory according to the standard operating procedures: Analysis of Haloacetic Acids and Trihalomethanes (Reckhow 2006). These methods are closely aligned with US EPA Method 551.1 and 552.2. These procedures involved sample preservation, extraction, and gas chromatography analysis.

3.3.3 Total Organic Carbon Analysis

The Shimadzu TOC/V at the UMass Laboratory was used for this measurement. Samples were collected, acidified to pH of 2 by adding 50 μ L of HCl 6N, and stored in a 4° C constant temperature room. The instrument was calibrated using six calibration standards which have concentrations as follows: 0, 0.5, 1, 2.5, 5, and 10 mg/L. Standard solutions were prepared using a 1000 mg/L carbon stock solution that was made by dissolving 2.125 g of reagent grade potassium hydrogen phthalate in 1 L of MilliQ water; the KHP was previously dried at 100C for approximately 1 hour and then cooled in a desiccator. The stock solution was then diluted with MilliQ water to achieve the desired concentration of 10 mg/L, which was then autodiluted for standards.

3.3.4 Media Surface Extraction Analysis

Extraction of surface metals was conducted for the media used in lab and pilot experiments. The extraction was conducted according to Knocke (1990). This procedure allowed for the measurement of the amount of constituents accumulated on the surface of the media by reduction and dissolution into solution. The concentrations of aluminum, manganese, and iron were determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis.

Calibration curves were determined for standards for each metal and used to accurately determine metal values. The following is a brief summary of the extraction procedure:

Media samples were collected for extraction analysis and were rinsed with de-ionized water to remove metal oxides that were not attached to the surface of the media. Approximately one gram of media was weighed and then dried in an oven at 105° C. After a 24 hour period the media sample was placed in a desiccator to cool and was then reweighed. The media was soaked in a 250 ml 0.5 % nitric acid and hydroxylamine sulfate solution for at least two hours to reduce the metal oxides to the dissolved forms. This solution was then filtered through a 0.7 micron Whatman fine glass-fiber filter. Manganese, iron, and aluminum concentrations in the filtered sample were analyzed using the ICP-MS. Once the concentrations were determined, the milligram of metal per gram of media was determined by multiplying the metal concentration by the volume of the solution and then dividing by the mass of the dried media sample.

Below is a brief description of each media tested, including sample name, how the media were used, when and where it was used, and the relative location of the sample in the media bed:

LH DM Anthracite 1 & 2 – Lantern Hill Dual Media Filter Anthracite Samples 1 & 2 – This anthracite has been in the DM filter since previous two-stage pilot work prior to 2011. This sample was taken at a media bed depth of about 8 inches.

LH DM Sand 1 & 2 – Lantern Hill Dual Media Filter Sand Samples 1 & 2 – This sand has been in the DM filter since previous two-stage pilot work prior to 2011. This sample was taken at a media bed depth of about 8 inches.

LH Macrolite 1 & 2 – Lantern Hill Second-Stage Contactor Media Macrolite Samples 1 & 2 – This media came from Fairmont Water Solutions with a Mn oxide coating. It was used during lab and pilot experiments from 2011-2012. This sample was taken at a media bed depth of about 4 inches.

LH Anthracite 1 & 2 – Lantern Hill Second-Stage Contactor Media Anthracite Samples 1 & 2 – This media was initially conditioned using potassium permanganate according the Knocke

(1990). It was used during lab and pilot experiments during 2011-2012. This sample was taken at a media bed depth of about 18 inches.

Siemens Anthracite 1 & 2 – This anthracite was conditioned according to the Siemens procedure using potassium permanganate and manganese sulfate. It was used during lab experiments in 2012. This sample was taken at a media bed depth of about 3 inches.

3.3.5 Plastic and Glassware Preparation

All of the plastic and glassware used during these experiments was properly prepared according to the UMass Lab Procedures prior to use. It was soaked in a soap bath and rinsed with de-ionized water. If it was to be used on the ICP-MS it was soaked in a soap bath, rinsed with de-ionized water, then soaked in a nitric acid bath, then rinsed with de-ionized water. Non-volumetric glassware was dried in an oven at 110° C. Plastic and volumetric glassware were dried in an oven at 50° C.

3.3.6 Metal Concentrations

3.3.6.1 HACH DR4000

Initially, a HACH DR/4000 spectrophotometer, set for the low range manganese method, was used to analyze water samples during column experiments in the lab. The low range Mn detection method, which has a measurement range of 0.006 to 0.7 mg/L Mn with a precision of 0.001 mg/L, was used. HACH reagent kits for manganese measurements, consisting of ascorbic acid pillows, hydrogen cyanide, and PAN indicator were used. A 10 ml volume of the sample was collected in a HACH sample cell. Ascorbic acid was added to the sample, 12 drops of hydrogen cyanide was added, followed by 12 drops of PAN Indicator. The sample was shaken and allowed to react for two minutes prior to being measured. A 10 ml sample of de-ionized water was prepared in a similar manner and used as a zero for the instrument.

3.3.6.2 HACH Pocket Colorimeter II

A HACH Pocket Colorimeter II for manganese was used to measure the manganese concentration towards the end of the laboratory study. The measurement range for this instrument was 0.01 to 0.7 mg/L Mn with a precision of 0.01 mg/L. This instrument was also used to determine the manganese concentration for pilot experiments at Lantern Hill. HACH reagents kits for manganese measurements, consisting of ascorbic acid pillows, hydrogen cyanide, and PAN indicator were used. A 10 ml volume of the sample was collected in a HACH sample cell. Ascorbic acid was added to the sample, 12 drops of hydrogen cyanide was added, followed by 12 drops of PAN Indicator. The sample was shaken and allowed to react for two minutes prior to being measured. A 10 ml sample of de-ionized water was prepared in a similar manner and used as a zero for each instrument.

For the pilot experiments at Lantern Hill, a HACH Pocket Colorimeter II for iron was used to measure the iron concentration in the field. The measurement range for this instrument was 0.01 to 5.0 mg/L Fe with a precision of 0.01 mg/L. This instrument used the HACH reagents kits for iron measurements, consisting of FerroVer reagent pillows. For each sample, two 10 ml volumes of the sample were collected in HACH cells. One sample was used as a zero and the FerroVer reagent was added to the other sample. The sample and reagent were shaken and allowed to react for three minutes prior to analysis. The instrument was zeroed for each sample prior to analysis.

3.3.6.3 Inductively Coupled Plasma Mass Spectrometer (ICP-MS)

For the media surface extraction experiments, the manganese concentration was measured using the ICP-MS in the UMass Laboratory. Due to chemicals used for the extraction procedure, a color based approach for concentration measurement could not be used. A 12 ml volume of the sample was collected in a vial and acidified with 2 % nitric acid, prior to analysis. Mn standards were prepared by diluting a known stock concentration for the ICP-MS. The concentrations of standards used were 0, 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 1.0, 2.5, 5.0, 10, 15, 20,

and 25 mg/L Mn. Calibration curves were created based on these standards and sample concentrations were determined accordingly.

The iron concentration for surface extraction experiments was measured in a similar manner. The ICP-MS was used because chemicals used for the extraction procedure inhibited a color based approach for concentration measurement. A 12 ml volume of the sample was collected in a vial and acidified with 2 % nitric acid, prior to analysis. Fe standards were prepared by diluting a known stock concentration for the ICP-MS. The concentrations of standards used were 0, 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 1.0, 2.5, and 5.0 mg/L Fe. Calibration curves were created based on these standards and sample concentrations were determined accordingly.

Aluminum concentrations were measured during media surface extraction experiments using the ICP-MS as well. A 12 ml volume of the sample was collected in a vial and acidified with 2 % nitric acid, prior to analysis. Al standards were prepared by diluting a known stock concentration for the ICP-MS. The concentrations of standards used were 0, 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, and 1.0 mg/L Al. Calibration curves were created based on these standards and sample concentrations were determined accordingly.

3.3.7 pH

The pH was periodically measured using a Thermo Electron Corp. Orion 520A with a Thermo Orion pH probe. This instrument was calibrated before each use with certified buffer standards of 4, 7, and 10. The probe solution was periodically filled and replaced as necessary.

3.3.8 Turbidity

The turbidity was measured during pilot experiments using a HACH 2100 Turbidimeter.

3.3.9 Ultraviolet Absorbance (UV₂₅₄)

The ultraviolet absorbance was measured using different instruments depending on the time and location of experiments. Samples were filtered through a 0.45 micron Whatman fiberglass

filter prior to analysis. For laboratory experiments, the UV_{254} was measured using a HACH 4000U spectrophotometer set for UV absorbance at a wavelength of 254 nm. For pilot experiments, the UV_{254} was measured using either a Milton Roy Spectronic 21D or a HACH 4000U Spectrophotometer. The wavelength of both instruments was set to 254 nm and each instrument was zeroed with de-ionized water prior to each use.

3.3.10 Chlorine Concentration

The chlorine concentration was measured as free chlorine using multiple instruments. Initially, during lab experiments, the chlorine was measured using an HF Scientific Pocket Photometer for Total and Free Chlorine. A DPD Free Chlorine Powder Pop dispenser was used to add the reagent. Initially, the 10 ml volume of sample was collected in a vial and the instrument was zeroed. The reagent was then added and the vial was inverted three times to mix the solution. The sample was then inserted into the instrument and the measurement was taken. During subsequent lab and field experiments, a HACH Chlorine Pocket Colorimeter 46700 was used to measure the free chlorine residual. The HACH free chlorine reagents were added to a 10 ml sample and the vial was inverted three times prior to the measurement.

3.3.11 Flow Rate

The flow rate was measured using a flow meter during laboratory and pilot experiments. The flow was also verified by filling a graduated cylinder with effluent and timing it with a stopwatch.

3.3.12 Head Loss

The head loss was measured using a differential pressure gauge during laboratory and pilot experiments.

CHAPTER 4: EXPERIMENTAL RESULTS AND DISCUSSION

This chapter presents and discusses the experimental results for the second-stage contactor experiments conducted in the water treatment laboratory at the University of Massachusetts – Amherst and the two-stage pilot plant experiments performed at Aquarion Water Company’s Lantern Hill facility in Stonington, CT. The UMass laboratory experimental results include assessment of manganese removal as a function of media bed depth for a variety of effluent chlorine residuals and hydraulic loading rates. The results for the Lantern Hill pilot plant experiments include assessment of manganese, iron, TOC, and turbidity removal. Optimization of chemical dosing and DBP analyses were also part of these pilot experiments.

4.1 University of Massachusetts – Amherst Second-Stage Contactor Laboratory Experiments

This section describes results for the second-stage contactor experiments conducted in the water treatment laboratory at the University of Massachusetts – Amherst.

4.1.1 Media Performance for All Operational Scenarios

Tap water was filtered by a GAC filter and was stored in the reserve tank. The UV_{254} and pH of the water in the reserve tank were 0.011 cm^{-1} and 6.68, respectively, and were considered appropriate for these experiments. Due to the use of different media depths during these experiments, all media comparisons were made at the minimum media depth of approximately 27 inches. The influent manganese concentration was kept constant at 0.2 mg/L. The fraction of influent manganese removed as a function of media depth was used as a measure of the media performance. In order to achieve the desired finished water manganese concentration of 0.02 mg/L or less, the value for the fraction of the initial manganese concentration needs to be approximately 0.1 or less. The four sets of data obtained for each hydraulic loading rate and chlorine residual were averaged to characterize performance for a set of conditions.

The overall performance of anthracite # 1 is shown in Figure 4-1, where the media performance at all of the hydraulic loading rates and chlorine residuals is compared. The media removed a

greater fraction of Mn at lower HLRs and higher Cl₂ residuals. The media performed best at an HLR of 10 GPM/ft² and a Cl₂ residual of 4.0 mg/L. Table A-1 in the Appendix shows the averaged data for each set of test runs for the anthracite # 1 column.

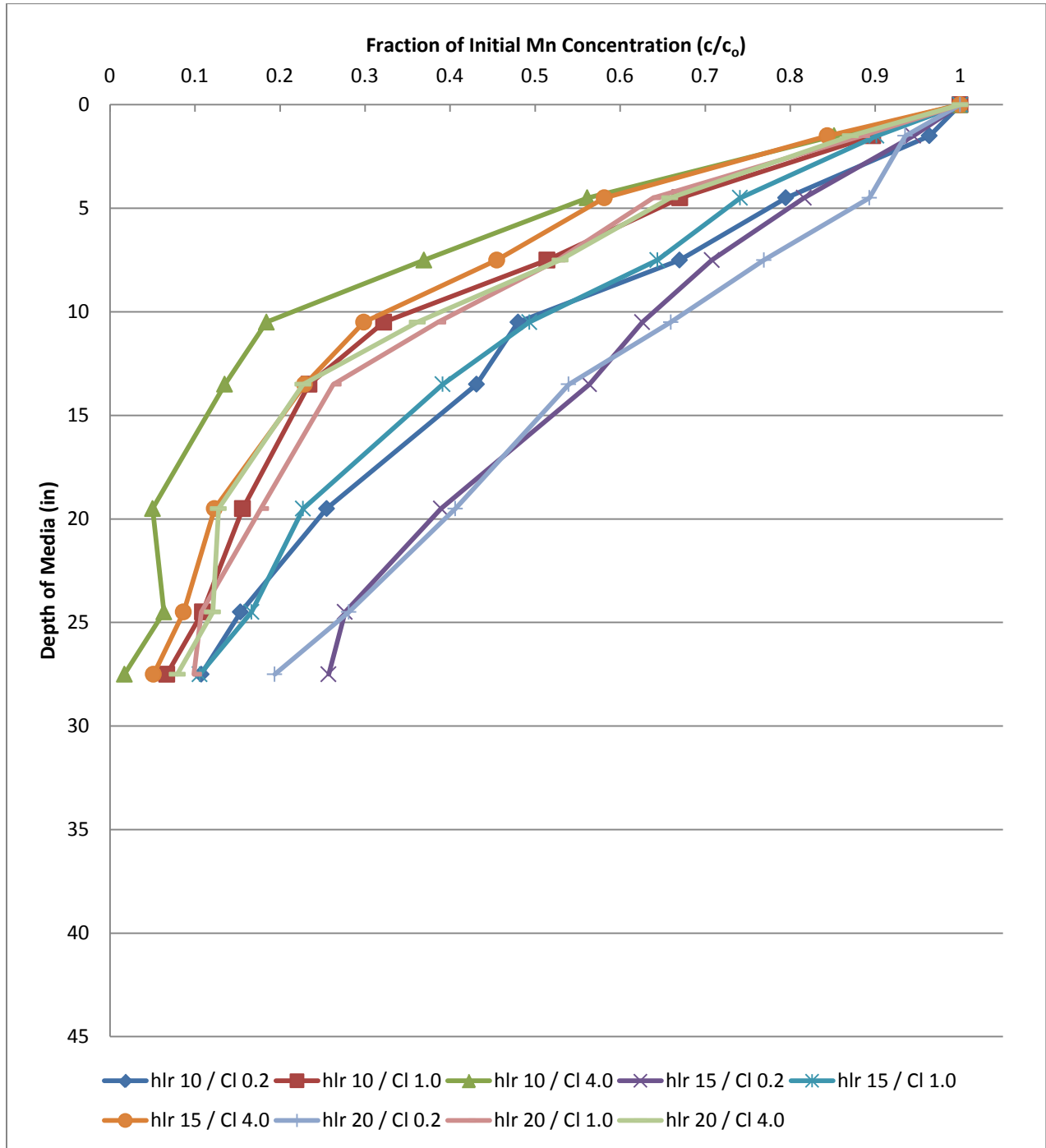


Figure 4-1: Effects of hydraulic loading rate (GPM/ft²) and effluent chlorine residual (mg/L) on the fraction of the initial Mn concentration versus column depth for anthracite # 1.

Figure 4-2 shows the performance of anthracite # 2 for all hydraulic loading rates and chlorine residuals. This media performed significantly better at lower HLRs and higher Cl₂ residuals. At an HLR of 10 GPM/ft² and a Cl₂ residual of 4.0 mg/L, the greatest fraction of influent Mn was removed. The averaged data for each set of test runs can be found in Table A-2 in the Appendix.

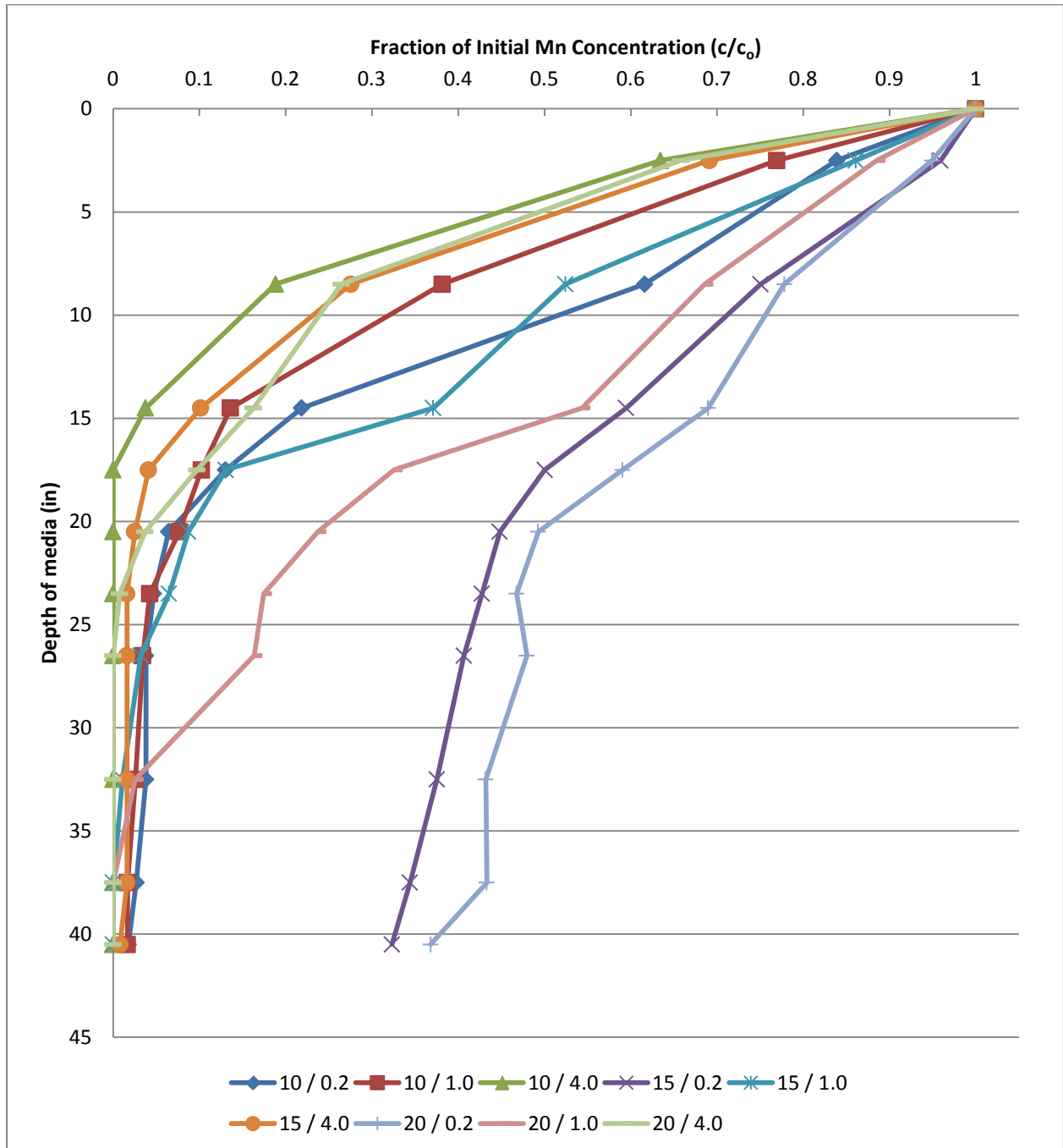


Figure 4-2: Effects of hydraulic loading rate (GPM/ft²) and effluent chlorine residual (mg/L) on the fraction of the initial Mn concentration versus column depth for anthracite # 2.

Figure 4-3 shows the performance of UMass Macrolite for all hydraulic loading rates and chlorine residuals. The media performed best at lower HLRs and higher Cl₂ residuals. At an HLR of 10 GPM/ft² and a Cl₂ residual of 4.0 mg/L, the greatest fraction of Mn was removed. It was observed for this set of data, as well as for other data sets, that the influent Mn concentration for the UMass Macrolite is less than or equal to the Mn concentration at the first port. This creates a fraction of initial Mn concentration greater than one at the first port in the column. It is suspected that some of the MnO_x on the surface of the media could have released during early test runs. This could be a result of the modified conditioning process and possibly insufficient backwashing of the conditioned media. The averaged data for each set of test runs can be found in Table A-3 in the Appendix.

The performance of the Fairmount conditioned Macrolite for all hydraulic loading rates and chlorine residuals can be seen in Figure 4-4. Compared to other media, the performance of the Macrolite was less dependent on the chlorine residual and moderately dependent on the HLR. The best performance occurred at an HLR of 15 GPM/ft² and a chlorine residual of 1.0 mg/L. This could potentially be due to the MnO_x coating becoming more developed during the previous 10 GPM/ft² test runs, resulting in greater Mn²⁺ adsorption. All of the profiles for this media displayed similar trends and resulted in satisfactory effluent Mn concentrations. Table A-4 in the Appendix shows the averaged data for each set of test runs for the Macrolite column.

Figure 4-5 shows the performance of the pyrolusite at all of the hydraulic loading rates and chlorine residuals. The pyrolusite performance improved at a lower hydraulic loading rate and higher chlorine residual. This media performed best at an HLR of 15 gpm/ft² and a Cl₂ residual of 4.0 mg/L. Also, it is evident in this data set, as well as some other data sets, that the influent Mn concentration for the pyrolusite is less than or equal to the Mn concentration at the first port. This creates a fraction of initial Mn concentration greater than one at the first port in the column. At the conclusion of the pyrolusite testing, it was noted that the influent test line had built up a significant MnO_x coating and was presumably lowering the influent Mn concentration by adsorption. This test line was replaced and the experiment continued. Table A-5 in the Appendix shows the averaged data for each set of test runs for the pyrolusite column.

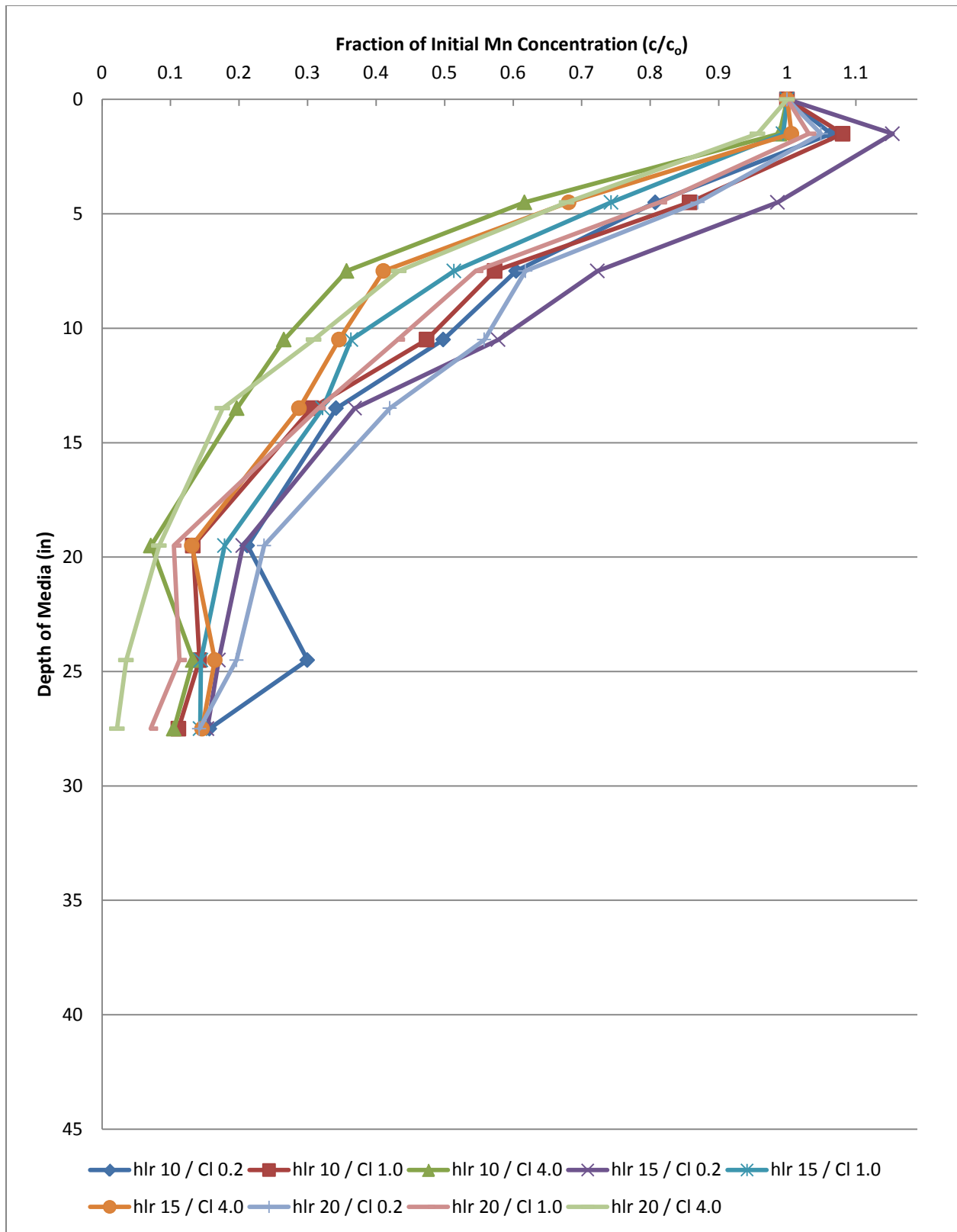


Figure 4-3: Effects of hydraulic loading rate (GPM/ft²) and effluent chlorine residual (mg/L) on the fraction of the initial Mn concentration versus column depth for UMass Macrolite.

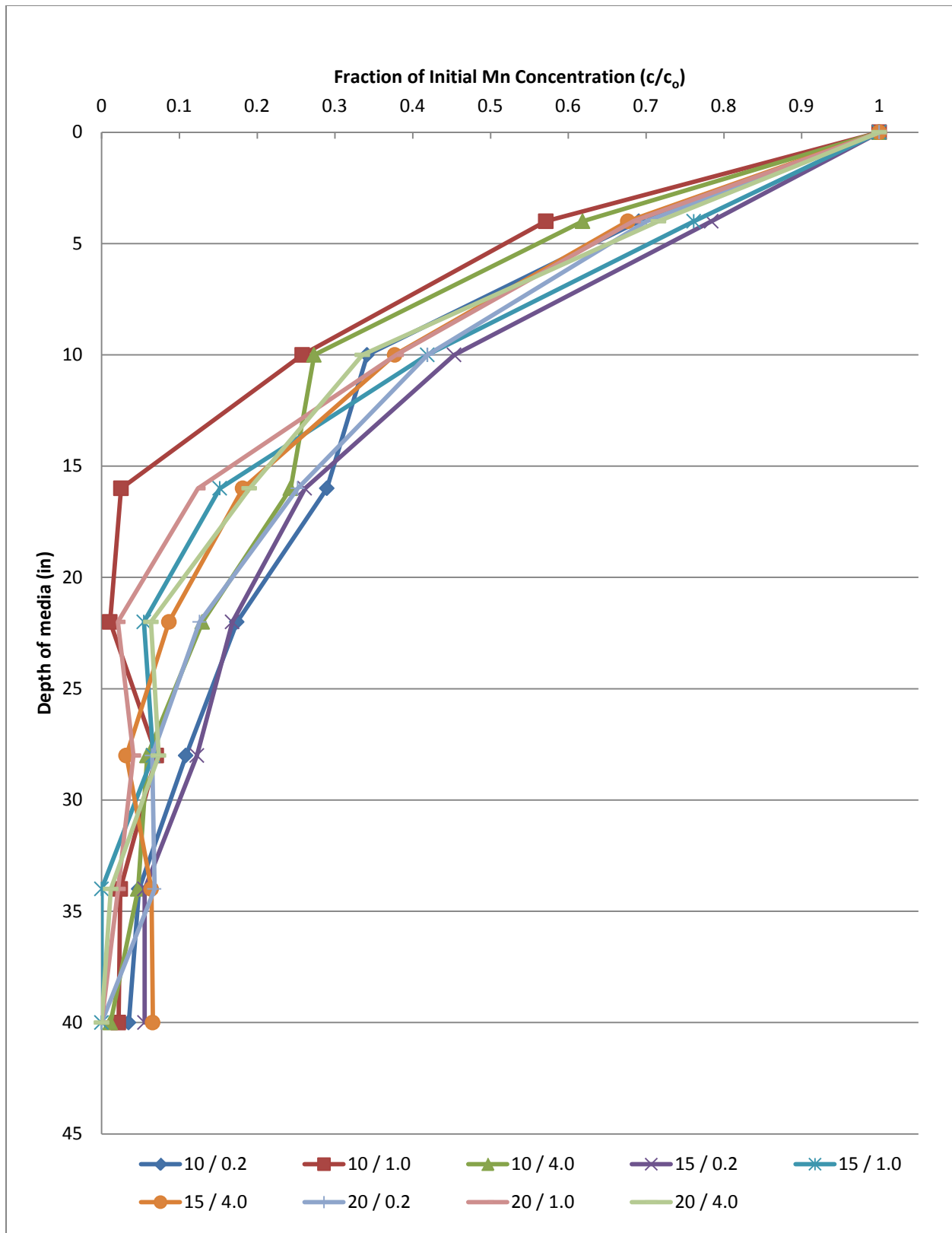


Figure 4-4: Effects of hydraulic loading rate (GPM/ft²) and effluent chlorine residual (mg/L) on the fraction of the initial Mn concentration versus column depth for Macrolite.

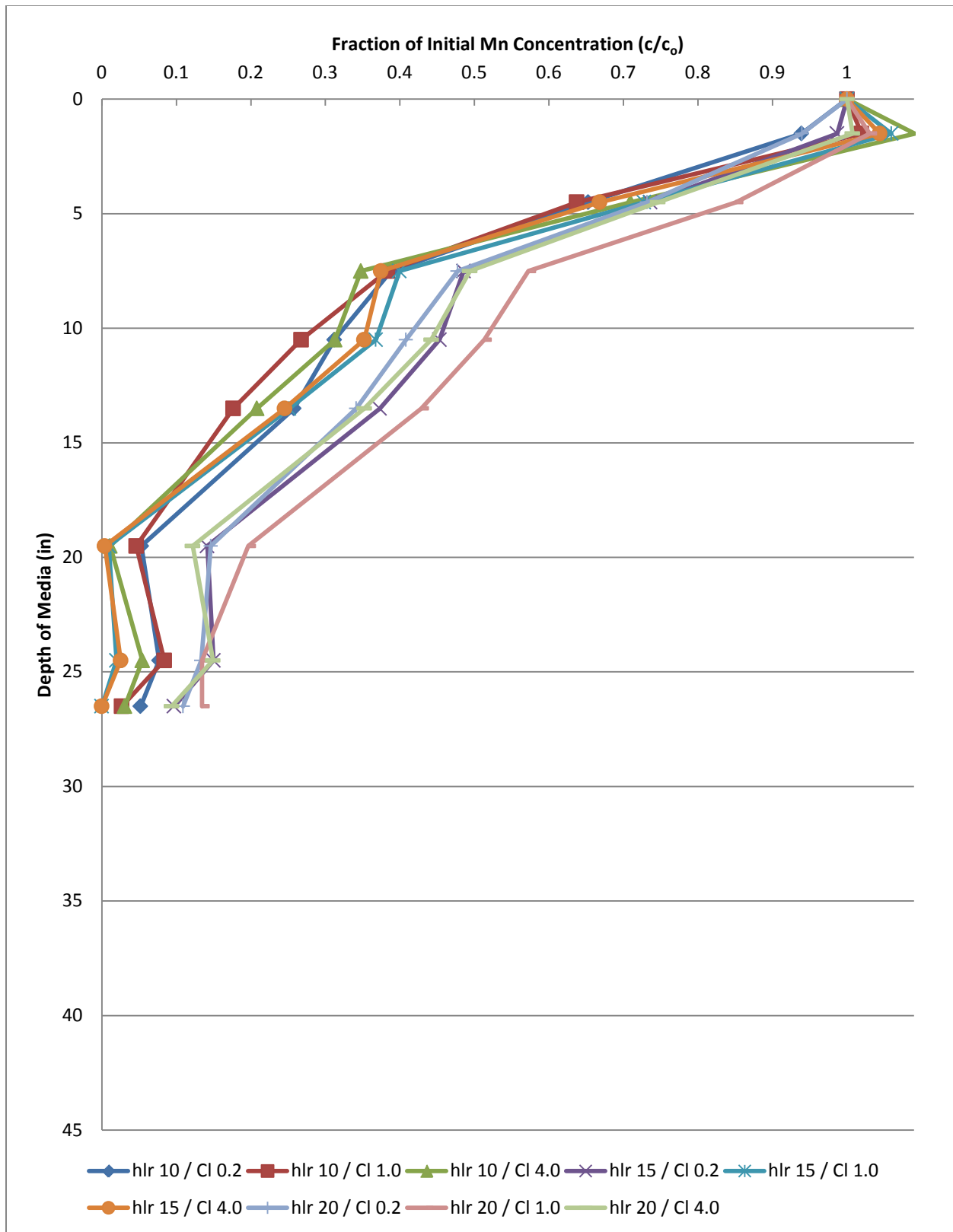


Figure 4-5: Effects of hydraulic loading rate (GPM/ft²) and effluent chlorine residual (mg/L) on the fraction of the initial Mn concentration versus column depth for pyrolusite.

4.1.2 Comparison of All Media at a Hydraulic Loading Rate of 10 GPM/ft²

Figure 4-6 shows plots of the fraction of the initial manganese concentration versus the depth of the media for all media types at a hydraulic loading rate of 10 GPM/ft² and a chlorine residual of 0.2 mg/L. The pyrolusite performed the best at these conditions and had an average contactor effluent Mn concentration of 0.01 mg/L.

Figure 4-7 shows plots of the fraction of the initial manganese concentration versus the depth of the media for all media types at a hydraulic loading rate of 10 GPM/ft² and a chlorine residual of 1.0 mg/L. These conditions are representative of full-scale conditions at the Lantern Hill water treatment plant. At a media depth of 26.5 inches, the pyrolusite had the lowest Mn concentration, with the anthracite # 2 performing in a very similar manner. Also, the Macrolite had a lower Mn concentration at the ports above and below the location used for comparison. This irregularity could have been due to manganese analysis precision. The average effluent Mn concentrations for the pyrolusite, anthracite # 2, and Macrolite were 0.01 mg/L.

Plots of the fraction of the initial manganese concentration versus the depth of the media for all media types at a hydraulic loading rate of 10 GPM/ft² and a chlorine residual of 4.0 mg/L can be seen in Figure 4-8. At these conditions, the anthracite # 2 performed best and had an average Mn effluent concentration that was non-detectable.

In general, the Macrolite, pyrolusite, and anthracite # 2 could achieve the desired effluent manganese concentration at a hydraulic loading rate of 10 GPM/ft² for any of the effluent chlorine residuals. The average head loss across the column at this hydraulic loading rate was 0.3 psi, at an average water temperature of 20° C.

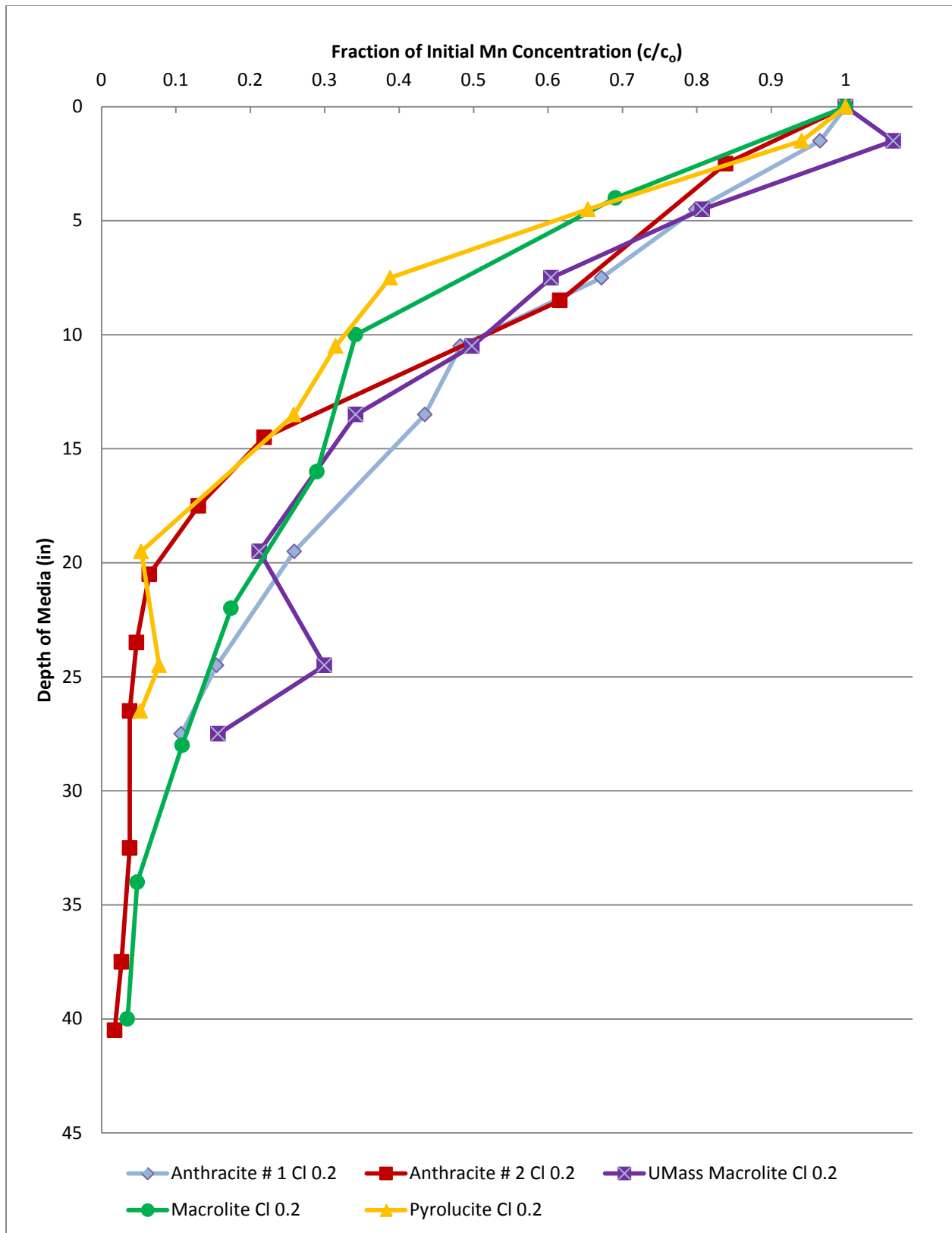


Figure 4-6: Mn profiles for the five media types with a 0.2 mg/L effluent chlorine residual at a hydraulic loading rate of 10 GPM/ft².

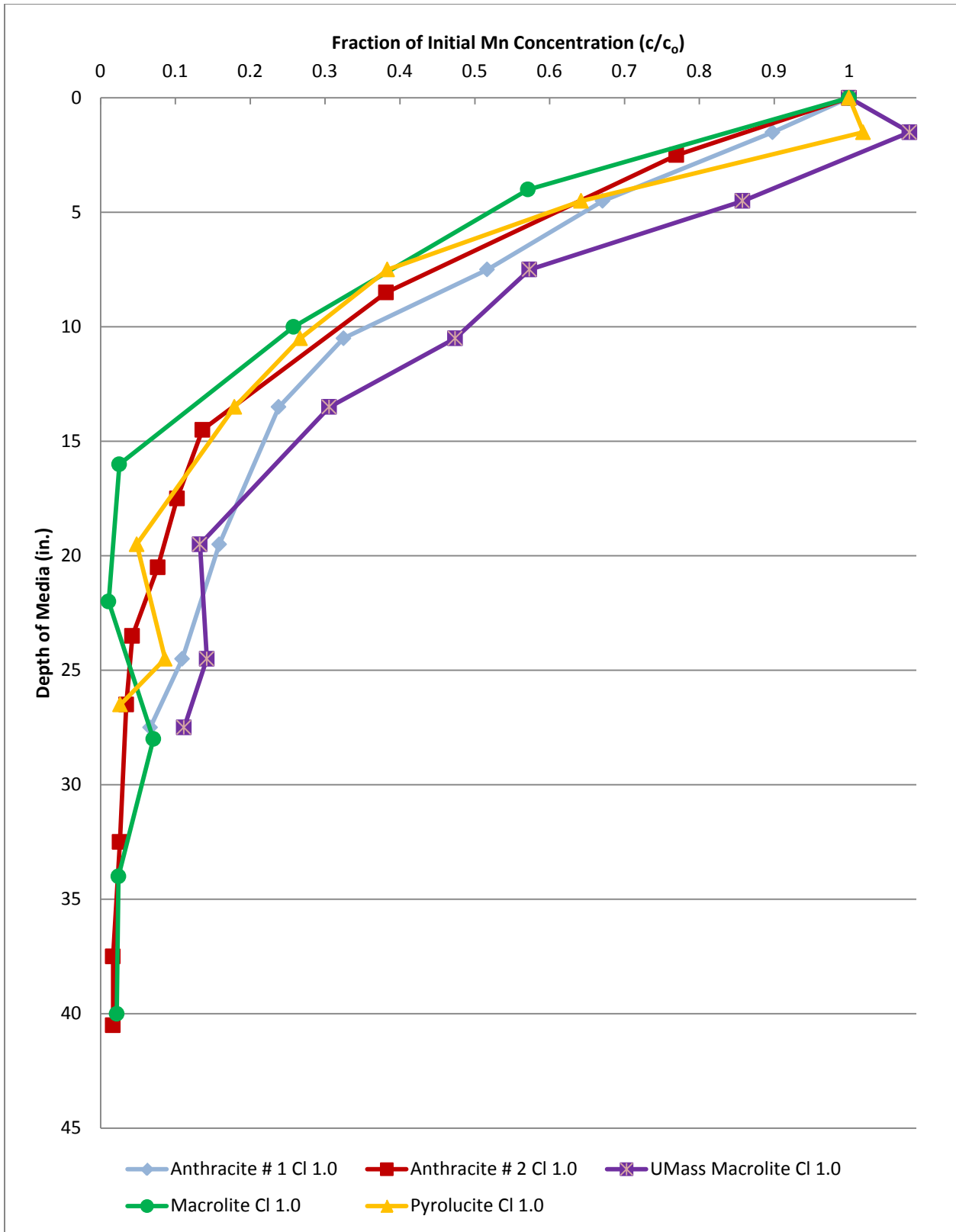


Figure 4-7: Mn profiles for the five media types with a 1.0 mg/L effluent chlorine residual at a hydraulic loading rate of 10 GPM/ft².

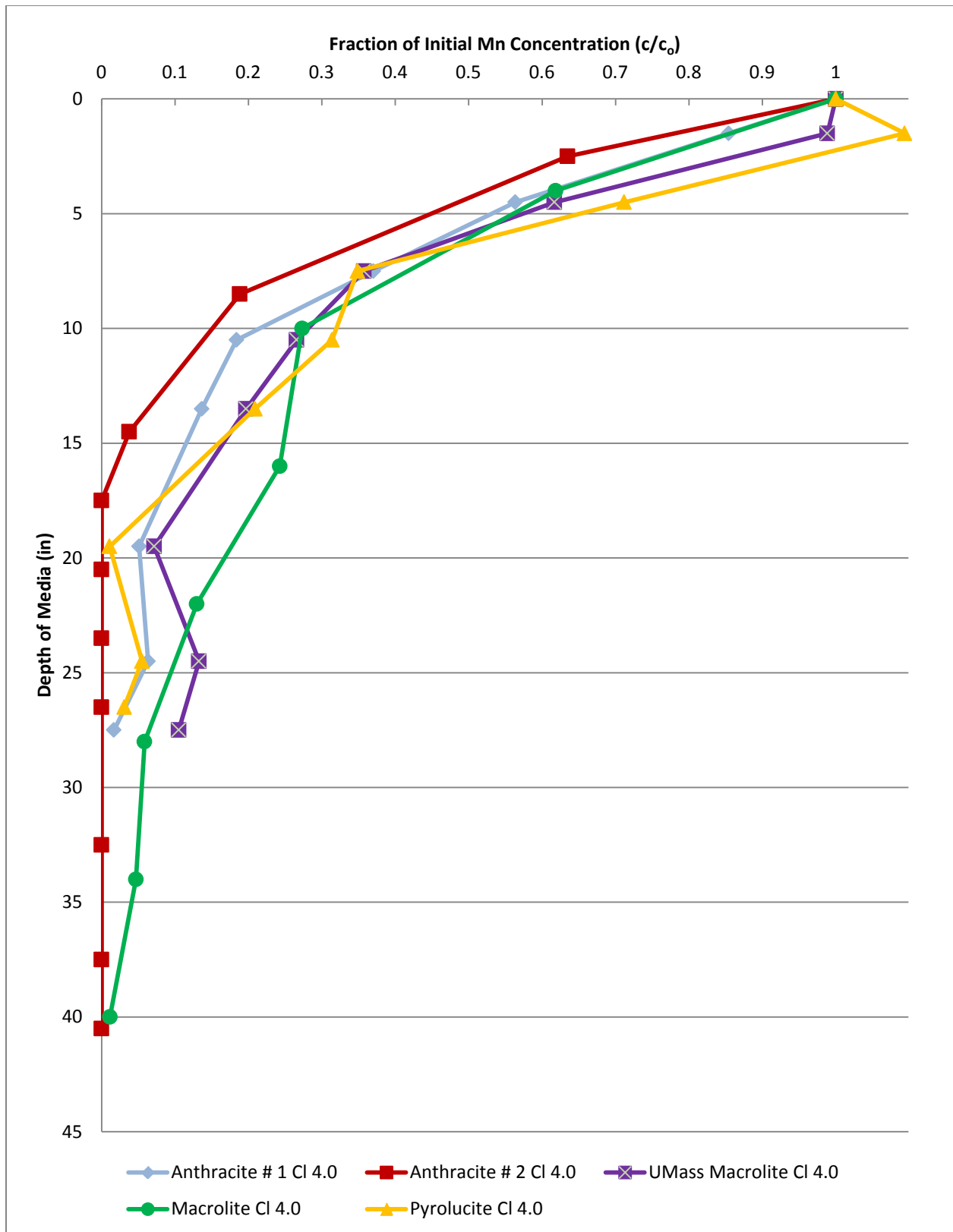


Figure 4-8: Mn profiles for the five media types with a 4.0 mg/L effluent chlorine residual at a hydraulic loading rate of 10 GPM/ft².

4.1.3 Comparison of All Media at a Hydraulic Loading Rate of 15 GPM/ft²

Figures 4-9, 4-10, and 4-11 show the Mn removal performance for all media types at a hydraulic loading rate of 15 GPM/ft² for effluent chlorine residuals of 0.2, 1.0, and 4.0 mg/L, respectively. For a chlorine residual of 0.2 mg/L, the pyrolusite performed best and had an average effluent Mn concentration of 0.02 mg/L. At a chlorine residual of 1.0 mg/L, the pyrolusite removed the greatest fraction of Mn and the average effluent Mn concentration was non-detectable. For a chlorine residual of 4.0 mg/L, the pyrolusite had the best performance and the average effluent Mn concentration was non-detectable. In general, the Macrolite and the pyrolusite could achieve the desired effluent manganese concentration at a hydraulic loading rate of 15 GPM/ft² for any of the effluent chlorine residuals. However, as noted previously, performance is worse for the lowest chlorine residual, 0.2 mg/L, and more similar for the 1.0 and 4.0 mg/L residuals.

4.1.4 Comparison of All Media at a Hydraulic Loading Rate of 20 GPM/ft²

Figures 4-12, 4-13, and 4-14 show the Mn removal performance for all media types at a hydraulic loading rate of 20 GPM/ft² for effluent chlorine residuals of 0.2, 1.0, and 4.0 mg/L, respectively. At a chlorine residual of 0.2 mg/L, the Macrolite had the best performance and the average effluent Mn concentration was non-detectable. For a chlorine residual of 1.0 mg/L, the Macrolite performed best and had an average effluent Mn concentration that was non-detectable. At a chlorine residual of 4.0 mg/L, the anthracite # 2 removed the greatest fraction of Mn and the average effluent Mn concentration was non-detectable. In general, the Macrolite could achieve the desired effluent manganese concentration at a hydraulic loading rate of 20 GPM/ft² for any of the effluent chlorine residuals. Again, performance is worst for the 0.2 mg/L chlorine residual and there is significant improvement from the 1.0 mg/L residual to the 4.0 mg/L residual. Thus as the hydraulic loading rate increases, the performance is more sensitive to the chlorine residual.

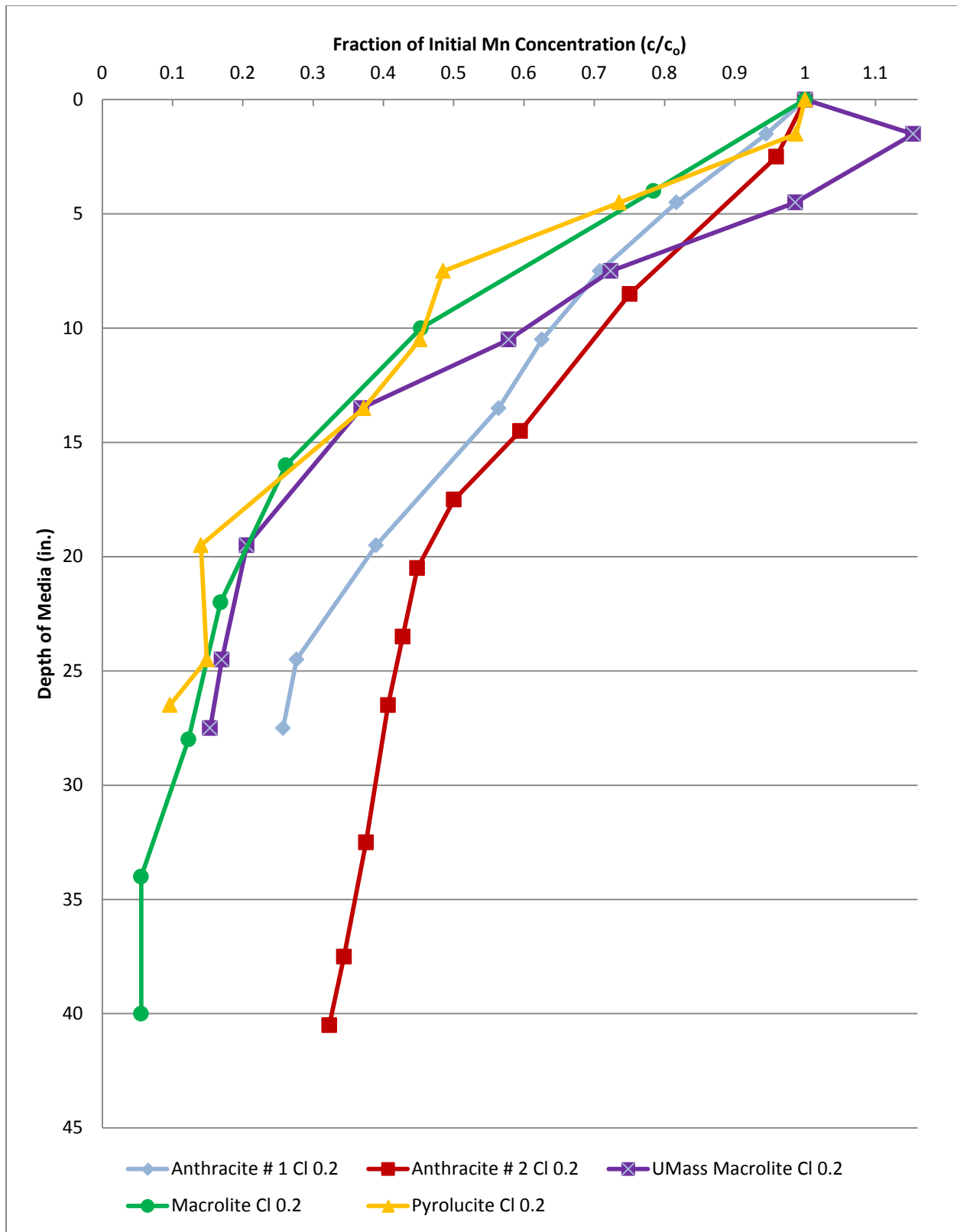


Figure 4-9: Mn profiles for the five media types with a 0.2 mg/L effluent chlorine residual at a hydraulic loading rate of 15 GPM/ft².

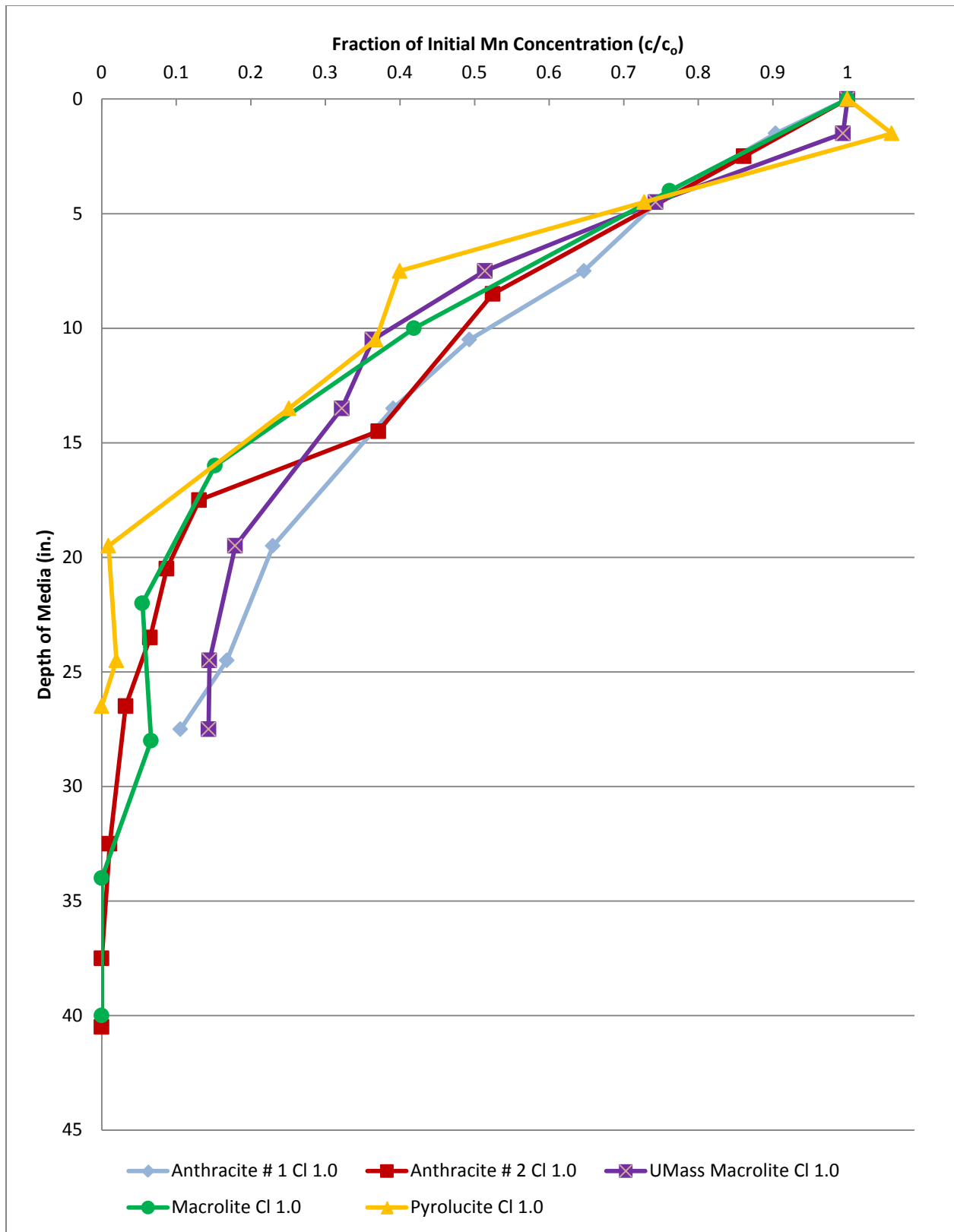


Figure 4-10: Mn profiles for the five media types with a 1.0 mg/L effluent chlorine residual at a hydraulic loading rate of 15 GPM/ft².

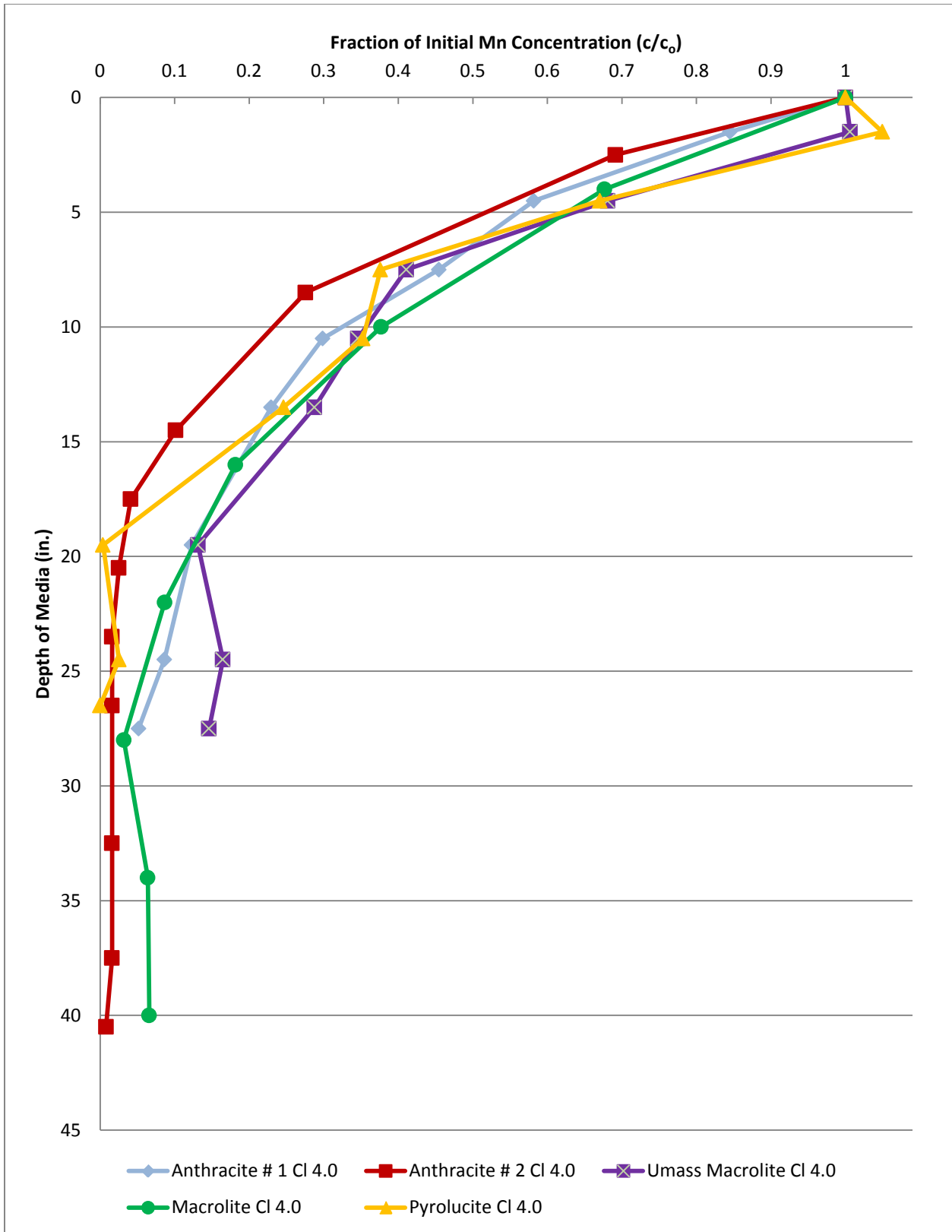


Figure 4-11: Mn profiles for the five media types with a 4.0 mg/L effluent chlorine residual at a hydraulic loading rate of 15 GPM/ft².

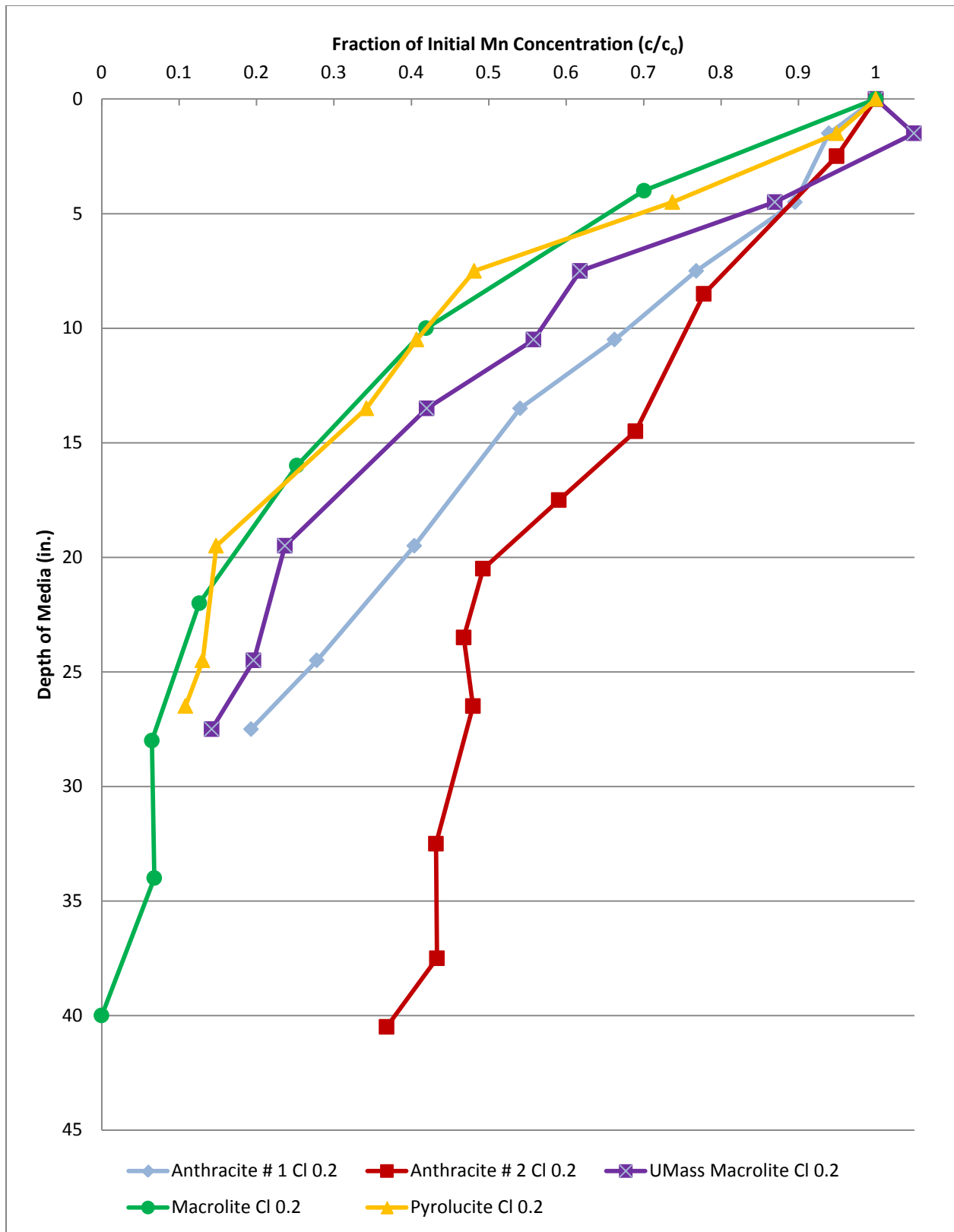


Figure 4-12: Mn profiles for the five media types with a 0.2 mg/L effluent chlorine residual at a hydraulic loading rate of 20 GPM/ft².

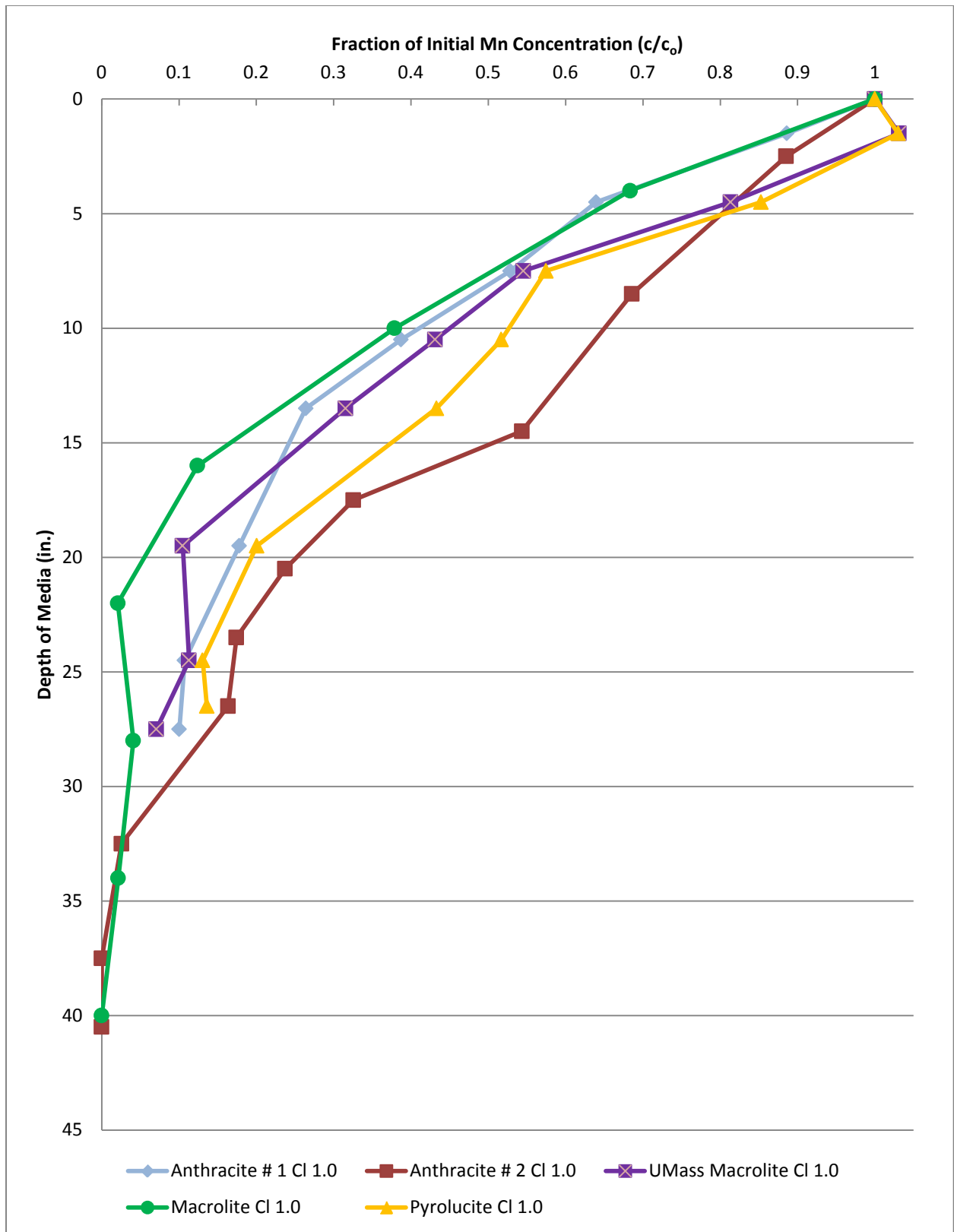


Figure 4-13: Mn profiles for the five media types with a 1.0 mg/L effluent chlorine residual at a hydraulic loading rate of 20 GPM/ft².

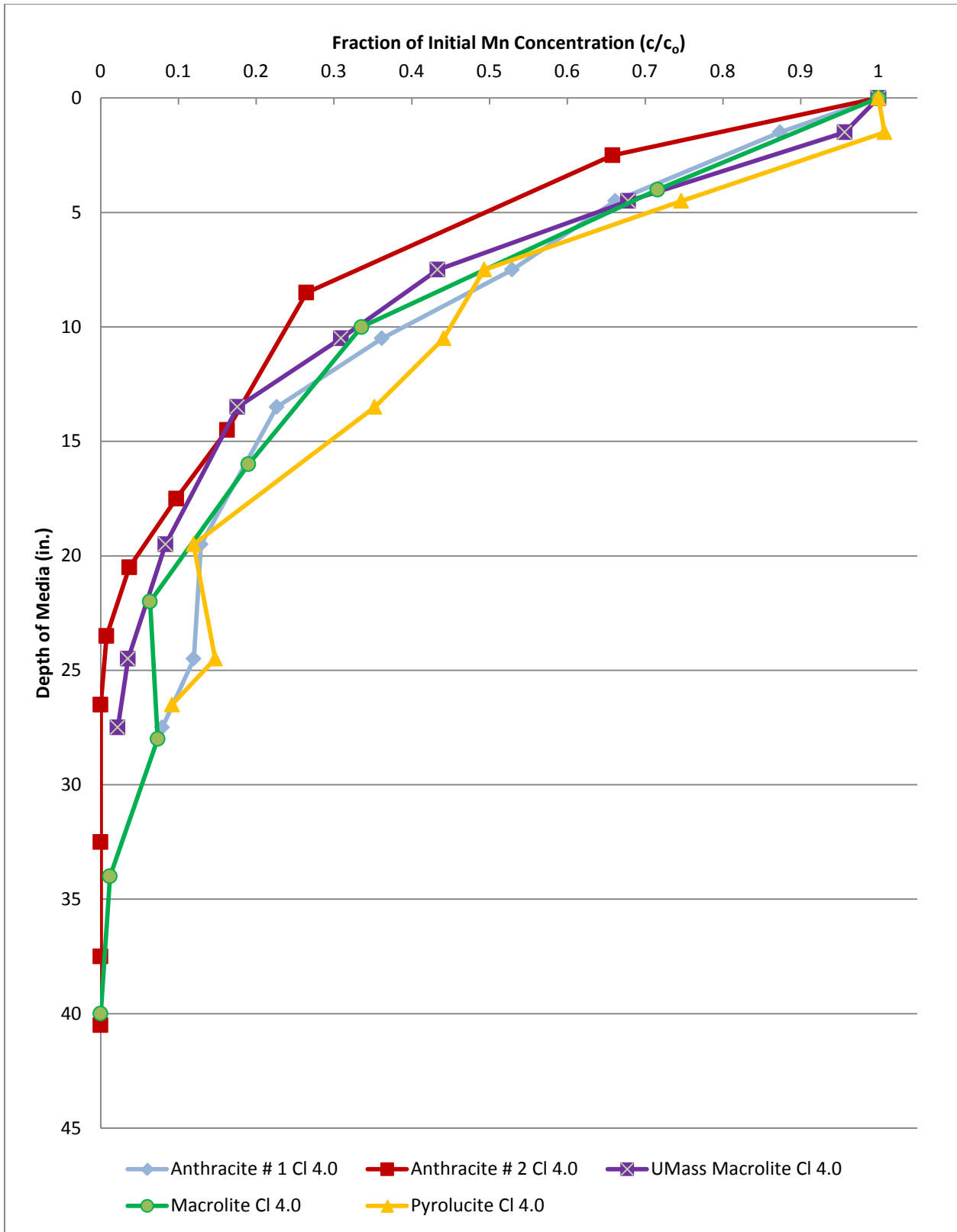


Figure 4-14: Mn profiles for the five media types with a 4.0 mg/L effluent chlorine residual at a hydraulic loading rate of 20 GPM/ft².

Table 4-1 shows the average chlorine demands measured during laboratory experiments for each set of test parameters and each media type. The chlorine demand was determined by the difference between chlorine concentrations in the influent and effluent sample lines. On average the pyrolusite exhibited the greatest chlorine demand overall. This could potentially be due to the fact that this media is Mn oxide throughout, as opposed to other media types containing only a Mn oxide coating, and with more MnO_x surface, there is more potential for catalytic oxidation by chlorine. For all media, the general trend was as the chlorine residual was increased for a given hydraulic loading rate, the chlorine demand increased. This is most likely a result of more chlorine being available for oxidation processes. Another relationship observed was as the hydraulic loading rate for a particular chlorine residual was increased, the chlorine demand decreased. This was potentially due to the physical limitations of the chlorine contacting the surface of the media at higher flow rates, limiting the catalytic oxidation by the chlorine at the surface of the media.

Table 4-1: The average chlorine demand for each set of test parameters and each media type. (Measured across the media bed)

	Anthracite # 1 (27.5-in bed depth)	Anthracite # 2 (40.5-in bed depth)	UMass Macrolite (27.5-in bed depth)	Macrolite (40-in bed depth)	Pyrolusite (26.5-in bed depth)
HLR/Cl₂	Cl ₂ demand (mg/L)	Cl ₂ demand (mg/L)	Cl ₂ demand (mg/L)	Cl ₂ demand (mg/L)	Cl ₂ demand (mg/L)
10/0.2	0.27	0.23	0.17	0.12	0.21
10/1.0	0.42	0.81	0.3	0.31	0.63
10/4.0	0.43	0.73	0.69	0.66	1.03
15/0.2	0.17	0.19	0.18	0.07	0.22
15/1.0	0.39	0.56	0.27	0.52	0.86
15/4.0	0.6	0.44	0.27	0.66	1.36
20/0.2	0.13	0.41	0.24	0.12	0.41
20/1.0	0.34	0.21	0.34	0.42	0.66
20/4.0	0.56	0.53	0.59	0.74	0.98

4.1.5 Effects of Chlorine Residual and Hydraulic Loading Rate on Manganese Removal for the Macrolite and Anthracite # 2 Media at Typical LH Full-Scale Conditions

Additional analyses were made to isolate the effects of the effluent chlorine residual and the hydraulic loading rate on manganese removal for the Macrolite and the anthracite # 2 media. These two media were selected for analysis because they were considered the most likely options for the final full-scale design based on their performance, physical properties, and availability.

4.1.5.1 Effects of Chlorine Residual on Manganese Removal for the Macrolite and Anthracite # 2 Media

Figures 4-15 and 4-16 show the effect of effluent chlorine residual on the fraction of initial Mn throughout the depth of the media for the Macrolite and the anthracite # 2, respectively. The hydraulic loading rate was held constant at 10 GPM/ft², which is typical of full-scale conditions, and the effluent chlorine residual was varied (0.2, 1.0, and 4.0 mg/L).

The performance of the Macrolite was moderately affected by varying the effluent chlorine residual. At an effluent chlorine residual of 0.2 mg/L, the least amount of manganese was removed throughout the profile. The greatest fraction of manganese was removed with an effluent chlorine residual of 1.0 mg/L, which is approximately the residual for full-scale operations. The fact that the manganese removal performance at a residual of 4.0 mg/L was worse than the performance at 1.0 mg/L was unexpected because at higher residuals more free chlorine is available for catalytic oxidation. The reason for this discrepancy is unknown; however, for the range of effluent chlorine residuals tested, all effluents had Mn concentrations of 0.02 mg/L or less.

The performance of the anthracite # 2 was moderately affected by varying the effluent chlorine residual. With an effluent chlorine residual of 0.2 mg/L, the least amount of manganese was removed throughout the profile. Performance improved for an effluent chlorine residual of 1.0 mg/L, which is typical of full-scale operations. The greatest fraction of manganese was removed with an effluent chlorine residual of 4.0 mg/L. For the range of effluent chlorine residuals tested, the manganese concentrations in the effluents were 0.02 mg/L or less.

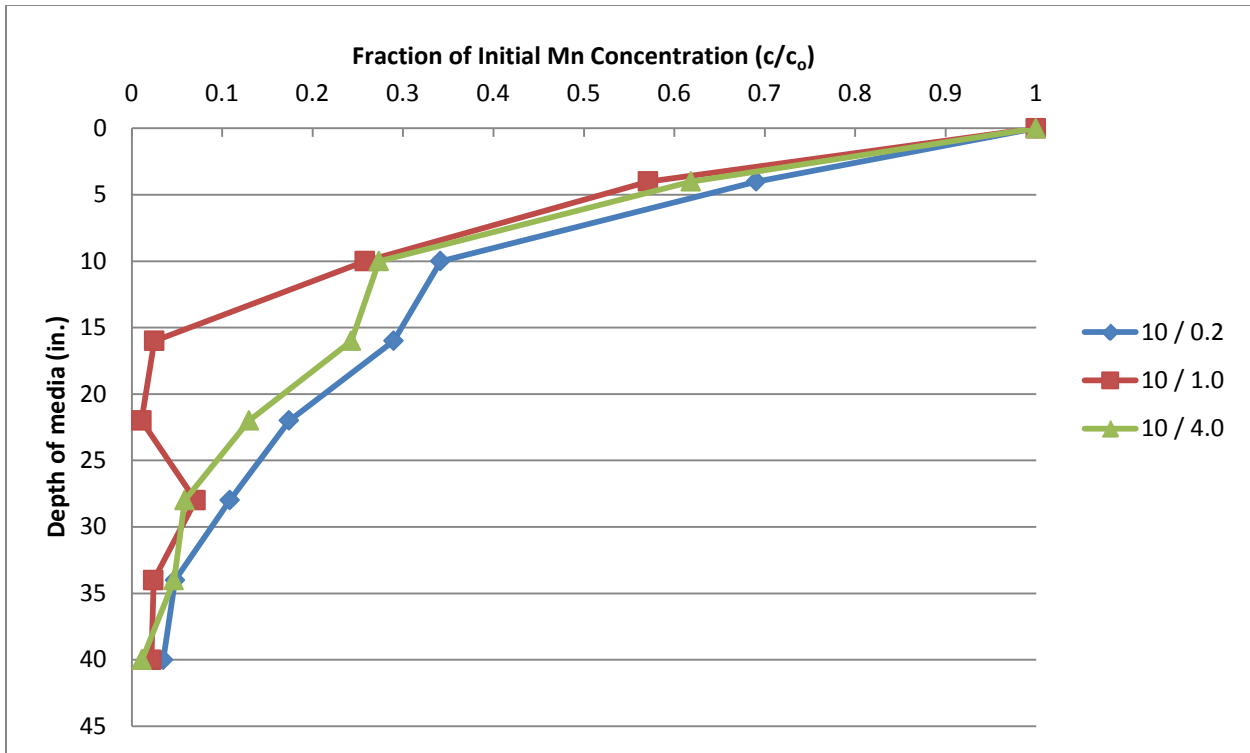


Figure 4-15: Effects of effluent chlorine residual (mg/L) on the fraction of the initial Mn concentration versus column depth for Macrolite at a hydraulic loading rate of 10 GPM/ft².

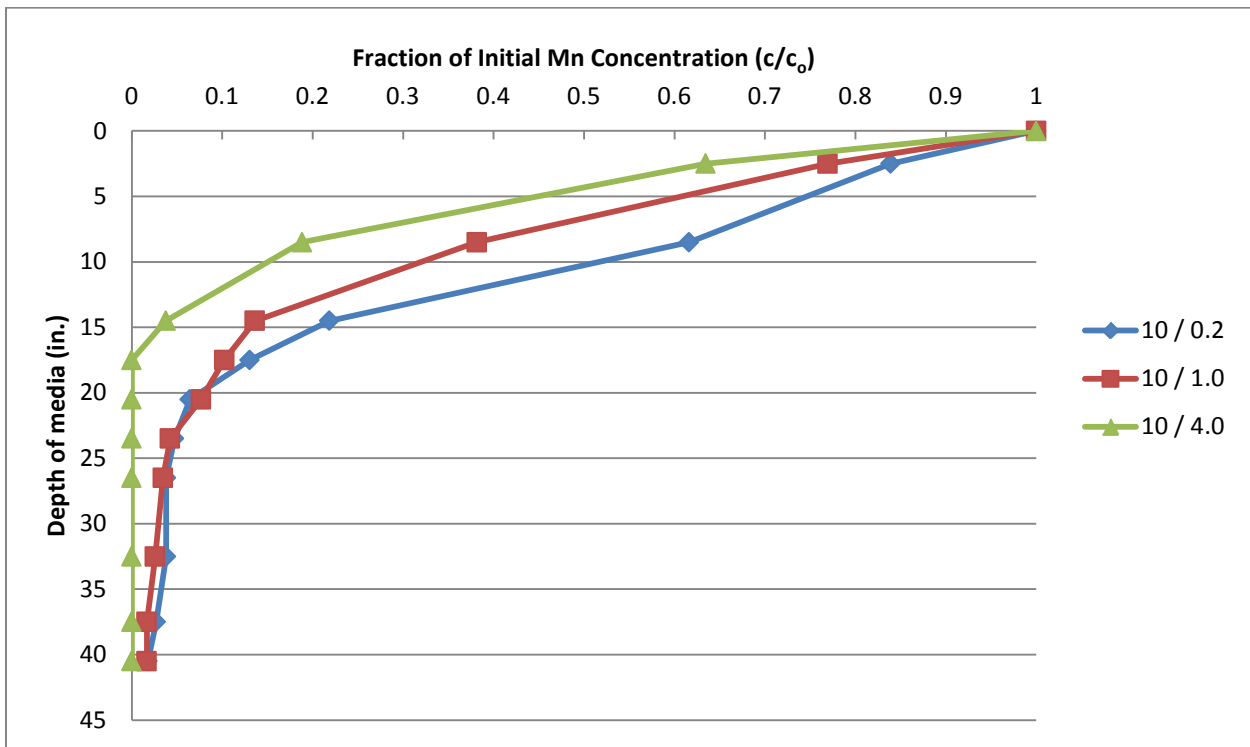


Figure 4-16: Effects of effluent chlorine residual (mg/L) on the fraction of the initial Mn concentration versus column depth for anthracite # 2 at a hydraulic loading rate of 10 GPM/ft².

4.1.5.2 Effects of Hydraulic Loading Rate on Manganese Removal for the Macrolite and Anthracite # 2 Media

The effects of hydraulic loading rate on the fraction of initial manganese remaining throughout the depth of the media for the Macrolite and anthracite # 2 can be seen in Figures 4-17 and 4-18, respectively. The effluent chlorine residual was held constant at 1.0 mg/L, which is typical of full-scale conditions, and the hydraulic loading rate was varied (10, 15, and 20 GPM/ft²). The performance of the Macrolite was not greatly affected by varying the hydraulic loading rate. Overall the profile for the hydraulic loading rate of 10 GPM/ft², which is the design rate for full-scale operations, displayed the best performance, even for a media bed depth of less than 20 inches. At a hydraulic loading rate of 20 GPM/ft², a greater fraction of manganese was removed than at a hydraulic loading rate of 15 GPM/ft². This was unexpected because at a higher hydraulic loading rate, there is less time for adsorption and oxidation on the media. The reason for this performance discrepancy is unknown; however, for the range of hydraulic loading rates tested, all effluents had Mn concentrations of 0.02 mg/L or less.

The performance of the anthracite # 2 was somewhat more dependent on the hydraulic loading rate. The greatest fraction of manganese was removed at a hydraulic loading rate of 10 GPM/ft². The performance of the media at a hydraulic loading rate of 15 GPM/ft² was better than that of 20 GPM/ft². It was evident that as the hydraulic loading rate was increased the resulting fraction of initial Mn concentration increased. This is a result of less contact time in the media bed for a given volume of water. For the range of hydraulic loading rates tested, all effluents had Mn concentrations of 0.02 mg/L or less.

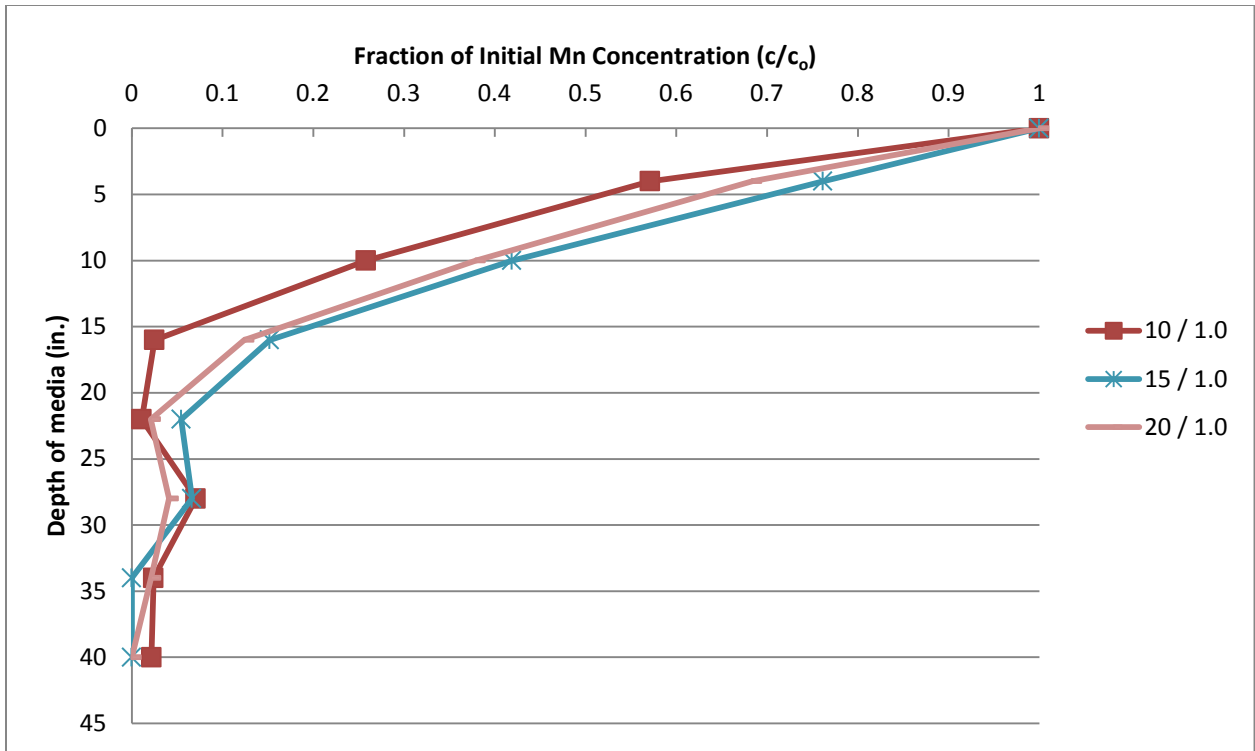


Figure 4-17: Effects of hydraulic loading rate (GPM/ft²) on the fraction of the initial Mn concentration versus column depth for Macrolite with an effluent chlorine residual of 1.0 mg/L.

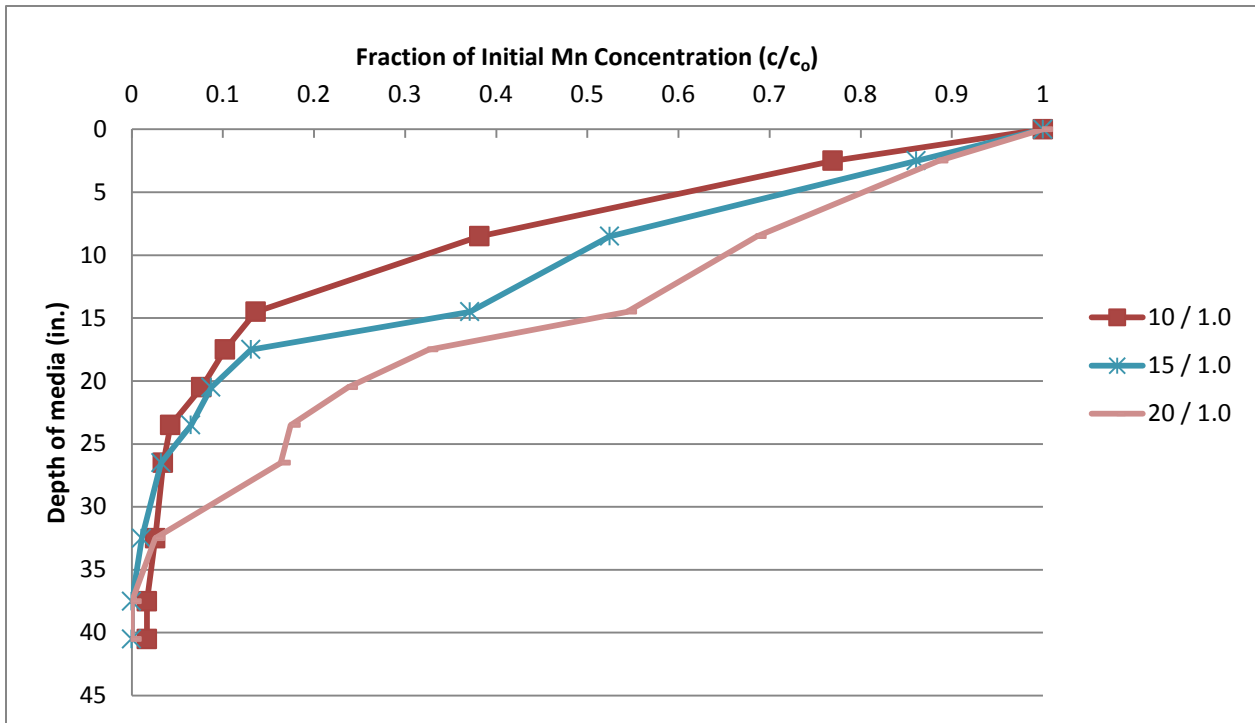


Figure 4-18: Effects of hydraulic loading rate (GPM/ft²) on the fraction of the initial Mn concentration versus column depth for anthracite # 2 with an effluent chlorine residual of 1.0 mg/L.

4.2 Lantern Hill Two-Stage Pilot Plant Contactor Media Experiments

This section describes results for the two-stage pilot plant experiments conducted at Aquarion Water Company's Lantern Hill Facility in Stonington, CT.

4.2.1 Water Quality and Plant Operation

Pre-Contactor Conditions

The average raw water quality at Lantern Hill during the pilot experiments can be seen in Table 4-2. The total manganese concentration ranged from 0.14 to 0.22 mg/L, with a reduced (dissolved) manganese (Mn^{2+}) concentration ranging from 0.12 to 0.22 mg/L, with averages of 0.17 and 0.17 mg/L, respectively. The total iron concentration ranged from 1.16 to 2.39, with a reduced (dissolved) iron (Fe^{2+}) concentration ranging from 1.03 to 2.34, with averages of 1.85 and 1.69 mg/L, respectively. The pH of the groundwater ranged from 6.35 to 6.67 with an average value of 6.51. The UV_{254} ranged from 0.128 to 0.165 cm^{-1} with an average value of 0.153 cm^{-1} . The TOC ranged from 3.03 to 4.30 mg/L with an average value of 3.48 mg/L.

Table 4-2: Average Lantern Hill raw water quality during pilot testing.

	Total Mn (mg/L)	Dissolved Mn (mg/L)	Total Fe (mg/L)	Dissolved Fe (mg/L)	pH	UV_{254} (cm^{-1})	TOC (mg/L)
Average	0.17	0.17	1.85	1.69	6.51	0.153	3.48
Range	0.14-0.22	0.12-0.22	1.16-2.39	1.03-2.34	6.35-6.67	0.128-0.165	3.03-4.30

Dissolved iron values were used to determine oxidant dosing for complete iron oxidation ahead of the dual media filter. The dissolved iron was oxidized to the particulate form and these iron particles were removed through filtration. The dissolved metal concentrations were most often determined from routine fractionations. Figures 4-19 and 4-20 show results of metal fractionations conducted across the pre- $KMnO_4$ / NaOCl pilot system during testing. The differences in the relative amounts of the particulate, colloidal, and dissolved forms of metals

are shown. A majority of the combined colloidal and dissolved fraction was dissolved, thus metals in the filtrate from the 0.2 micron syringe filter were considered dissolved. Almost all of the raw water metals were dissolved.

When KMnO_4 was used as the pre-oxidant, it was found that it could be dosed at a sub-stoichiometric level and yield complete iron oxidation. The increase in total Mn caused by KMnO_4 addition is shown in Figures 4-19 and 4-20 as the 0.2 mg/L raw water level increased to 0.55 mg/L ahead of the filter. The Figure 4-19 data indicated that the DM filter influent contained mostly particulate Mn, with only 0.11 mg/L dissolved Mn; the particulate Mn could result from reduction of the Mn(VII) in the KMnO_4 , possible oxidation of the raw water Mn, or adsorption of the Mn^{2+} by the precipitated Fe. In contrast, Figure 4-20 shows a much greater fraction of the dissolved Mn in the DM filter influent. Increases in the dissolved and total Mn concentrations were sometimes observed across the DM filter, as seen in Figures 4-19 and 4-20. This phenomenon could possibly be attributed to excessive KMnO_4 dosing or the possible release of Mn^{2+} from the surface of the media inside the DM filter, as a result of an undetermined reduction process.

The dissolved iron concentration for the DM filter influent and effluent were measured and dosing was adjusted until all of the iron was oxidized, without excess oxidant addition. When NaOCl was used as the pre-oxidant, stoichiometric dosing was used to minimize the addition of Cl_2 and creation of associated DBPs. The dissolved iron concentration and Cl_2 residual of the DM filter effluent were measured and dosing was adjusted to oxidize all iron without a Cl_2 residual. The pH of both systems was adjusted to approximately 7.3 by adding NaOH . C572 polymer dosing was conducted in order to decrease turbidity and improve removal of organic matter and particles. The dosing was dependent on the UV_{254} value for the raw water and was adjusted according to the desired DM filter effluent turbidity of 0.1 NTU or less.

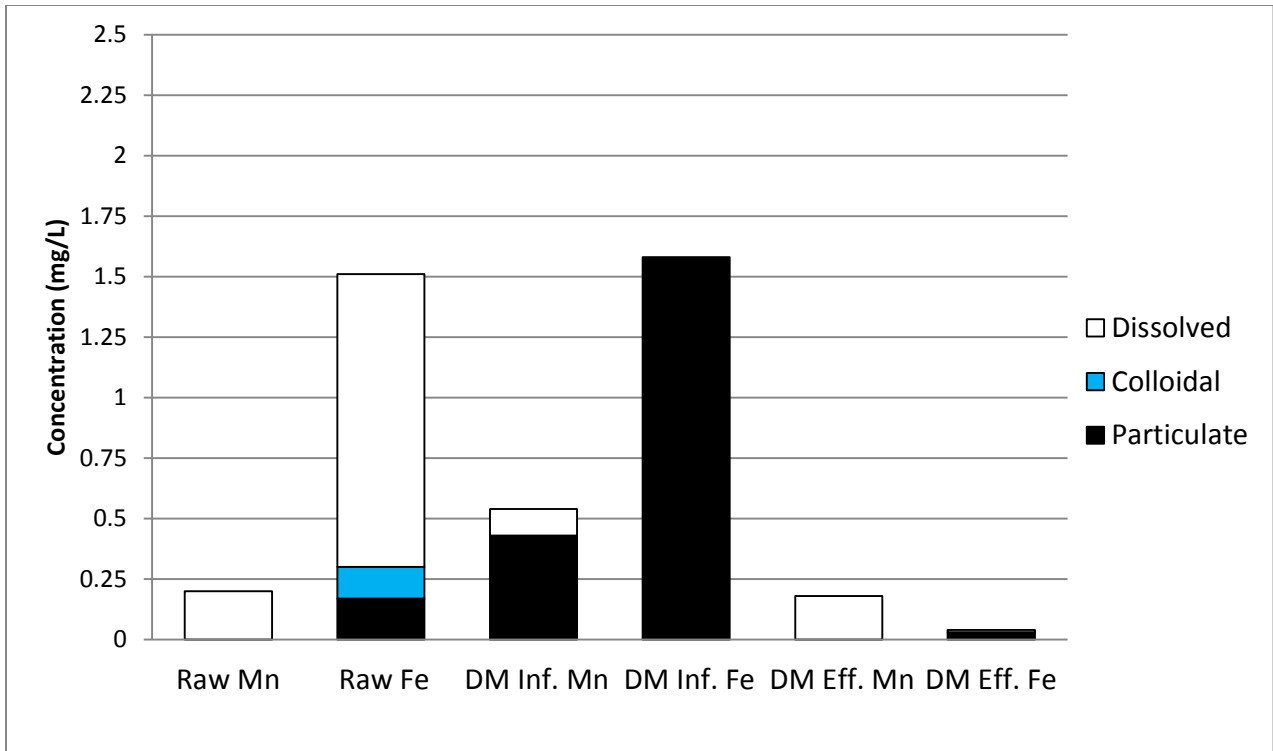


Figure 4-19: Results for field fractionation of the Mn and Fe concentrations across the pre-KMnO₄ / NaOCl pilot system on 12/21/11. (1.2 mg/L pre-KMnO₄ / 3.4 mg/L NaOCl)

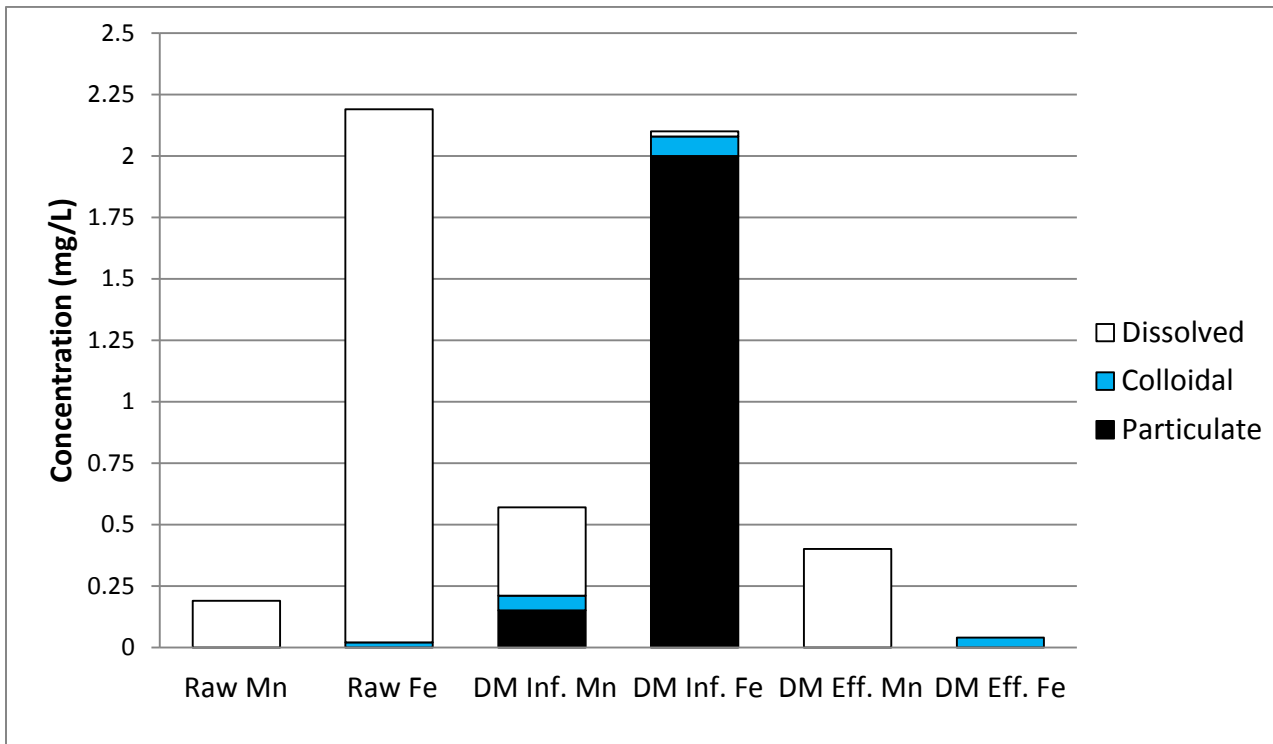


Figure 4-20: Results for field fractionation of the Mn and Fe concentrations across the pre-KMnO₄ / NaOCl pilot system on 08/17/11. (1.2 mg/L pre-KMnO₄ / 4.2 mg/L NaOCl)

4.2.2 KMnO₄ / Chlorine System

4.2.2.1 Chemical Dosing and Plant Optimization

For some pilot plant experiments, KMnO₄ was used as the pre-filter oxidant followed by post-dual media filter chlorination (pre-KMnO₄ / NaOCl) ahead of the second-stage contactors; a process schematic is shown in Figure 4-21. The NaOH dose ranged from 23.7 to 29.4 mg/L, with an average dose of 25.0 mg/L. The KMnO₄ dosing used to oxidize the Fe²⁺ ranged from 1.0 to 1.5 mg/L, with an average value of 1.1 mg/L. The C572 polymer dose ranged from 5.0 to 7.8 mg/L, with an average dose of 6.9 mg/L. The resulting DM filter effluent total Fe concentration ranged from non-detectable to 0.14 mg/L, with an average of 0.07 mg/L. The post-filter chlorine dosing ranged from 3.1 to 4.6 mg/L NaOCl, with an average value of 4.0 mg/L. The average contactor effluent Cl₂ residual was 1.2 mg/L. The hydraulic loading rates of the DM filter and second-stage contactors were 3 and 10 GPM/ft², respectively.

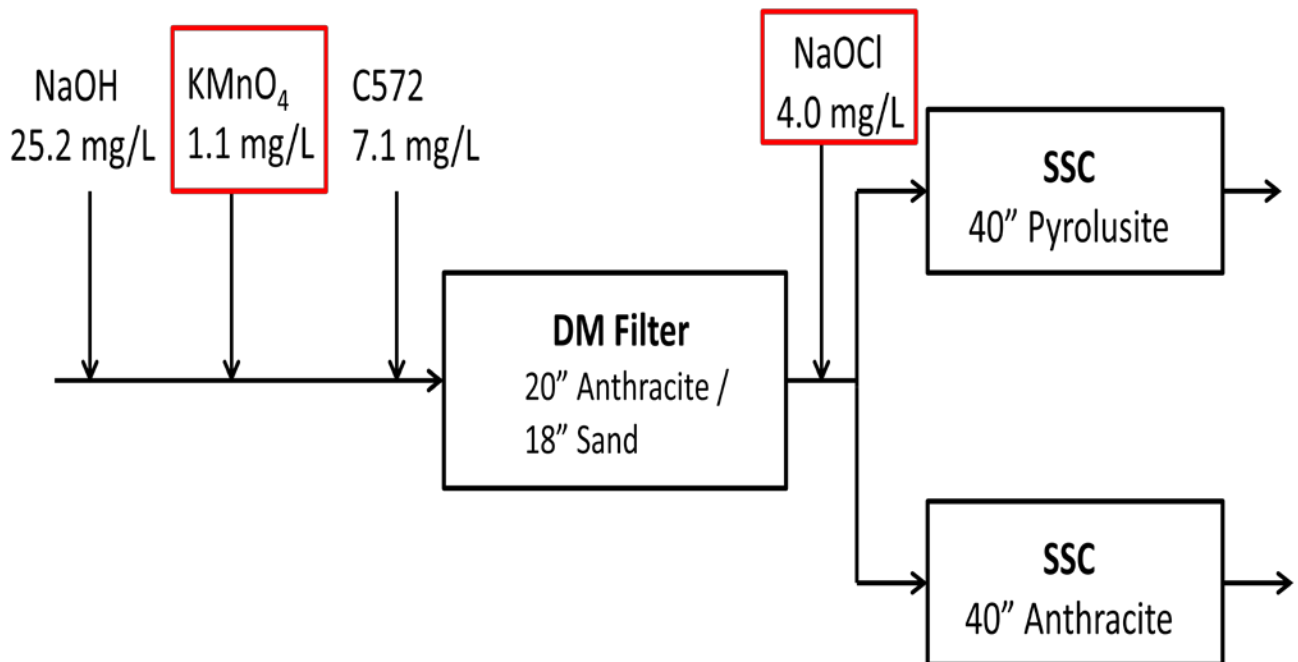


Figure 4-21: The pre-KMnO₄ / NaOCl pilot plant chemical dosing.

4.2.2.2 Overall Comparison of Media Performance

Evaluation of Second-Stage Contactor Media

Initially, the anthracite # 1 and pyrolusite media were compared for the pre-KMnO₄ / NaOCl system. Figure 4-22 shows the fraction of initial Mn concentration versus the depth of the media for experiments conducted on 08/03/11, where the contactor influent Mn concentration was 0.66 mg/L. The pyrolusite performed better than anthracite # 1 and the Mn concentrations of the contactor effluents were 0.01 and 0.06 mg/L, respectively.

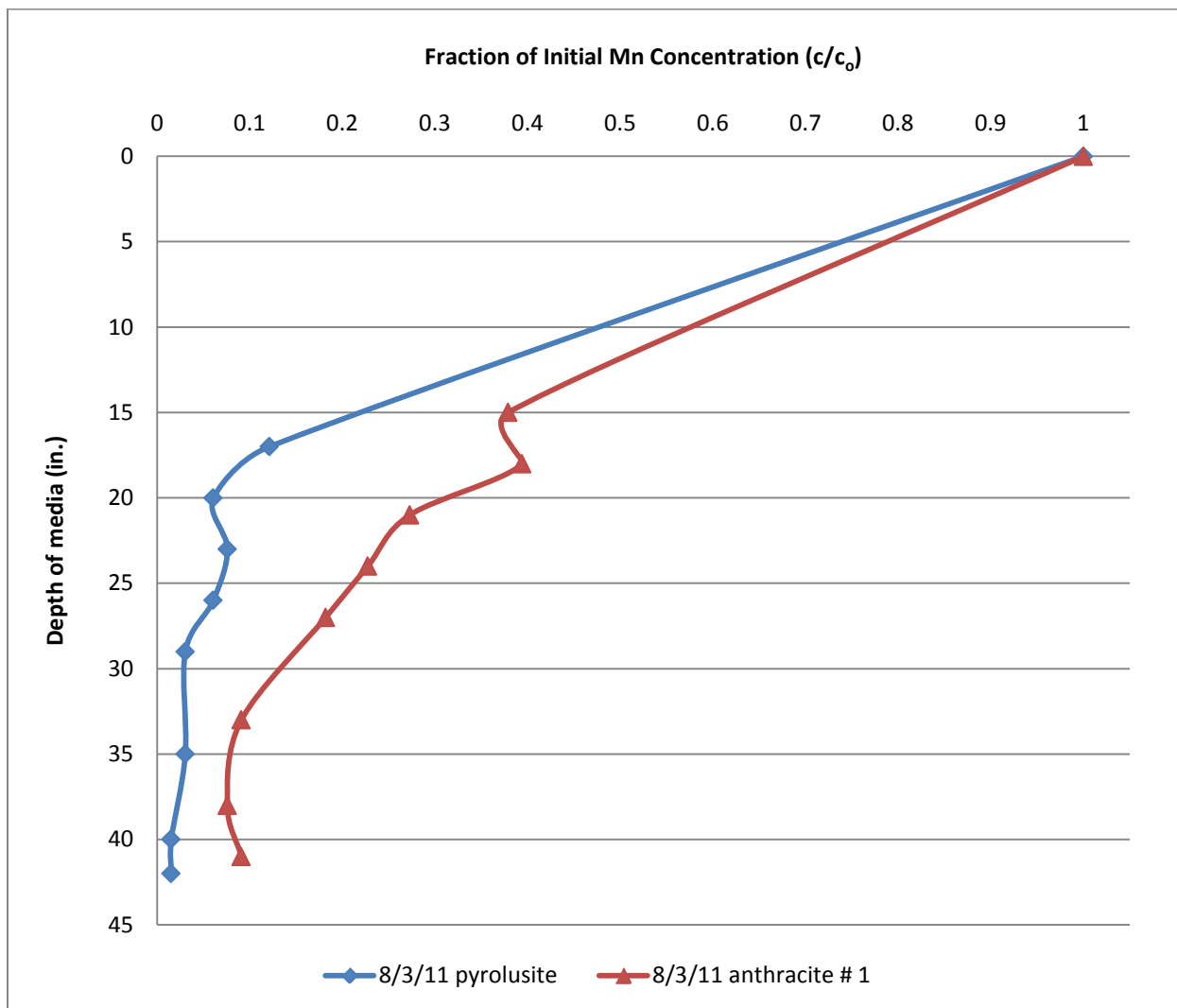


Figure 4-22: A comparison of Mn profiles for the pyrolusite and anthracite # 1 contactors for the pre-KMnO₄ / NaOCl pilot plant system at Lantern Hill on 08/03/11. (HLR = 10 GPM/ft²; c₀ = 0.66 mg/L Mn)

The average fraction of initial Mn concentration versus the depth of the media for the pre-KMnO₄ / NaOCl system for tests conducted on 08/09/11 through 08/11/11 can be seen in Figure 4-23. The contactor influent Mn concentration ranged from 0.52 to 0.53 mg/L, with an average of 0.53 mg/L. The pyrolusite performed better than anthracite # 1 and the Mn concentrations of the contactor effluents were 0.04 and 0.11 mg/L, respectively. However, on 08/09/11 the depth of the media bed in the anthracite # 1 column was decreased due to media lost during backwash. The Mn effluent concentration values for the anthracite # 1 column for this testing period were based on a 34.5 inch bed depth.

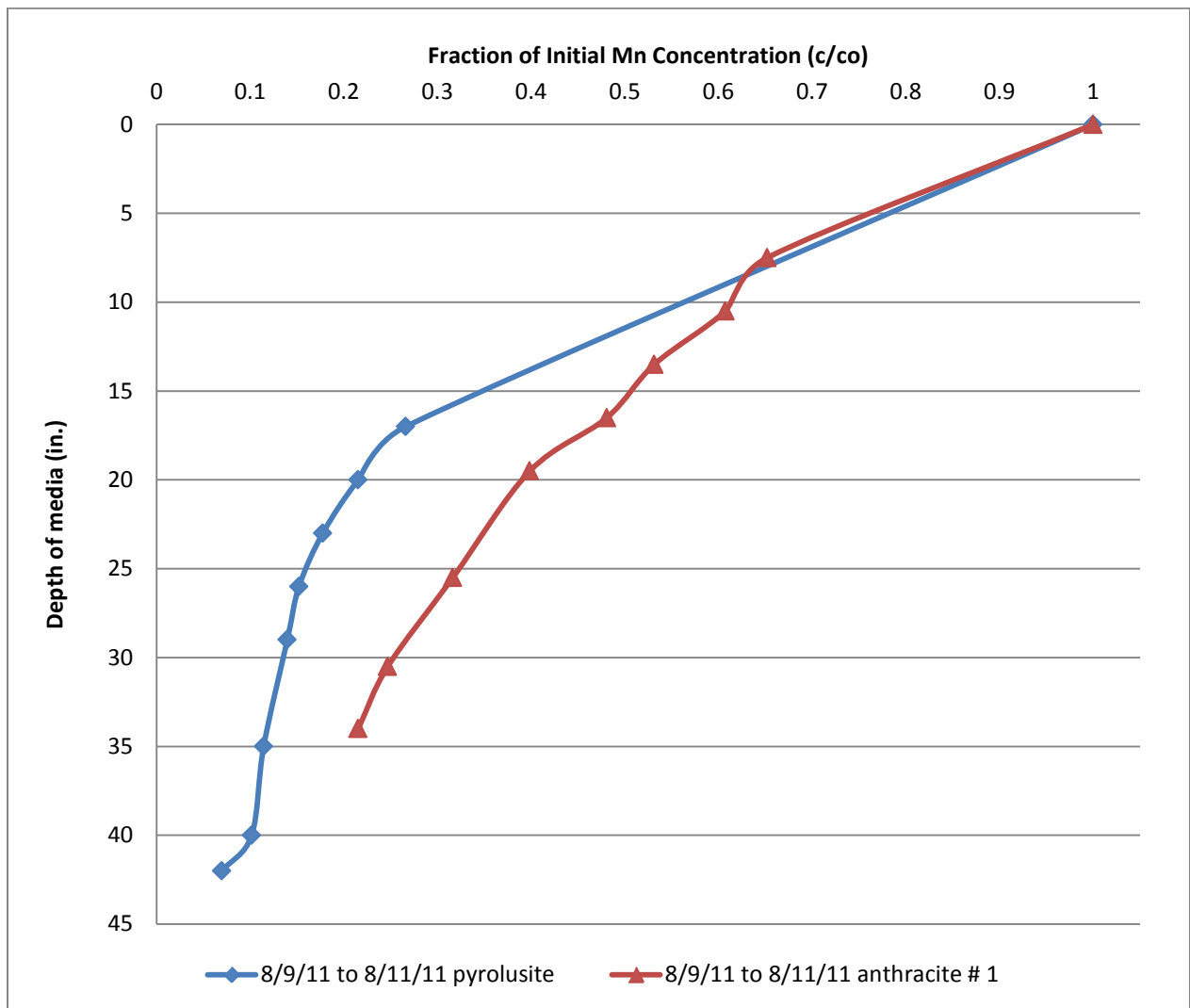


Figure 4-23: A comparison of the average Mn profiles for the pyrolusite and anthracite # 1 contactors for the pre-KMnO₄ / NaOCl pilot plant system at Lantern Hill for 08/09/11 to 08/11/11. (HLR = 10 GPM/ft²; c_o = 0.53 mg/L Mn)

Figure 4-24 shows the average fraction of initial Mn concentration versus the depth of the media for the pre-KMnO₄ / NaOCl system for tests conducted on 08/16/11 through 08/18/11. The contactor influent Mn concentration ranged from 0.31 to 0.39 mg/L, with an average of 0.35 mg/L. The pyrolusite performed slightly better than anthracite # 1 and the Mn concentrations of the contactor effluents were 0.03 and 0.05 mg/L, respectively. Additional MnO_x coated anthracite media was added to the column prior to testing in order to obtain a bed depth of 40 inches.

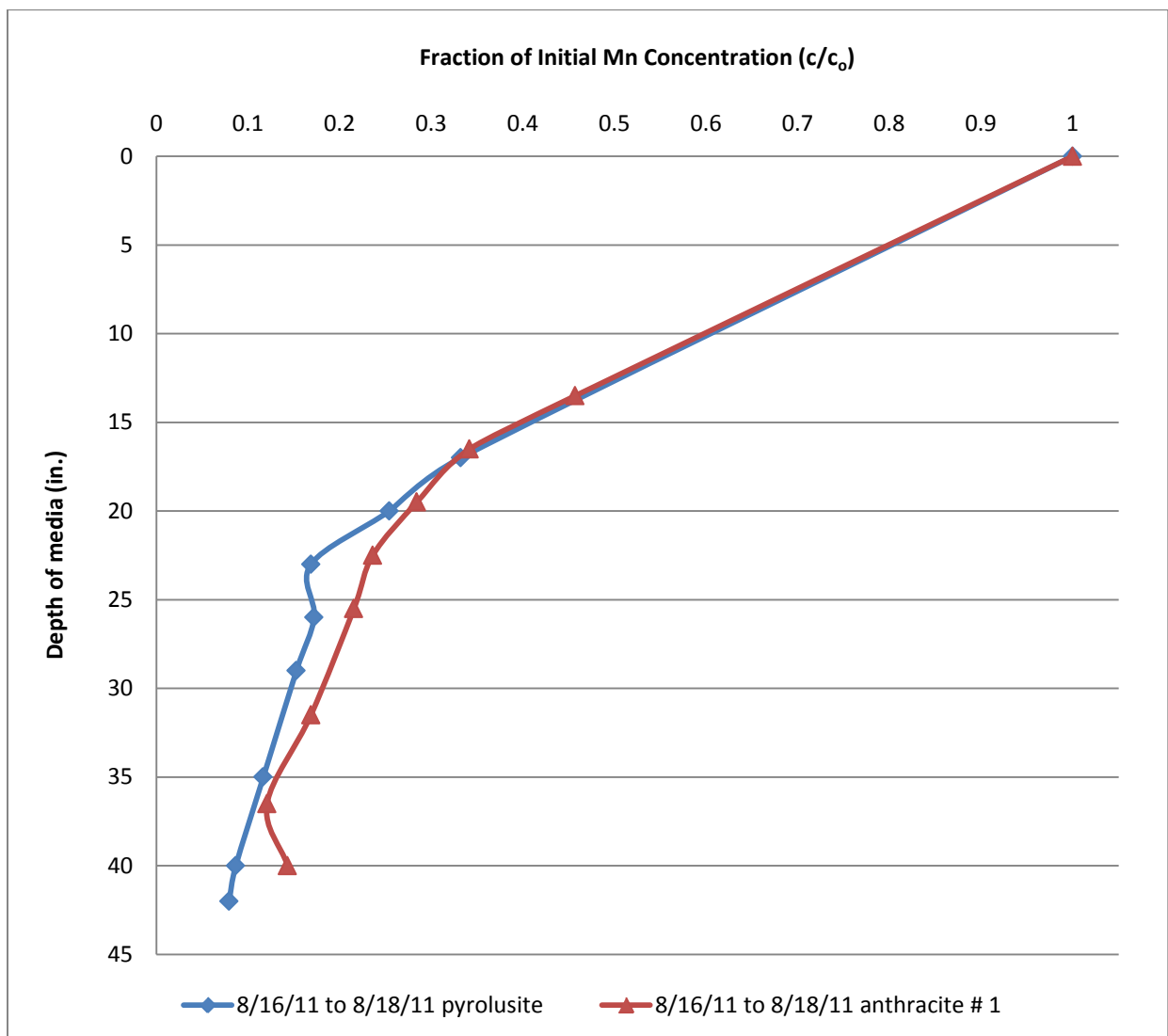


Figure 4-24: A comparison of the average Mn profiles for the pyrolusite and anthracite # 1 contactors for the pre-KMnO₄ / NaOCl pilot plant system at Lantern Hill for 08/16/11 to 08/18/11. (HLR = 10 GPM/ft²; c_0 = 0.35 mg/L Mn)

Next, the pyrolusite and Macrolite media were also compared for the pre-KMnO₄ / NaOCl system. Figure 4-25 shows the average fraction of initial Mn concentration versus the depth of the media for the pre-KMnO₄ / NaOCl system for tests conducted on 12/20/11 through 12/22/11. The contactor influent Mn concentration ranged from 0.12 to 0.16 mg/L, with an average of 0.14 mg/L. The Macrolite performed better than the pyrolusite and the Mn concentrations of the contactor effluents were 0.01 and 0.02 mg/L, respectively.

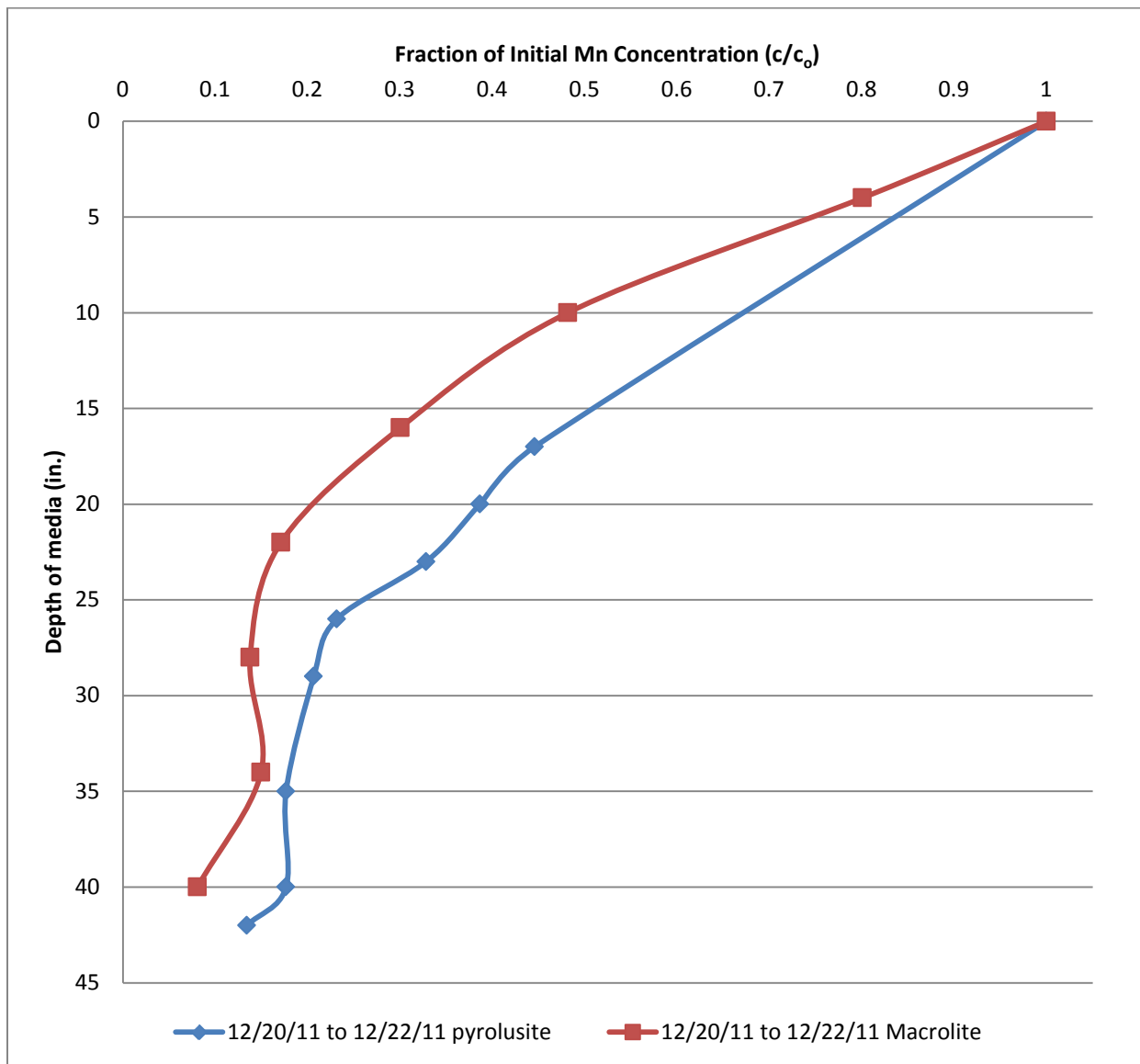


Figure 4-25: A comparison of the average Mn profiles for the pyrolusite and Macrolite contactors for the pre-KMnO₄ / NaOCl pilot plant system at Lantern Hill for 12/20/11 to 12/22/11. (HLR = 10 GPM/ft²; c₀ = 0.14 mg/L Mn)

The average fraction of initial Mn concentration versus the depth of the media for the pre-KMnO₄ / NaOCl system for tests conducted on 01/03/12 through 01/05/12 can be seen in Figure 4-26. The contactor influent Mn concentration ranged from 0.09 to 0.15 mg/L, with an average of 0.12 mg/L. The Macrolite performed better than the pyrolusite and the Mn concentrations of the contactor effluents were 0.01 and 0.02 mg/L, respectively.

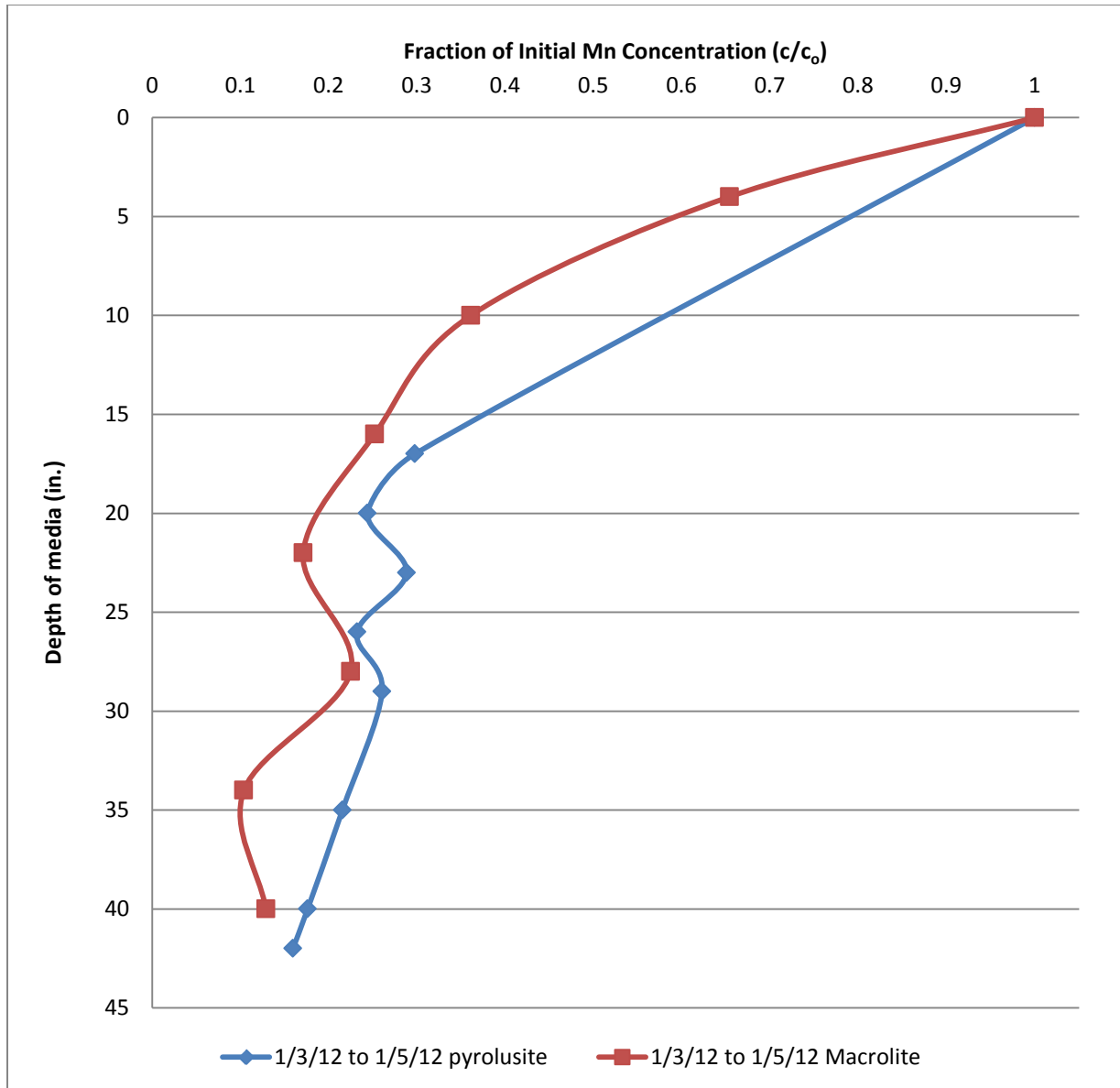


Figure 4-26: A comparison of the average Mn profiles for the pyrolusite and Macrolite contactors for the pre-KMnO₄ / NaOCl pilot plant system at Lantern Hill for 01/03/12 to 01/05/12. (HLR = 10 GPM/ft²; c₀ = 0.12 mg/L Mn)

Lastly, the anthracite # 2 and Macrolite media were compared for the pre-KMnO₄ / NaOCl system. The average fraction of initial Mn concentration versus the depth of the media for the pre-KMnO₄ / NaOCl system for tests conducted on 08/28/12 through 08/29/12 can be seen in Figure 4-27. The contactor influent Mn concentration ranged from 0.26 to 0.28 mg/L, with an average of 0.27 mg/L. The Macrolite performed better than anthracite # 2 and the Mn concentrations of the contactor effluents were 0.01 and 0.02 mg/L, respectively.

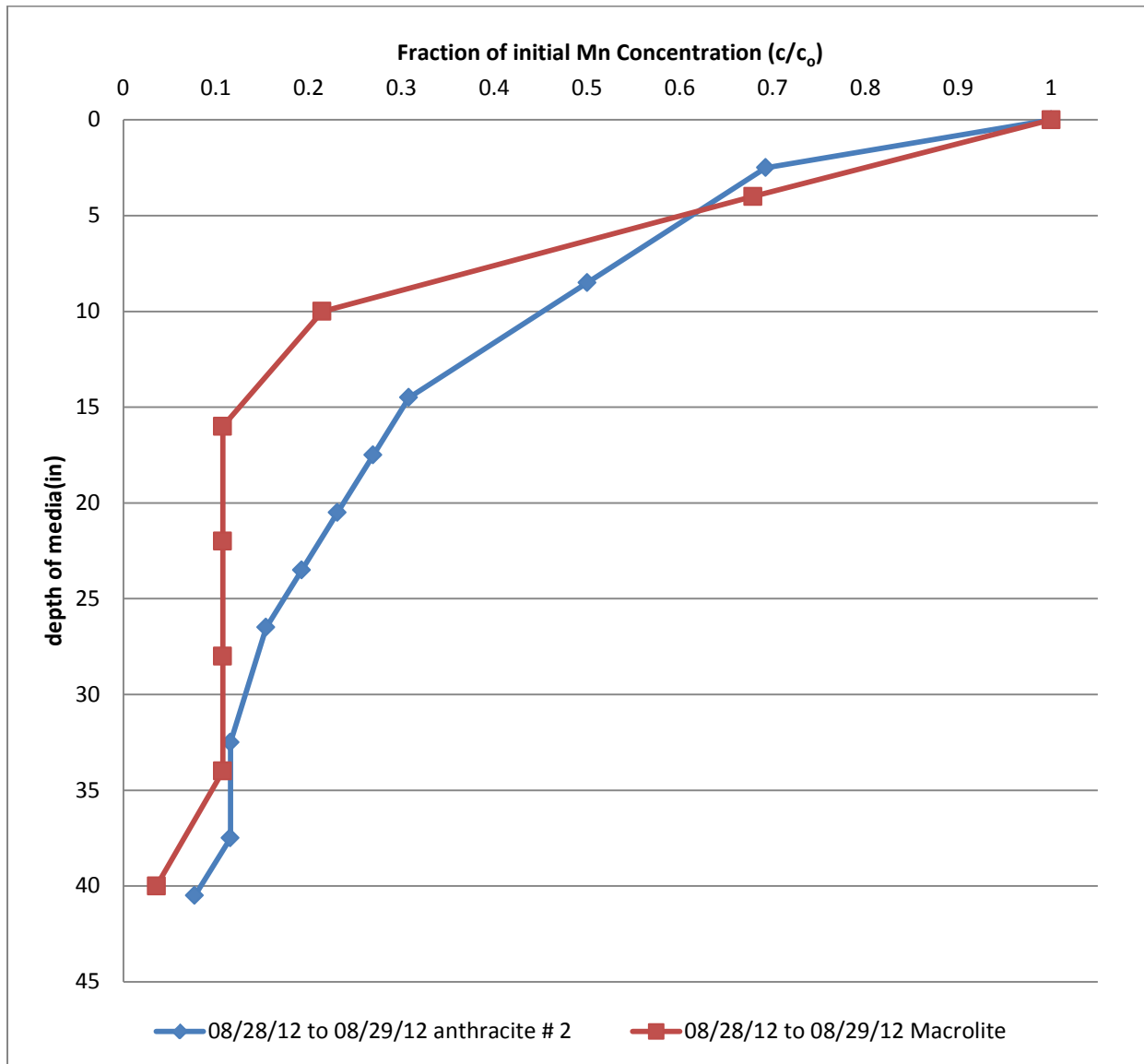


Figure 4-27: A comparison of the average Mn profiles for the anthracite # 2 and Macrolite contactors for the pre-KMnO₄ / NaOCl pilot plant system at Lantern Hill for 08/28/12 to 08/29/12. (HLR = 10 GPM/ft²; c₀ = 0.27 mg/L Mn)

4.2.2.3 TOC Removal

The total organic carbon (TOC) concentration was measured for the pre-KMnO₄ / NaOCl pilot system on 01/04/12. The average TOC concentration of the raw water was 4.3 mg/L, while the average TOC concentration of the dual media filter effluent was 3.3 mg/L. The dual media filter removed 1 mg/L of the raw water TOC, a 23 % decrease. The TOC concentration was also measured for the pre-KMnO₄ / NaOCl pilot system on 08/29/12. The average TOC concentration of the raw water was 3.1 mg/L, while the average TOC concentration of the dual media filter effluent was 2.0 mg/L. The dual media filter removed 1.1 mg/L of the raw water TOC, a 35 % decrease. Thus, the average overall TOC removal by the dual media filter was 28 %.

4.2.2.4 DBP Results

During the first round of DBP analysis for both pilot systems in January 2012, the full-scale Lantern Hill facility was not in operation, in order to avoid DBP compliance issues. As a result, DBP analysis was conducted only for the pilot systems and not the full-scale plant during this time. Full-scale DBP analysis was conducted on 08/23/12 and 08/29/12 during the second round of DBP analysis for the pilot systems. Table 4-3 shows the instantaneous, 24 hour hold, and 48 hour hold values for THM and HAA concentrations for full-scale plant effluent on 08/23/12, 08/29/12, and the average for these visits, along with the US EPA MCLs. All of the instantaneous, 24 hour hold, and 48 hour hold THM and HAA concentrations for the full-scale analysis exceeded the respective EPA MCLs of 80 and 60 µg/L. For the purpose of comparing full-scale and pilot-scale results during the first round of sampling in January 2012, the average full-scale values for August 2012 were used to determine the decreases in DBP concentration associated with each pilot plant experiment.

Table 4-3: Instantaneous, 24 hour hold, and 48 hour hold DBP concentrations for the full-scale Lantern Hill plant effluent and the associated EPA DBP limits.

DBP Parameter	Concentration (µg/L)			EPA MCL
	08/23/12 Full-Scale	08/29/12 Full-Scale	Aug. 2012 Full-Scale Average	
Inst. THM	116	96	106	n/a
Inst. HAA	123	120	122	n/a
24 hr THM	105	97	101	80
24 hr HAA	125	127	126	60
48 hr THM	102	102	102	80
48 hr HAA	127	119	123	60

The first set of DBP analysis for the pre-KMnO₄ / NaOCl pilot system was conducted on 01/04/12. The pre-oxidant dosing for this day was 1.1 mg/L KMnO₄ and the post-dual media filter dosing was 3.7 mg/L NaOCl. The raw water UV₂₅₄ was 0.154 cm⁻¹ and the TOC was 4.3 mg/L. The contactor effluent Cl₂ residuals were 1.31 mg/L for the Macrolite and 1.35 mg/L for the pyrolusite. Instantaneous and 24 hour hold samples from the contactor effluents were analyzed for THM and HAA concentrations.

Figures 4-28 and 4-29 compare the instantaneous and 24 hour hold DBP concentrations for the contactor effluents and average full-scale plant effluent values. The average instantaneous THM and HAA concentrations were 27 and 23 µg/L, respectively, for the Macrolite contactor. The average 24 hour hold THM and HAA concentrations were 38 and 54 µg/L, respectively. For the pyrolusite contactor, the average instantaneous THM and HAA concentrations were 26 and 23 µg/L, respectively. The average 24 hour hold THM and HAA concentrations were 44 and 58 µg/L, respectively. After 24 hours, the chlorine residuals for the Macrolite and pyrolusite contactor effluents were 0.33 and 0.26 mg/L, respectively.

Table 4-4 shows the average DBP values for the pre-KMnO₄ / NaOCl system for both contactors, as well as full-scale values. The corresponding percent decrease in 24 hr hold values with respect to the full-scale values is in parentheses next to each pilot value. There were average decreases of 75 % and 81 % for the instantaneous THM and HAA concentrations, respectively. There were average decreases of 59 % and 56 % in the 24 hour hold THM and HAA values for this system. These results show that the two-stage pre-KMnO₄ / NaOCl pilot system can effectively meet the effluent goals for metals and turbidity while greatly decreasing the amount of DBPs created compared to full-scale operations.

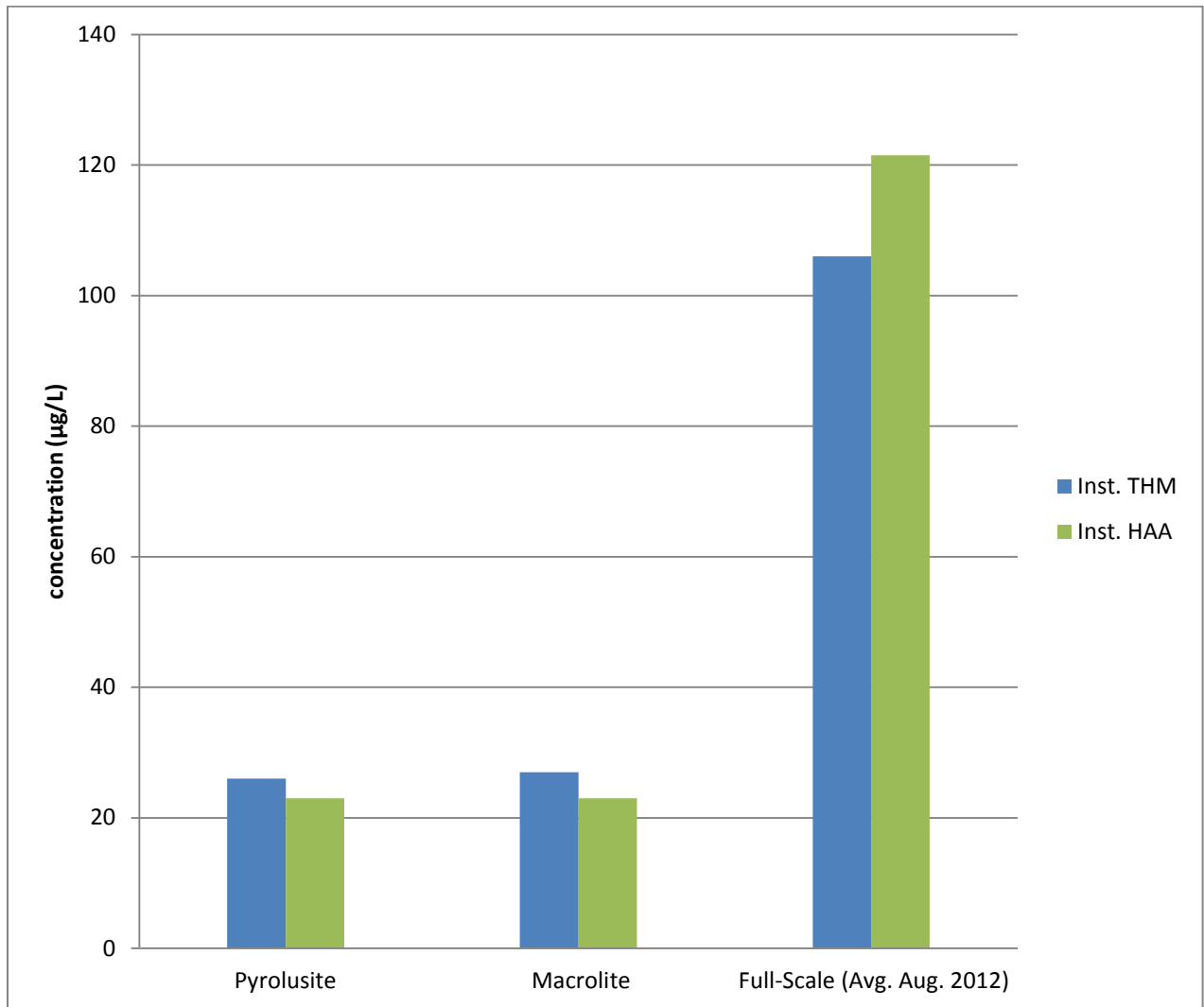


Figure 4-28: Instantaneous THM and HAA concentrations for the pre-KMnO₄ / NaOCl pilot system at Lantern Hill on 01/04/12 and the average August 2012 full-scale plant values.

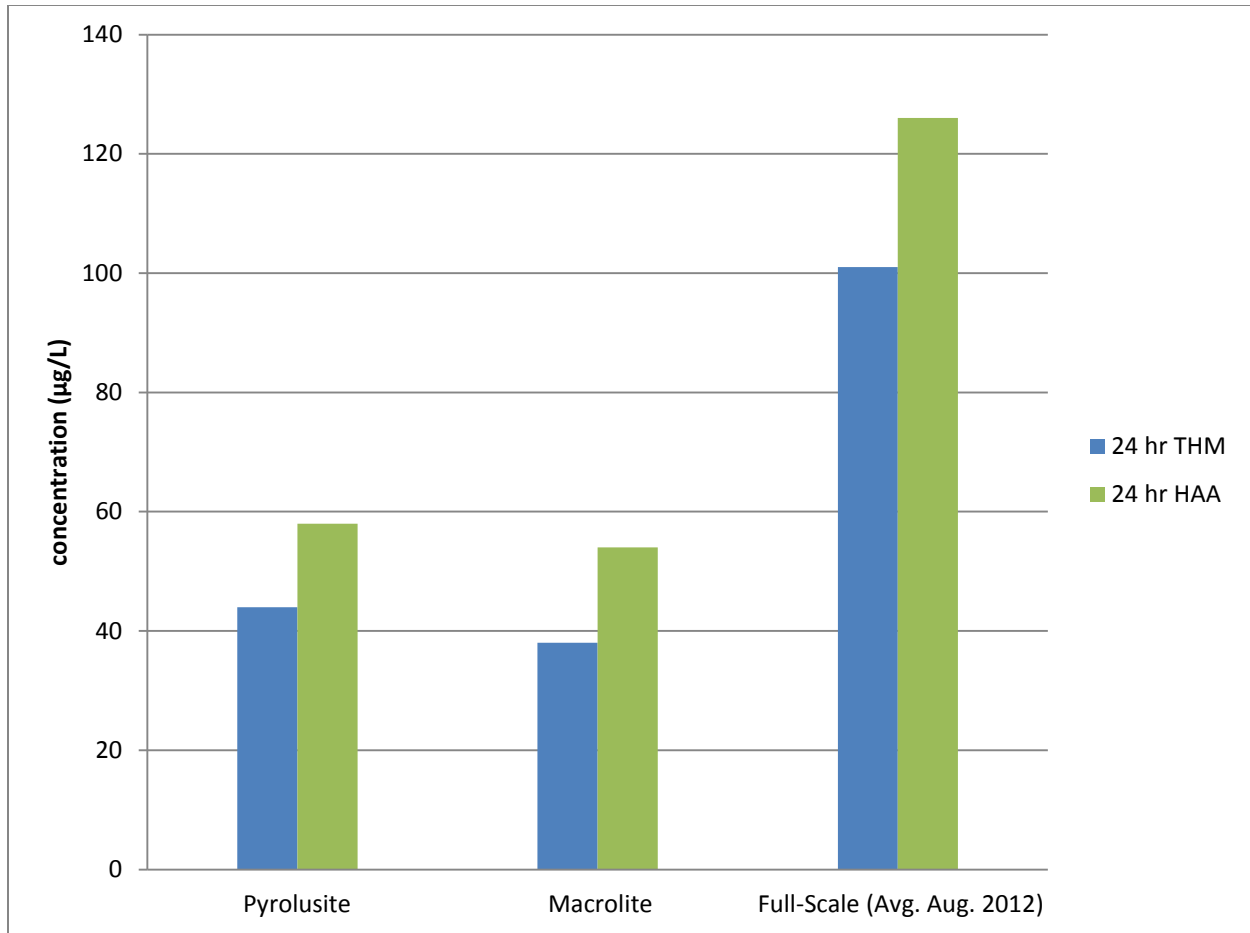


Figure 4-29: 24 hour hold THM and HAA concentrations for the pre-KMnO₄ / NaOCl pilot system at Lantern Hill on 01/04/12 and the average August 2012 full-scale plant values.

Table 4-4: DBP values for the pre-KMnO₄ / NaOCl two-stage pilot system on 01/04/12 and the average August 2012 full-scale plant values.

DBP Parameter	Concentration (µg/L) (% Decrease)		
	01/04/12 Pilot Pyrolusite	01/04/12 Pilot Macrolite	Aug. 2012 Full-Scale Average
Inst. THM	26	27	106
Inst. HAA	23	23	122
24 hr THM	44 (56 %)	38 (62 %)	101
24 hr HAA	58 (54 %)	54 (57 %)	126

The second set of DBP analysis for the pre-KMnO₄ / NaOCl pilot system was conducted on 08/29/12. DBP analysis was also conducted for the full-scale Lantern Hill facility on this date. The pre-oxidant dosing for this day was 1.2 mg/L KMnO₄ and the post-dual media filter dosing was 3.9 mg/L NaOCl. The raw water UV₂₅₄ was 0.155 cm⁻¹ and the TOC was 3.1 mg/L. The contactor effluent Cl₂ residuals were 1.10 mg/L for the anthracite # 2 and 1.12 mg/L for the Macrolite. Instantaneous, 24 hour hold, and 48 hour hold samples from the contactor effluents were analyzed for THM and HAA concentrations.

Figures 4-30, 4-31, 4-32 compare the instantaneous, 24 hour hold, and 48 hour hold DBP concentrations for the contactor effluents and the full-scale plant effluent. For the anthracite # 2 contactor, the average instantaneous THM and HAA concentrations were 14 and 33 µg/L, respectively. The average 24 hour hold THM and HAA concentrations were 35 and 43 µg/L, respectively. The average 48 hour hold THM and HAA concentrations were 40 and 50 µg/L, respectively. For the Macrolite contactor, the average instantaneous THM and HAA concentrations were 12 and 31 µg/L, respectively. The average 24 hour hold THM and HAA concentrations were 33 and 40 µg/L, respectively. The average 48 hour hold THM and HAA concentrations were 38 and 48 µg/L, respectively. After 24 hours, the chlorine residuals for the anthracite # 2 and Macrolite contactor effluents were 0.40 and 0.34 mg/L, respectively. After 48 hours, the chlorine residuals were 0.35 and 0.30 mg/L.

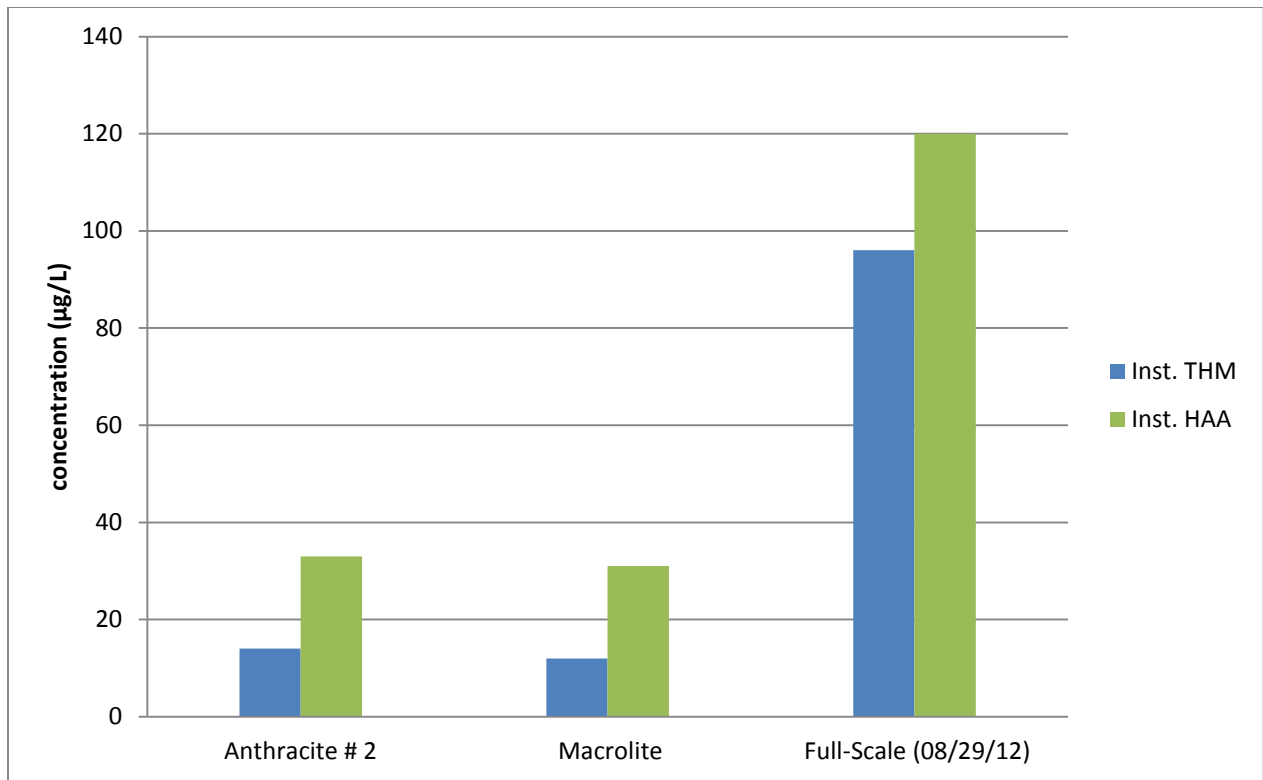


Figure 4-30: Instantaneous THM and HAA concentrations for the pre-KMnO₄ / NaOCl pilot system at Lantern Hill and the full-scale plant on 08/29/12.

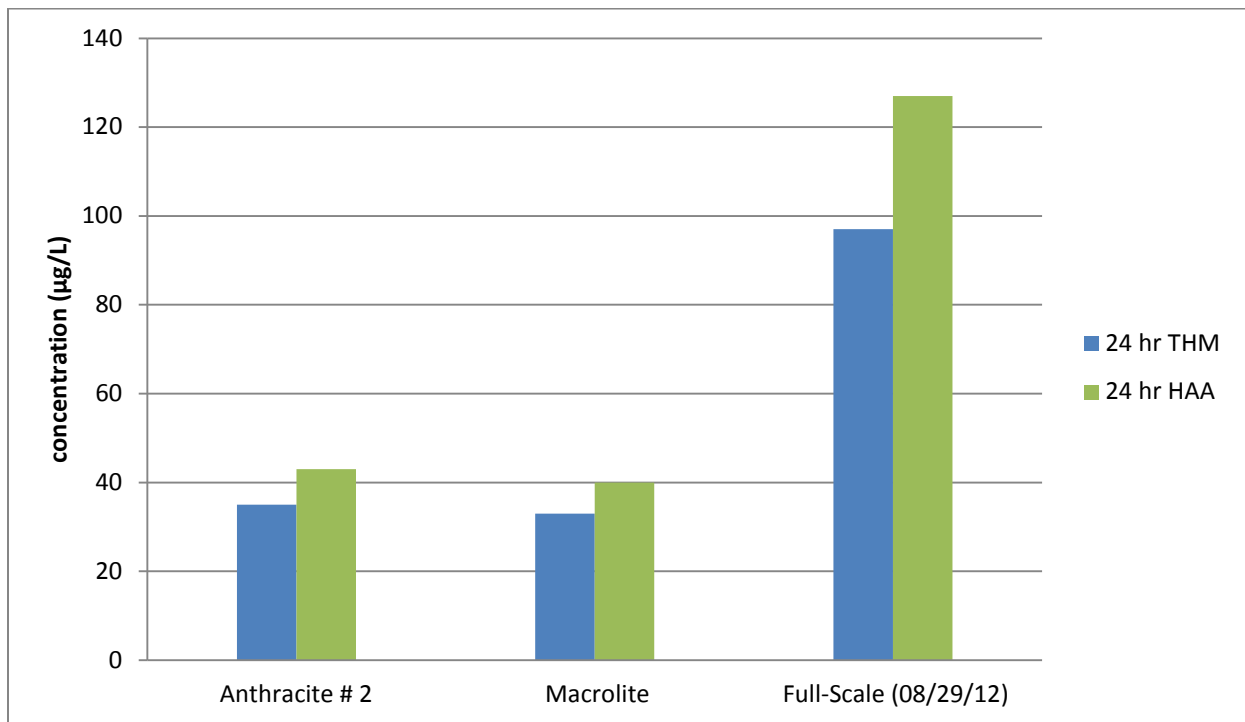


Figure 4-31: 24 hour hold THM and HAA concentrations for the pre-KMnO₄ / NaOCl pilot system at Lantern Hill and the full-scale plant on 08/29/12.

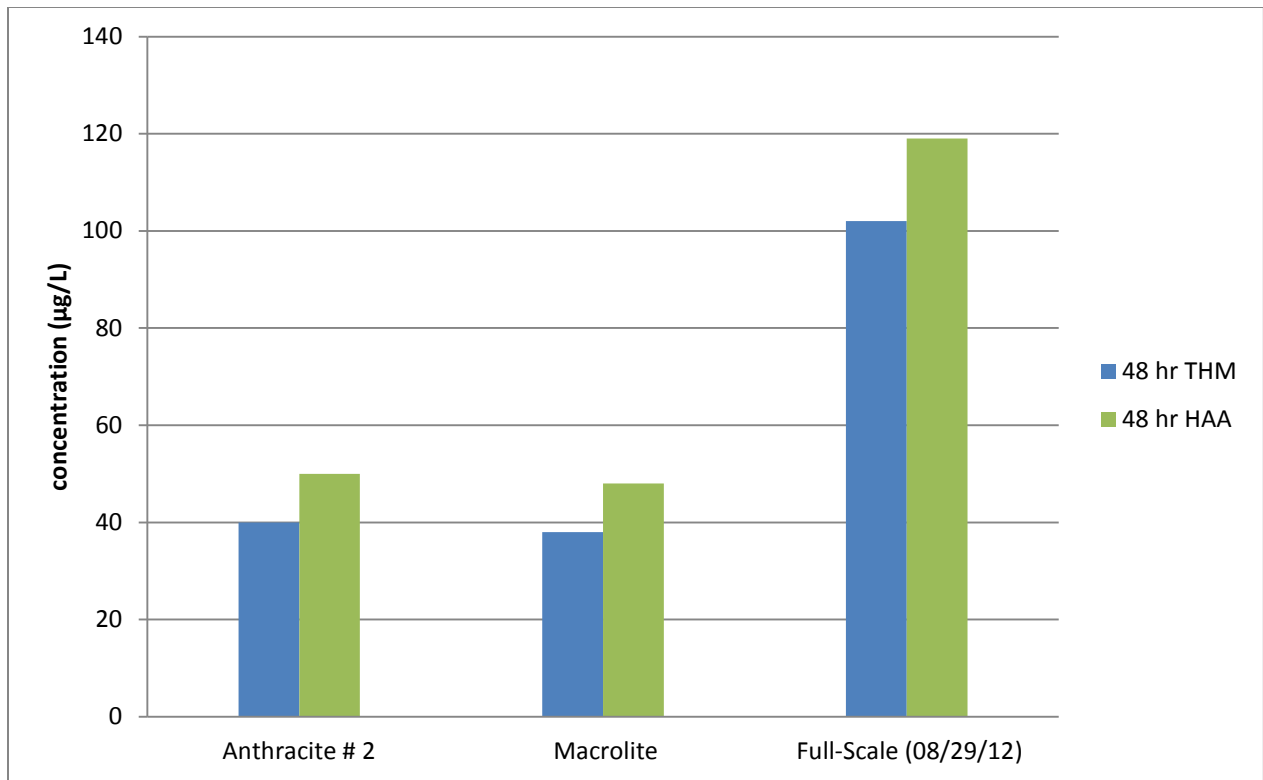


Figure 4-32: 48 hour hold THM and HAA concentrations for the pre-KMnO₄ / NaOCl pilot system at Lantern Hill and the full-scale plant on 08/29/12.

Table 4-5 shows the average DBP values for the pre-KMnO₄ / NaOCl system for both contactors. The corresponding percent decrease in 24 hr hold and 48 hour hold values with respect to the full-scale values is in parentheses next to each pilot value. There were average decreases of 86 % and 73 % for the instantaneous THM and HAA concentrations, respectively. There were average decreases of 65 % and 68 % in the 24 hour hold THM and HAA values for this system. There were average decreases of 62 % and 59 % in the 48 hour hold THM and HAA values for this system. These results confirm previous results for this system and show that the two-stage pre-KMnO₄ / NaOCl pilot system can effectively meet the effluent goals for metals and turbidity while greatly decreasing the amount of DBPs created compared to full-scale operations.

Table 4-5: DBP values for the pre-KMnO₄ / NaOCl two-stage pilot system effluent and the full-scale plant effluent on 08/29/12.

DBP Parameter	Concentration (µg/L) (% Decrease)		
	08/29/12 Pilot Anthracite # 2	08/29/12 Pilot Macrolite	08/29/12 Full-Scale
Inst. THM	14	12	96
Inst. HAA	33	31	120
24 hr THM	35 (64%)	33 (66%)	97
24 hr HAA	43 (66%)	40 (69%)	127
48 hr THM	40 (61%)	38 (63%)	102
48 hr HAA	50 (58%)	48 (60%)	119

4.2.2.5 Head Loss

Head loss across the dual media filter, between backwashes, was observed and measured during each pilot experiment, approximately a 24 hour period. For the pre-KMnO₄ / NaOCl system, the head loss ranged from 0 to 3 psi. Results for laboratory experiments at UMass showed that the head loss across the second-stage contactors was approximately 0.3 psi at the 10 GPM/ft² loading rate, at an average water temperature of 20° C.

4.2.3 Chlorine / Chlorine System

4.2.3.1 Chemical Dosing and Plant Optimization

For other pilot plant experiments, NaOCl was used as the pre-filter oxidant followed by post-filter chlorination (pre-NaOCl / NaOCl) ahead of the second-stage contactors; a process

schematic is shown in Figure 4-33. The NaOH dosing ranged from 24.3 to 27.1 mg/L, with an average dose of 26.5 mg/L. The pre-NaOCl dosing used to oxidize the Fe^{2+} ranged from 1.3 to 3.0 mg/L, with an average value of 2.0 mg/L. The C572 polymer dosing ranged from 5.1 to 5.5 mg/L, with an average dose of 5.2 mg/L. The resulting dual media filter effluent total Fe concentration ranged from 0.01 to 0.1 mg/L, with an average of 0.03 mg/L. The post-filter chlorine dosing ranged from 2.4 to 3.1 mg/L NaOCl, with an average value of 2.8 mg/L. The average contactor effluent Cl_2 residual was 1.3 mg/L.

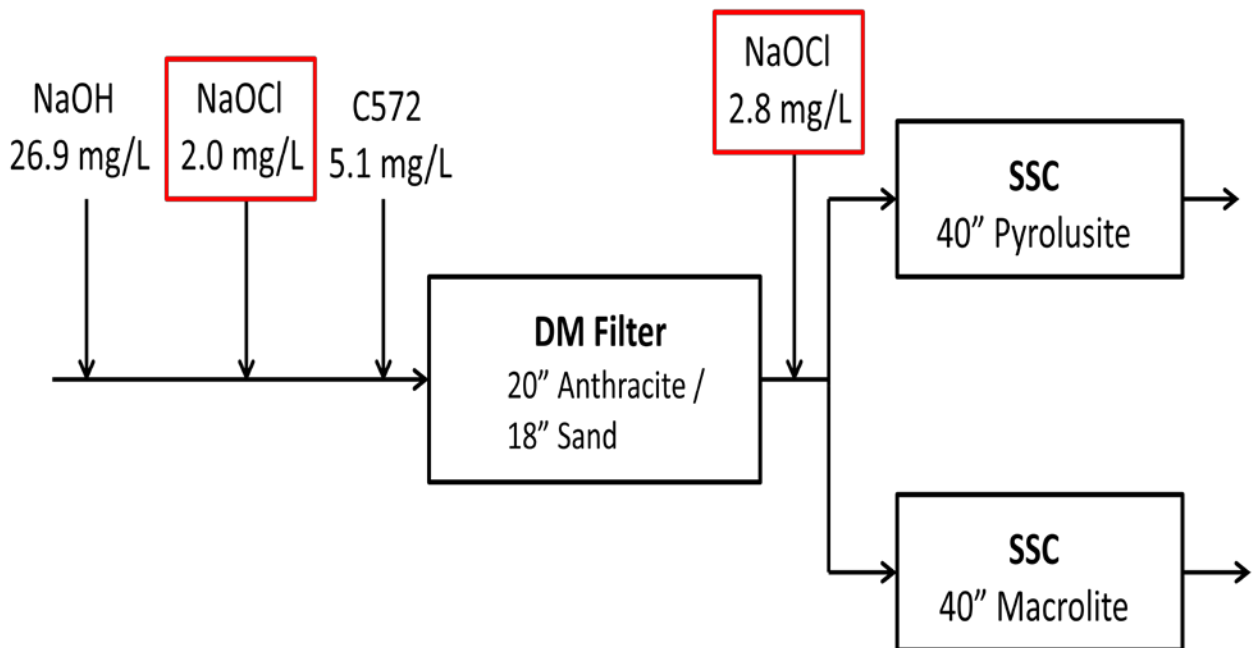


Figure 4-33: The pre-NaOCl / NaOCl pilot plant chemical dosing.

4.2.3.2 Overall Comparison of Media Performance

Evaluation of Second-Stage Contactor Media

The pyrolusite and Macrolite media were compared for the pre-NaOCl / NaOCl system. Figure 4-34 shows the average fraction of initial Mn concentration versus the depth of the media for experiments conducted on 01/10/12 to 01/12/12, where the contactor influent Mn concentration ranged from 0.15 to 0.16 mg/L, with an average of 0.16 mg/L. The Macrolite performed better than the pyrolusite and the Mn concentrations of the contactor effluents

were 0.02 and 0.01 mg/L, respectively. Although the Macrolite effluent Mn concentration was slightly higher than for the pyrolusite, the overall profile and smaller bed depth exhibit a better performance.

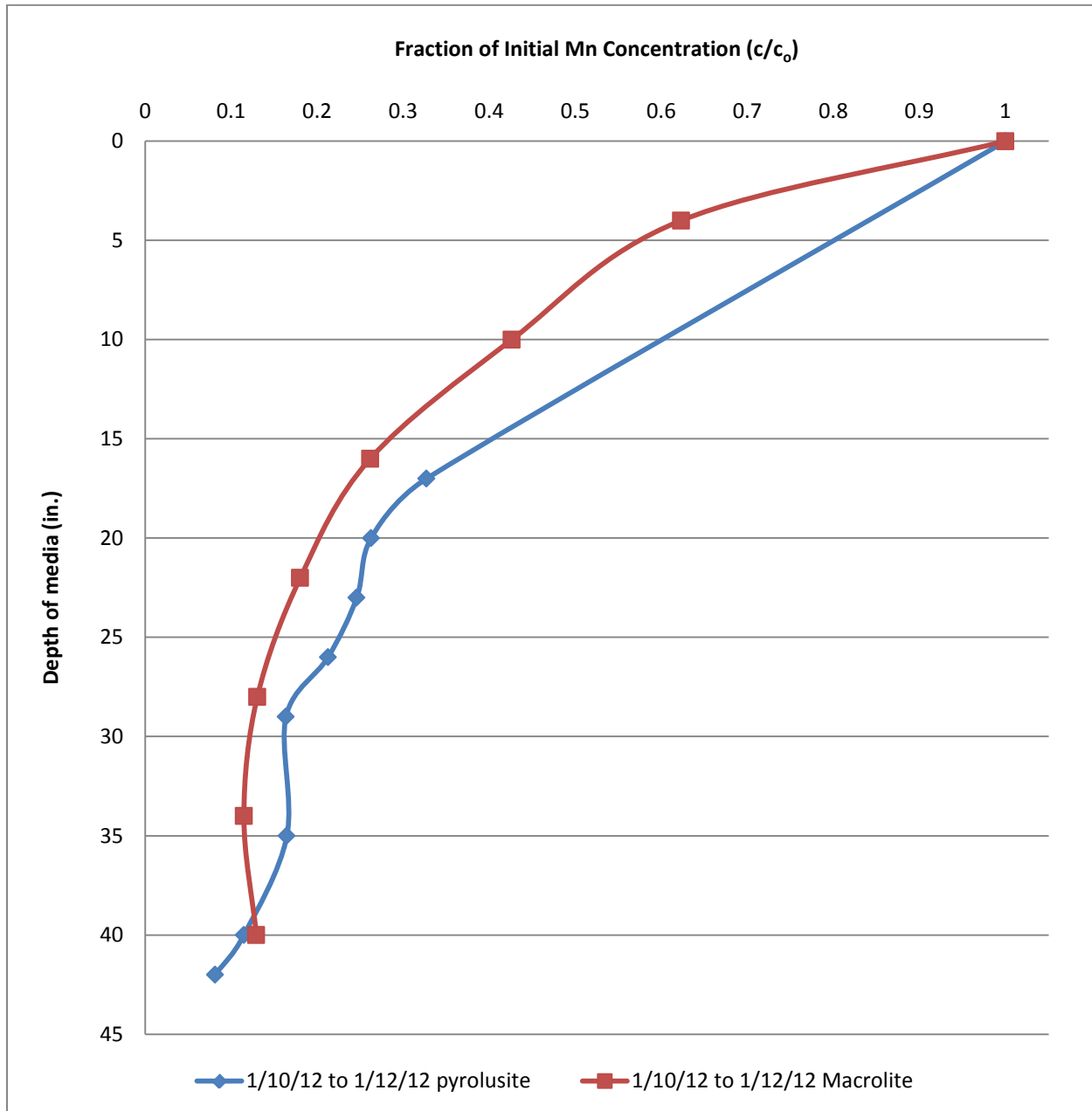


Figure 4-34: A comparison of the average Mn profiles for the pyrolusite and Macrolite contactors for the pre-NaOCl / NaOCl pilot plant system at Lantern Hill for 01/10/12 to 01/12/12. (HLR = 10 GPM/ft²; c₀ = 0.16 mg/L Mn)

The average fraction of initial Mn concentration versus the depth of the media for the pre-NaOCl / NaOCl system for tests conducted on 01/17/12 through 01/18/12 can be seen in Figure 4-35. The contactor influent Mn concentration ranged from 0.15 to 0.16 mg/L, with an average of 0.16 mg/L. The Macrolite performed better than the pyrolusite and the Mn concentrations of the contactor effluents were 0.01 and 0.02 mg/L, respectively.

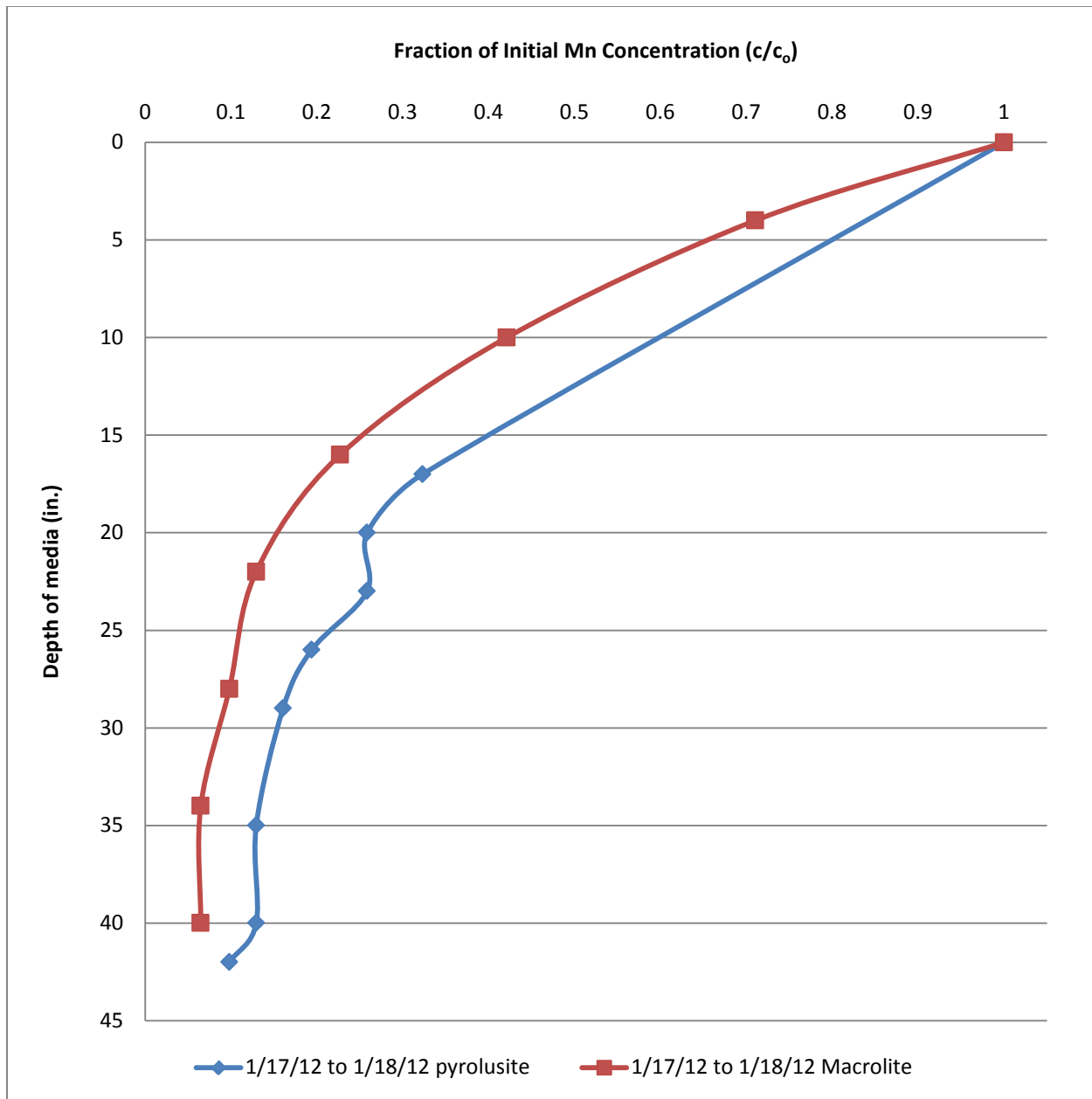


Figure 4-35: A comparison of the average Mn profiles for the pyrolusite and Macrolite contactors for the pre-NaOCl / NaOCl pilot plant system at Lantern Hill for 01/17/12 to 01/18/12. (HLR = 10 GPM/ft²; c_0 = 0.16 mg/L Mn)

Additionally, the anthracite # 2 and Macrolite media were compared for the pre-NaOCl / NaOCl system. Figure 4-36 shows the average fraction of initial Mn concentration versus the depth of the media for tests conducted on 08/22/12 to 08/23/12, where the contactor influent Mn concentration ranged from 0.12 to 0.15 mg/L, with an average of 0.15 mg/L. The Macrolite performed slightly better than anthracite # 2 and the Mn concentrations of the contactor effluents were 0.01 and 0.01 mg/L, respectively.

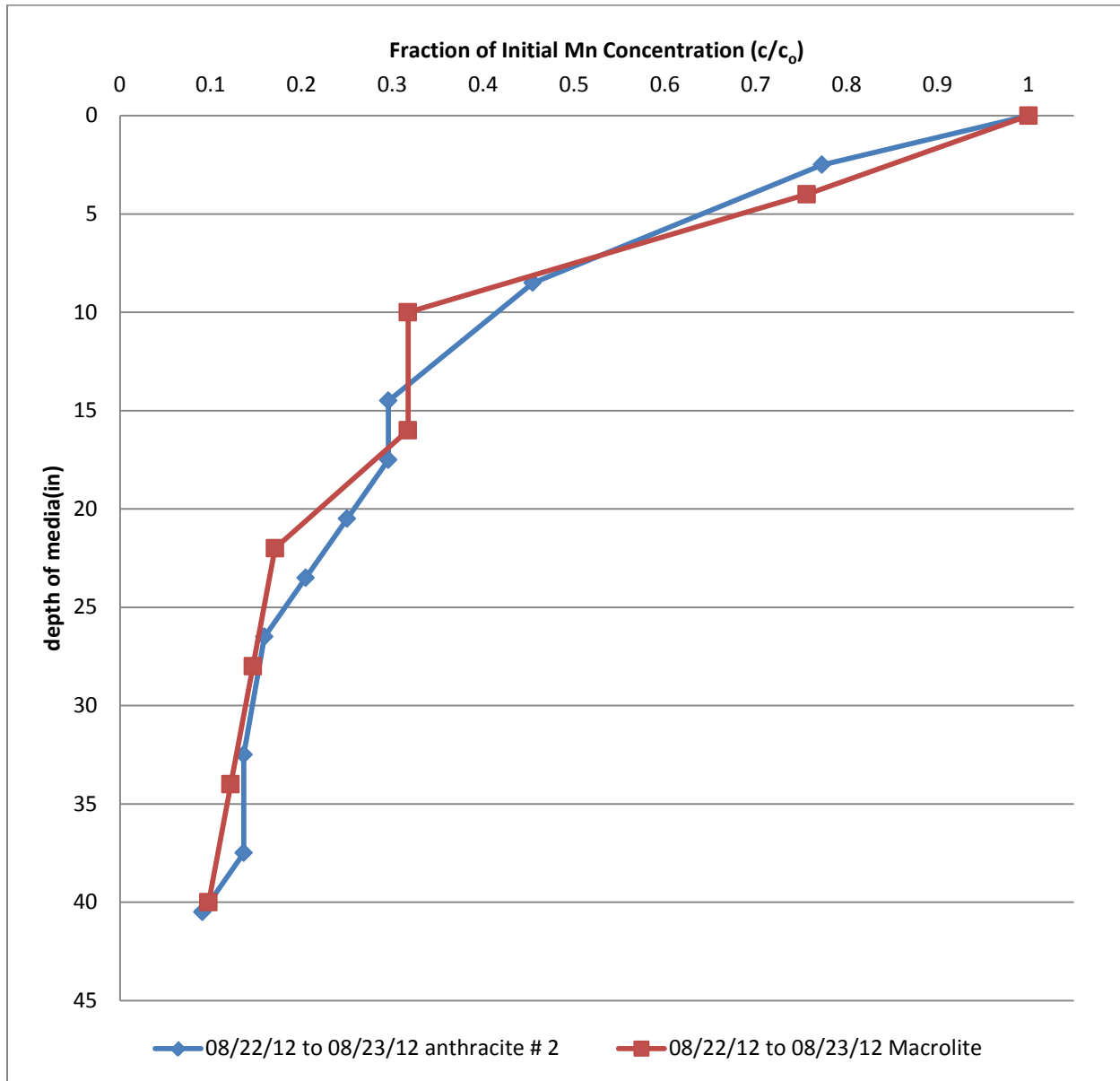


Figure 4-36: A comparison of the average Mn profiles for the anthracite # 2 and Macrolite contactors for the pre-NaOCl / NaOCl pilot plant system at Lantern Hill for 08/22/12 to 08/23/12. (HLR = 10 GPM/ft²; c₀ = 0.15 mg/L Mn)

4.2.3.3 TOC Removal

The total organic carbon (TOC) concentration was measured for the pre-NaOCl / NaOCl pilot system on 01/18/12. The average TOC concentration of the raw water was 3.5 mg/L, while the average TOC concentration of the dual media filter effluent was 2.5 mg/L. The dual media filter removed 1 mg/L of the raw water TOC, a 29 % decrease. The TOC concentration was also measured for the pre-NaOCl / NaOCl pilot system on 08/23/12. The average TOC concentration of the raw water was 3.0 mg/L, while the average TOC concentration of the dual media filter effluent was 2.0 mg/L. The dual media filter removed 1 mg/L of the raw water TOC, a 33 % decrease. Thus, the average overall TOC removal by the dual media filter was 31 %.

4.2.3.4 DBP Results

The first set of DBP analysis for the pre-NaOCl / NaOCl pilot system on was conducted on 01/18/12. The pre- and post-dual media filter chlorine dosing for this day was 1.3 mg/L NaOCl and 3.0 mg/L NaOCl, respectively. The raw water UV_{254} was 0.161 cm^{-1} and the TOC was 3.5 mg/L. The DM filter influent had a chlorine residual of 0.04 mg/L. Instantaneous DBP samples were analyzed for the DM filter influent and effluent as well as the contactor effluents for THM and HAA concentrations. 24 hour hold DBP samples were analyzed for the contactor effluents for THM and HAA concentrations.

Figure 4-37 shows a plot comparing the instantaneous DBP values across the pilot plant and the average August 2012 full-scale values. Figure 4-38 shows a plot comparing 24 hour hold DBP concentrations for the contactor effluents and the average August 2012 full-scale plant effluent values. The average instantaneous THM and HAA concentrations for the DM filter influent were 10 and 14 $\mu\text{g/L}$, respectively. The average instantaneous THM and HAA concentrations for the DM filter effluent were 11 and 21 $\mu\text{g/L}$, respectively. The contactor effluent chlorine residuals were 1.28 mg/L for the Macrolite and 1.39 mg/L for the pyrolusite. For the Macrolite contactor effluent, the average instantaneous THM and HAA concentrations were 24 and 40 $\mu\text{g/L}$, respectively. The average 24 hour hold THM and HAA concentrations were 43 and 56 $\mu\text{g/L}$, respectively. For the pyrolusite contactor effluent, the average instantaneous THM and HAA

concentrations were 23 and 45 µg/L, respectively. The average 24 hour hold THM and HAA concentrations were 41 and 58 µg/L, respectively. After 24 hours, the chlorine residuals for the Macrolite and pyrolusite contactor effluents were 0.44 and 0.66 mg/L, respectively.

Table 4-6 shows the average DBP values for the pre-NaOCl / NaOCl system for both contactors. The percent decrease from full-scale DBP values for the 24 hour hold THM and HAA concentrations are also shown in parentheses. There were average decreases of 78 % and 65 % for the instantaneous THM and HAA concentrations, respectively. There were average decreases of 58 % and 55 % for the 24 hour hold THM and HAA concentrations, respectively. These results show that the two-stage pre-NaOCl / NaOCl pilot system can effectively meet the effluent water goals for metals and turbidity while greatly decreasing the amount of DBPs created with respect to full-scale operations.

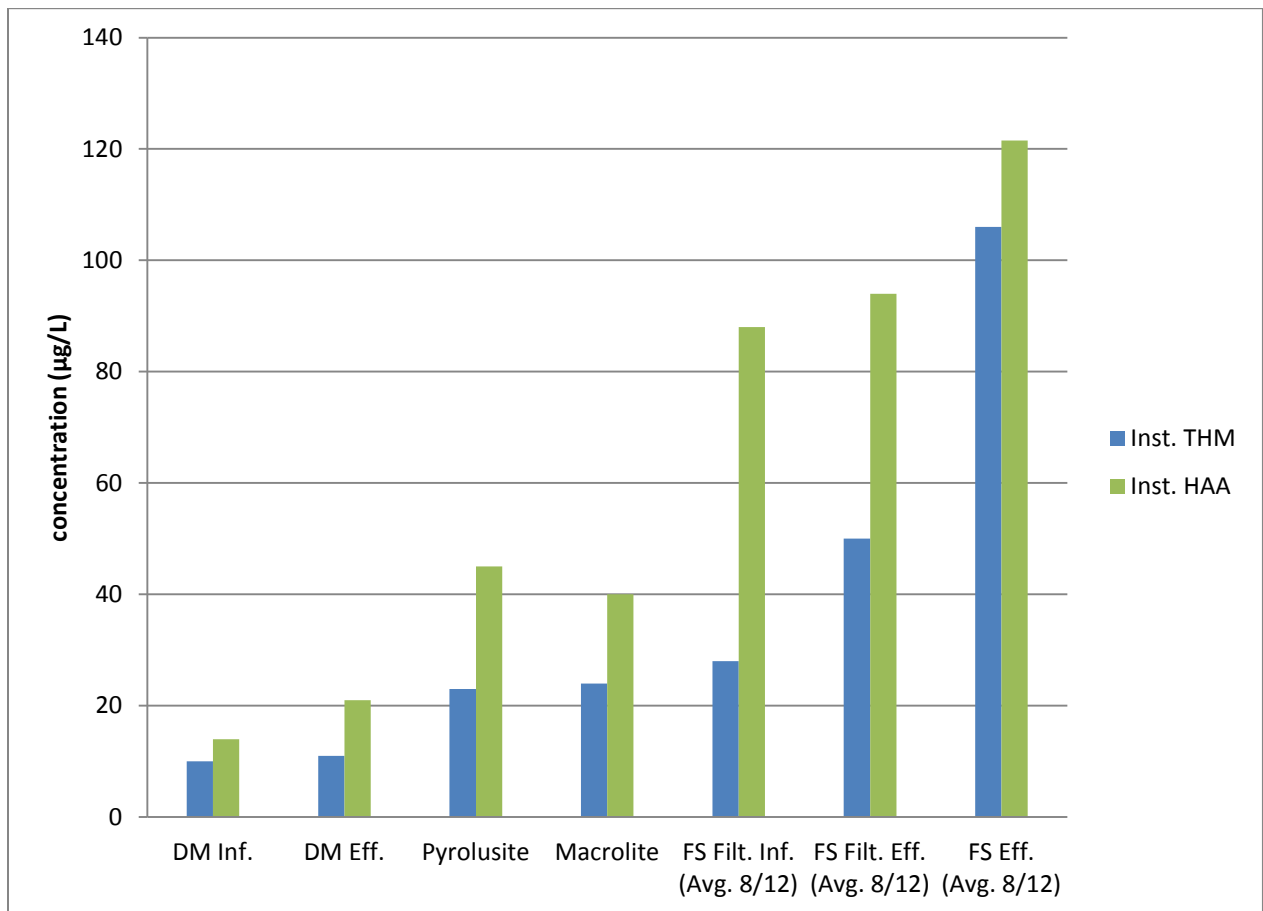


Figure 4-37: Instantaneous THM and HAA concentrations for the pre-NaOCl / NaOCl pilot system at Lantern Hill on 01/18/12 and the average August 2012 full-scale plant values.

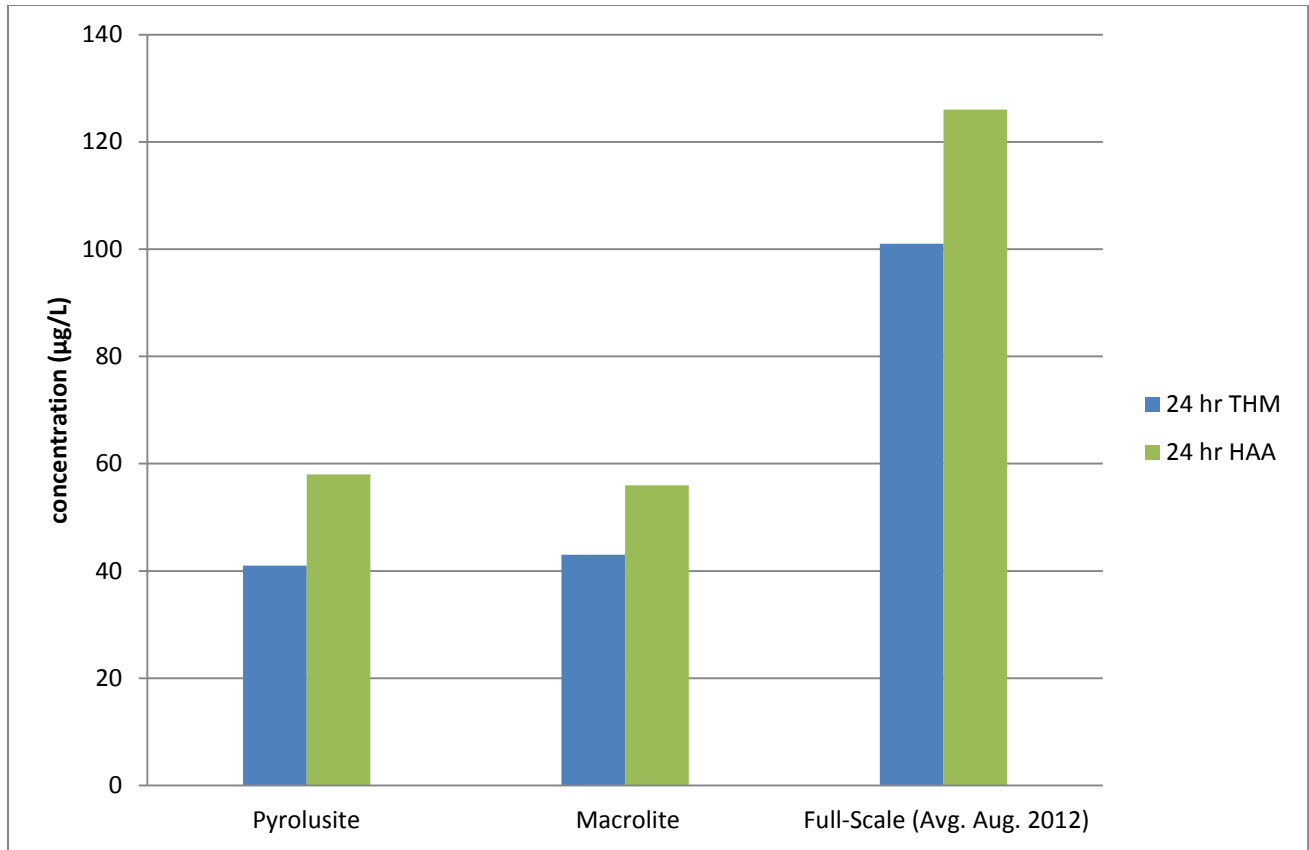


Figure 4-38: 24 hour hold THM and HAA concentrations for the pre-NaOCl / NaOCl pilot system at Lantern Hill on 01/18/12 and the average August 2012 full-scale plant values.

Table 4-6: DBP values for the pre-NaOCl / NaOCl two-stage pilot system at Lantern Hill on 01/18/12 and the average full-scale plant values.

DBP Parameter	Concentration (µg/L) (% Decrease)						
	Pilot				Full-Scale		
	<i>DM Inf.</i>	<i>DM Eff.</i>	<i>Pyrolusite</i>	<i>Macrolite</i>	<i>Filter Inf.</i>	<i>Filter Eff.</i>	<i>FS Eff.</i>
<i>Inst. THM</i>	10	11	23	24	28	50	106
<i>Inst. HAA</i>	14	21	45	40	88	94	122
<i>24 hr THM</i>	<i>n/a</i>	<i>n/a</i>	41 (59%)	43 (57%)	<i>n/a</i>	<i>n/a</i>	101
<i>24 hr HAA</i>	<i>n/a</i>	<i>n/a</i>	58 (54%)	56 (56%)	<i>n/a</i>	<i>n/a</i>	126

The second set of DBP analysis for the pre-NaOCl / NaOCl pilot system was conducted on 08/23/12. DBP analysis was also conducted for the full-scale Lantern Hill plant on this date. The pre- and post-dual media filter chlorine dosing for this day was 3.0 mg/L NaOCl and 3.1 mg/L NaOCl, respectively. The raw water UV_{254} was 0.165 cm^{-1} and the TOC was 3.0 mg/L. The DM filter influent had a chlorine residual that was not detectable. Instantaneous DBP samples were analyzed for the DM filter influent and effluent as well as the contactor effluents for THM and HAA concentrations. 24 hour and 48 hour hold DBP samples were also analyzed for the contactor effluents for THM and HAA concentrations. DBP sampling across the full-scale plant was conducted in a similar manner.

Figure 4-39 shows a plot comparing the instantaneous DBP values across the pilot plant and the full-scale plant. Figure 4-40 shows a plot comparing 24 hour hold DBP concentrations for the contactor effluents and the full-scale values. Figure 4-41 shows a plot comparing 48 hour hold DBP concentrations for the contactor effluents and the full-scale values. The average instantaneous THM and HAA concentrations for the DM filter influent were 6 and 17 $\mu\text{g/L}$, respectively. The average instantaneous THM and HAA concentrations for the LH filter influent were 28 and 89 $\mu\text{g/L}$, respectively. The average instantaneous THM and HAA concentrations for the DM filter effluent were 7 and 19 $\mu\text{g/L}$, respectively. The average instantaneous THM and HAA concentrations for the LH filter effluent were 53 and 96 $\mu\text{g/L}$, respectively. For the anthracite # 2 contactor effluent, the average instantaneous THM and HAA concentrations were 18 and 37 $\mu\text{g/L}$, respectively. The average 24 hour hold THM concentration was not obtained and the HAA concentration was 53 $\mu\text{g/L}$. The average 48 hour hold THM concentration was not obtained and the HAA concentration was 60 $\mu\text{g/L}$. For the Macrolite contactor effluent, the average instantaneous THM and HAA concentrations were 17 and 36 $\mu\text{g/L}$, respectively. The average 24 hour hold THM and HAA concentrations were 40 and 45 $\mu\text{g/L}$, respectively. The average 48 hour hold THM and HAA concentrations were 43 and 59 $\mu\text{g/L}$, respectively. The instantaneous, 24 hour, and 48 hour effluent chlorine residuals for the anthracite # 2 contactor were 1.21, 0.43, and 0.37 mg/L, respectively. The instantaneous, 24 hour, and 48 hour effluent chlorine residuals for the Macrolite contactor were 1.26, 0.31, and 0.27 mg/L, respectively.

Table 4-7 shows the average DBP values for the pre-NaOCl / NaOCl system for the pilot system and full-scale plant. The percent decreases from full-scale DBP values for the pilot system are shown in this table. There were average decreases of 85 % and 70 % for the instantaneous THM and HAA concentrations, respectively. There were average decreases of 62 % and 61 % for the 24 hour hold THM and HAA concentrations, respectively. There were average decreases of 58 % and 54 % for the 48 hour hold THM and HAA concentrations, respectively. These results confirm previous results for this system and show that the two-stage pre-NaOCl / NaOCl pilot system can effectively meet the effluent water goals for metals and turbidity while greatly decreasing the amount of DBPs created with respect to full-scale operations.

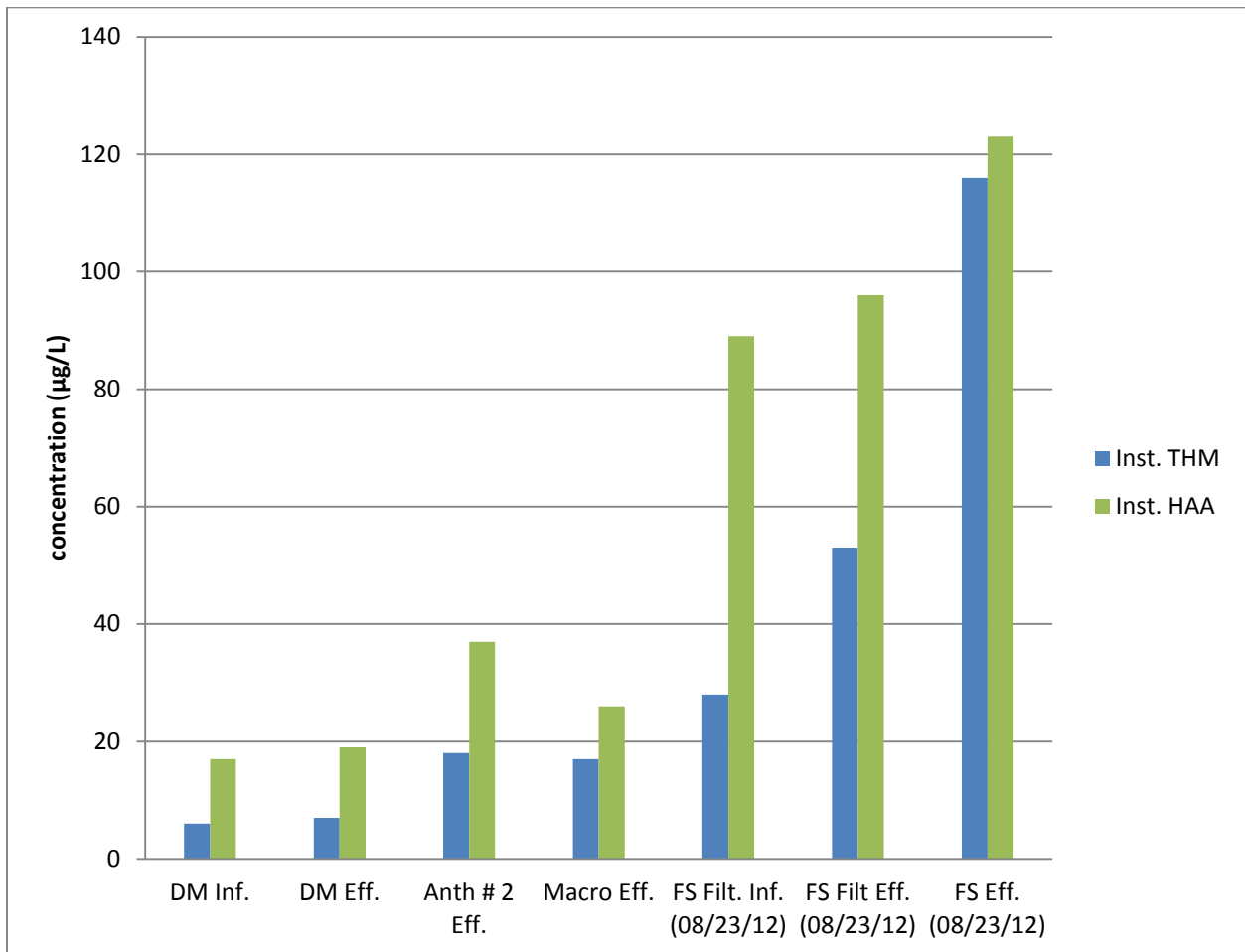


Figure 4-39: Instantaneous THM and HAA concentrations for the pre-NaOCl / NaOCl pilot system at Lantern Hill and the full-scale (FS) plant on 08/23/12.

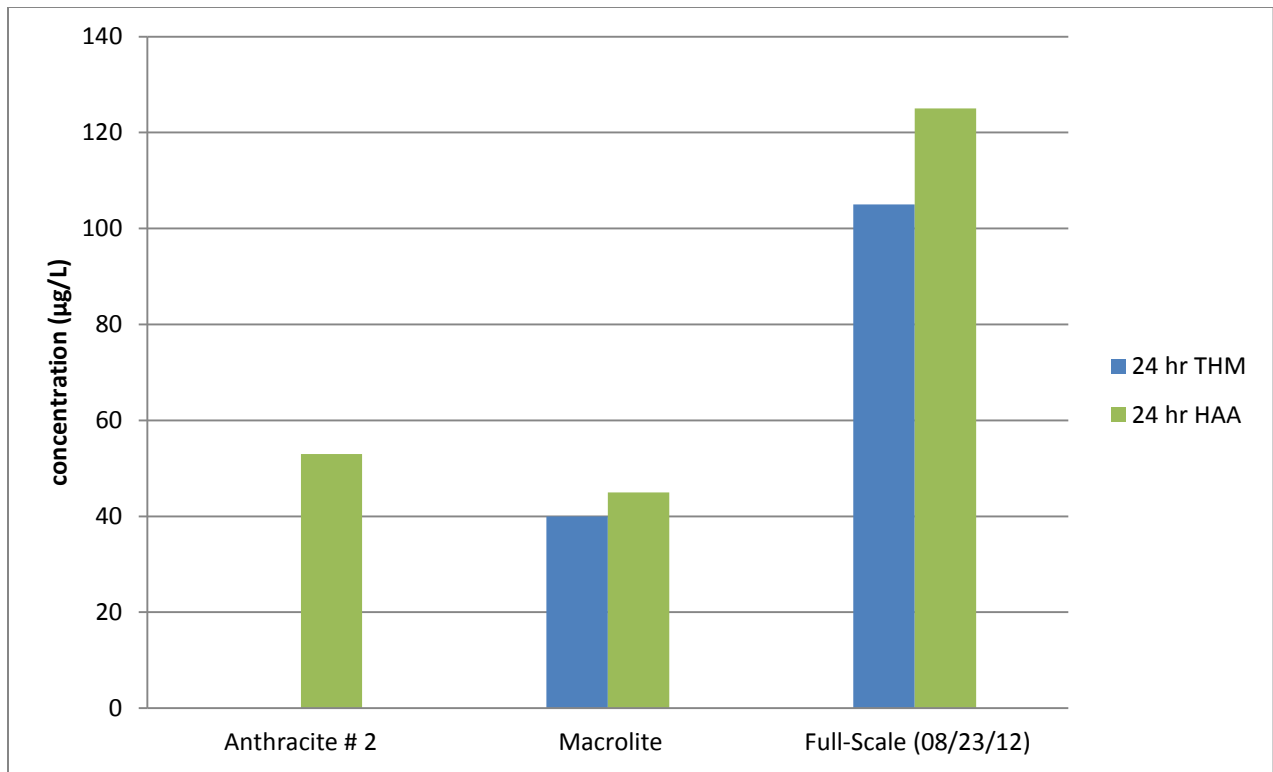


Figure 4-40: 24 hour hold THM and HAA concentrations for the pre-NaOCl / NaOCl pilot system at Lantern Hill and the full-scale plant on 08/23/12.

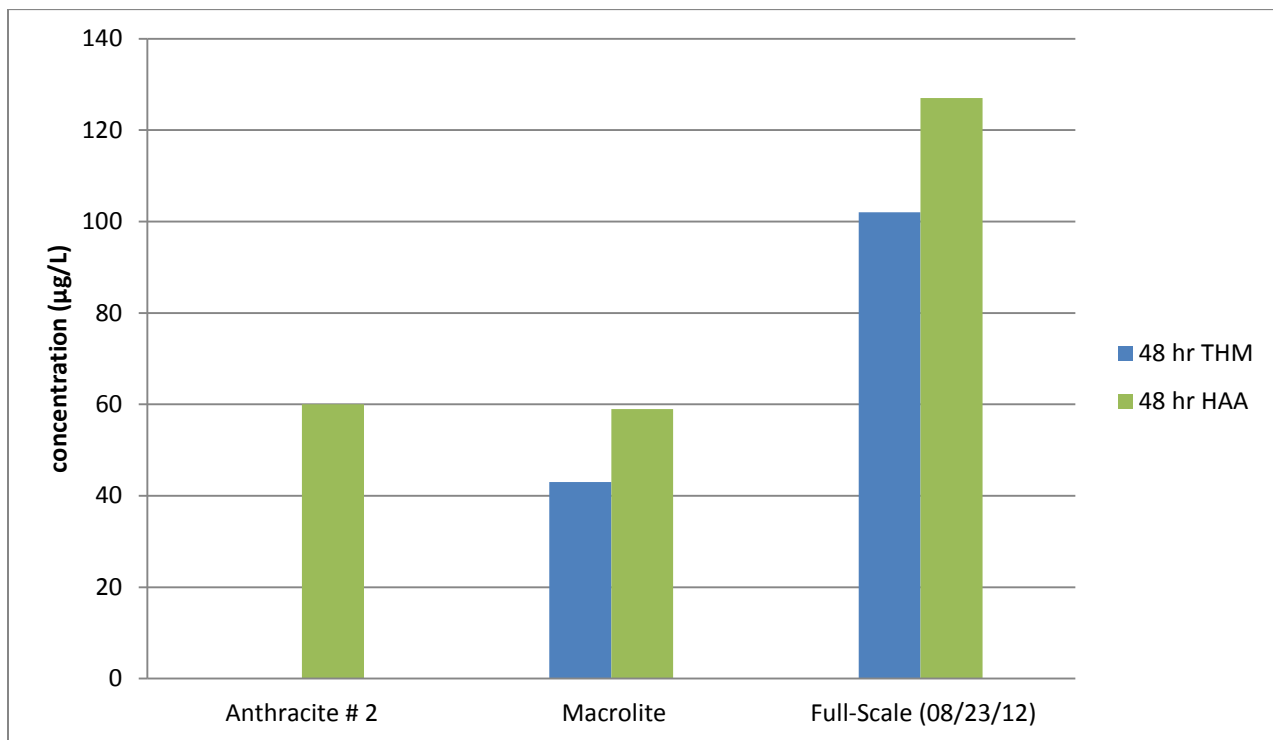


Figure 4-41: 48 hour hold THM and HAA concentrations for the pre-NaOCl / NaOCl pilot system at Lantern Hill and the full-scale plant on 08/23/12.

Table 4-7: DBP values for the pre-NaOCl / NaOCl two-stage pilot system at Lantern Hill and the full-scale plant on 08/23/12.

	Concentration (µg/L) (% Decrease)						
	Pilot				Full-Scale		
DBP Parameter	<i>DM Inf.</i>	<i>DM Eff.</i>	<i>Anthracite # 2</i>	<i>Macrolite</i>	<i>Filter Inf.</i>	<i>Filter Eff.</i>	<i>FS Eff.</i>
<i>Inst. THM</i>	6	7	18	17	28	53	116
<i>Inst. HAA</i>	17	19	37	36	89	96	123
24 hr THM	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>	40 (62 %)	<i>n/a</i>	<i>n/a</i>	105
24 hr HAA	<i>n/a</i>	<i>n/a</i>	53 (58 %)	45 (64 %)	<i>n/a</i>	<i>n/a</i>	125
48 hr THM	<i>n/a</i>	<i>n/a</i>	<i>n/a</i>	43 (58 %)	<i>n/a</i>	<i>n/a</i>	102
48 hr HAA	<i>n/a</i>	<i>n/a</i>	60 (53 %)	59 (54 %)	<i>n/a</i>	<i>n/a</i>	127

4.2.3.5 Head Loss

Head loss across the dual media filter was observed and measured during each pilot experiment between backwashes, approximately a 24 hour period. For the pre-NaOCl / NaOCl system, the head loss ranged from 0 to 1 psi. As noted previously, during laboratory experiments at UMass, the head loss across the second-stage contactors was approximately 0.3 psi, at an average water temperature of 20° C.

4.2.4 Overall Lab and Pilot Comparison and Summary

At the completion of the laboratory experiments, it was determined that all media types, with the exception of the UMass Macrolite, could obtain the desired effluent Mn concentration of 0.02 mg/L or less, based on a conservative full-scale design bed depth of 40 inches and a hydraulic loading rate of 10 GPM/ft². Table 4-8 shows the average Mn concentration as a function of bed depth for each media type during laboratory experiments at full-scale

conditions of a hydraulic loading rate of 10 GPM/ft² and a chlorine residual of 1.0 mg/L. The Macrolite performed best in the laboratory experiments, followed closely by anthracite # 2 (the Siemens conditioned anthracite).

Table 4-8: Average Mn removal profiles for all media types tested during laboratory experiments. (HLR = 10 GPM/ft²; Cl₂ = 1.0 mg/L)

Anthracite # 1		Anthracite # 2		UMass Macrolite		Macrolite		Pyrolusite	
depth of media (in.)	(mg/L Mn)	depth of media (in.)	(mg/L Mn)	depth of media (in.)	(mg/L Mn)	depth of media (in.)	(mg/L Mn)	depth of media (in.)	(mg/L Mn)
0	0.20	0	0.24	0	0.22	0	0.22	0	0.21
1.5	0.18	2.5	0.18	1.5	0.24	4	0.12	1.5	0.21
4.5	0.14	8.5	0.09	4.5	0.19	10	0.06	4.5	0.13
7.5	0.10	14.5	0.03	7.5	0.13	16	0.01	7.5	0.08
10.5	0.07	17.5	0.02	10.5	0.10	22	0.00	10.5	0.06
13.5	0.05	20.5	0.02	13.5	0.07	28	0.02	13.5	0.04
19.5	0.03	23.5	0.01	19.5	0.03	34	0.01	19.5	0.01
24.5	0.02	26.5	0.01	24.5	0.03	40	0.01	24.5	0.02
27.5	0.01	32.5	0.01	27.5	0.02			26.5	0.01
		37.5	0.00						
		40.5	0.00						

Table 4-9 shows a comparison for dosing and performance of each pilot system as well as for recent full-scale operations. For the pre-KMnO₄ / NaOCl pilot, it was determined that an average sub-stoichiometric dose of 1.1 mg/L KMnO₄ ahead of the dual media filter could effectively oxidize all of the raw water iron. Also, for this system it was determined that an

average C572 polymer dose of 6.9 mg/L could achieve a desired effluent turbidity of 0.1 NTU or less, as well as remove about 1 mg/L of TOC. An average post-filter chlorine dose of 4.0 mg/L was sufficient to regenerate the oxide coated media and result in a desired finished water effluent chlorine residual of about 1.2 mg/L. For the pre-NaOCl / NaOCl pilot, it was determined that an average dose of 2.0 mg/L NaOCl ahead of the dual media filter could effectively oxidize all of the raw water iron. Also, for this system it was determined that an average C572 polymer dose of 5.2 mg/L could achieve a desired effluent turbidity of 0.1 NTU or less, as well as remove about 1 mg/L of TOC. An average post-filter chlorine dose of 2.8 mg/L was sufficient to regenerate the oxide coated media and result in a desired finished water effluent chlorine residual of about 1.3 mg/L. When the pre-NaOCl / NaOCl approach was used, a total chlorine dose of only 4.8 mg/L was required for successful pilot operation. This chlorine dose is not much more than the pre-KMnO₄ / NaOCl chlorine dosing requirements, however, it is much lower than the full-scale chlorine dosing at Lantern Hill, approximately 6.9 mg/L.

Table 4-9: Average chemical dosing and operation for the two pilot systems and the full-scale Lantern Hill system.

Parameter	Concentration (mg/L)		
	Pre-KMnO ₄ / NaOCl Pilot System	Pre-NaOCl / NaOCl Pilot System	Full-Scale LH (2012)
NaOH (dose)	25.0	26.5	37.1
KMnO ₄ (pre-filter dose)	1.1	n/a	1.0
Cl ₂ (pre-filter dose)	n/a	2.0	5.2
C572 Polymer (dose)	6.9	5.2	6.0
Cl ₂ (post-filter dose)	4.0	2.8	1.7
Fe (effluent)	0.07	0.03	0.04
Mn (effluent)	0.02	0.01	0.01

The performance of all media types tested during the pilot experiments was considered satisfactory, based on the desired finished water manganese concentration of 0.02 mg/L or less. This is a result of the conservative system design including a 40 inch media bed depth and a hydraulic loading rate of 10 GPM/ft². The Macrolite media performed best during the pilot experiments for both the pre-KMnO₄ / NaOCl and the pre-NaOCl / NaOCl systems; average effluent manganese concentrations were 0.01 mg/L.

Both pilot systems produced significantly less DBPs than the full-scale operations at Lantern Hill. A summary of the DBP results can be seen in Figures 4-42 and 4-43. The pre-KMnO₄ / NaOCl system produced 63 and 61 % decreases in the 24 hour hold values for THMs and HAAs, respectively. This system also produced 62 and 60 % decreases in the 48 hour hold values for THMs and HAAs, respectively. The pre-NaOCl / NaOCl system produced 59 and 58 % decreases in the 24 hour hold values for THMs and HAAs, respectively. This system also produced 58 and 52 % decreases in the 48 hour hold values for THMs and HAAs, respectively. The HAA concentrations for all samples measured during this study consisted almost entirely of compounds from the HAA₅ group. From this group, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) made up the majority of each measurement. The pre-KMnO₄ / NaOCl system produced slightly less DBPs than the pre-NaOCl / NaOCl system. However, the overall results show that the two-stage approach, with either KMnO₄ or NaOCl dosing ahead of the filter for iron oxidation, can meet effluent goals without exceeding regulated DBP values. This substantial decrease in DBP production is most likely the result of DBP precursors being removed by the dual media filter during the first-stage, as well as lower concentrations of chlorine reacting with NOM throughout the pilot systems.

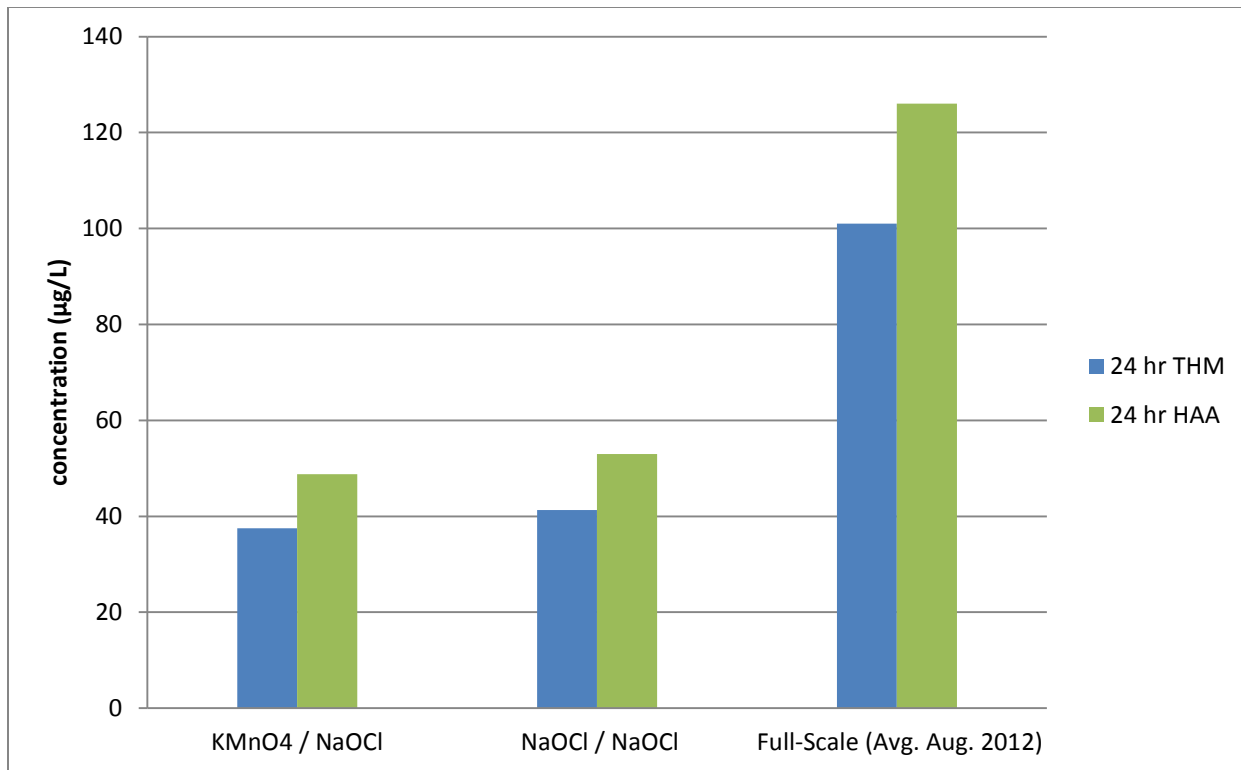


Figure 4-42: The average 24 hour hold THM and HAA results for both pilot systems and the full-scale plant.

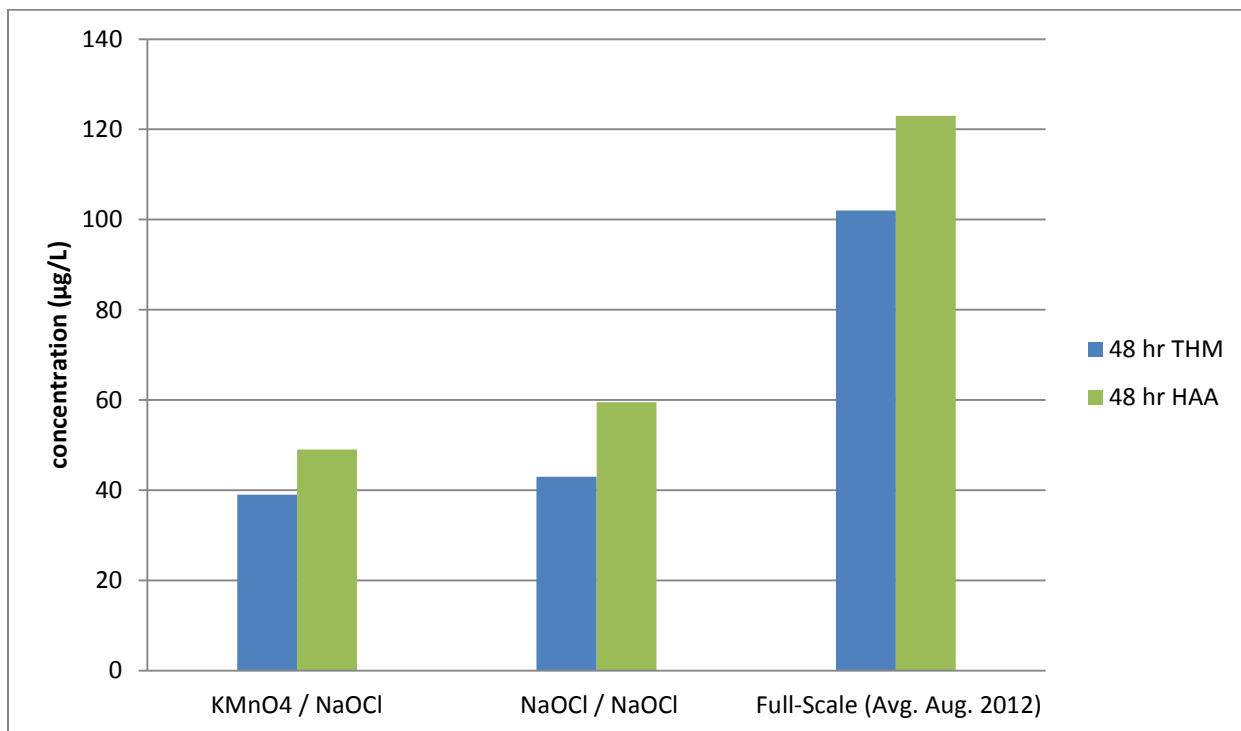


Figure 4-43: The average 48 hour hold THM and HAA results for both pilot systems and the full-scale plant.

4.2.5 Media Surface Extraction Results

Media samples were collected from the dual media filter and the second-stage contactor columns at the completion of all the laboratory experiments and most of the pilot experiments and analyzed on 06/08/12. The manganese, iron, and aluminum on the surface of the media were extracted and measured according to a procedure by Knocke (1990). The results for this analysis can be seen in Table 4-10. Media types that had longer operational times had higher coating levels of metals. The manganese coatings levels were typically much higher than the iron and aluminum for a given media. The dual media filter influent had relatively high levels of dissolved manganese and low levels of dissolved iron. The DM Anthracite experienced higher dissolved metal concentrations than the DM Sand. This should have resulted in the DM Anthracite having higher metal coating levels than the DM Sand. This was the case for the iron coating level, however, the opposite was observed with respect to manganese. After further investigation, it was determined that a significant amount of the DM Anthracite had been lost during a previous backwash procedure and new DM Anthracite was installed. This possibly resulted in a much shorter operational period in comparison to the DM Sand.

The SSC Anthracite # 1 media had developed a more significant coating level of manganese and iron compared to SSC Anthracite # 2. This is most likely the result of a longer operational time. The SSC Anthracite # 1 had been used in previous UMass pilot experiments as well as recent laboratory and pilot experiments, while the SSC Anthracite # 2 had only been used in recent laboratory experiments, at the time of analysis. The SSC Macrolite had the highest manganese coating level and a considerable iron coating level. The SSC Macrolite had been used in recent laboratory and pilot experiments. The high manganese level was most likely the result of the coating process used at the factory. There was not a significant aluminum coating level on any of the media, as was expected.

Table 4-10: Metal coating levels for the media surface extraction analysis.

Media Description	Coating Level		
	mg Mn/g media	mg Fe/g media	mg Al/g media
DM Anthracite*	0.07	0.61	0.02
DM Sand	0.42	0.16	0.01
SSC Anthracite # 1	2.61	0.50	0.02
SSC Macrolite	5.55	0.31	0.15
SSC Anthracite # 2**	0.39	0.05	0.05

* Very low Mn on DM Anthracite may be due to media replacement after loss due to backwash. Expected it to be higher than Mn on DM Sand.

**Used only in UMass laboratory experiments (at time of analysis)

CHAPTER 5: SUMMARY, CONCLUSION, AND RECOMMENDATIONS

5.1 Summary

The objective of this research was to evaluate different types of manganese oxide coated media for manganese removal by a second-stage contactor for a variety of operational scenarios. Laboratory experiments allowed for preliminary assessment of the media. The best performing media types were identified during these experiments. Next, pilot plant experiments were conducted for the two-stage pilot system constructed at the Lantern Hill water treatment facility. These experiments included treatment optimization, second-stage contactor media evaluation, and DBP analysis.

5.2 Conclusion

At the completion of the laboratory experiments, it was determined that all media types, with the exception of the UMass Macrolite, could obtain the desired effluent Mn concentration of 0.02 mg/L or less, based on a conservative full-scale design bed depth of 40 inches and a hydraulic loading rate of 10 GPM/ft². The Macrolite performed best in the laboratory experiments, followed closely by the Siemens conditioned anthracite (anthracite # 2). In general, the performance of all media types at a given hydraulic loading rate improved with higher effluent chlorine residuals. Also, for a given effluent chlorine residual, the media performed better at lower hydraulic loading rates.

Once pilot plant experiments were conducted, the treatment process was optimized, second-stage contactor media was evaluated, and DBP analyses were conducted. For the pre-KMnO₄ / NaOCl pilot, it was determined that an average sub-stoichiometric dose of 1.1 mg/L KMnO₄ ahead of the dual media filter could effectively oxidize all of the raw water iron. Also, for this system it was determined that an average C572 polymer dose of 6.9 mg/L could achieve a desired effluent turbidity of 0.1 NTU or less, as well as remove about 1 mg/L of TOC. An average post-filter chlorine dose of 4.0 mg/L was sufficient to regenerate the oxide coated media and result in a desired finished water effluent chlorine residual of about 1.2 mg/L. For the pre-

NaOCl / NaOCl pilot, it was determined that an average dose of 2.0 mg/L NaOCl ahead of the dual media filter could effectively oxidize all of the raw water iron. Also, for this system it was determined that an average C572 polymer dose of 5.2 mg/L could achieve a desired effluent turbidity of 0.1 NTU or less, as well as remove about 1 mg/L of TOC. An average post-filter chlorine dose of 2.8 mg/L was sufficient to regenerate the oxide coated media and result in a desired finished water effluent chlorine residual of about 1.3 mg/L. When the pre-NaOCl / NaOCl approach was used, a total chlorine dose of only 4.8 mg/L was required for successful pilot operation. This chlorine dose is not much more than the pre-KMnO₄ / NaOCl chlorine dosing requirements; however, it is much lower than the full-scale chlorine dosing at Lantern Hill, approximately 6.9 mg/L.

The performance of all second-stage contactor media types tested during the pilot experiments was considered satisfactory, based on the desired finished water manganese concentration of 0.02 mg/L or less. This is a result of the conservative system design including a 40 inch media bed depth and a hydraulic loading rate of 10 GPM/ft². The Macrolite media performed best during the pilot experiments for both the pre-KMnO₄ / NaOCl and the pre-NaOCl / NaOCl systems; average effluent manganese concentrations were 0.01 mg/L.

Both pilot systems produced significantly less DBPs than the full-scale operations at Lantern Hill. The pre-KMnO₄ / NaOCl system produced 63 and 61 % decreases in the 24 hour hold values for THMs and HAAs, respectively. This system also produced 62 and 60 % decreases in the 48 hour hold values for THMs and HAAs, respectively. The pre-NaOCl / NaOCl system produced 59 and 58 % decreases in the 24 hour hold values for THMs and HAAs, respectively. This system also produced 58 and 52 % decreases in the 48 hour hold values for THMs and HAAs, respectively. The pre-KMnO₄ / NaOCl system produced slightly less DBPs than the pre-NaOCl / NaOCl system. However, the overall results show that the two-stage approach, with either KMnO₄ or NaOCl dosing ahead of the filter for iron oxidation, can meet effluent goals without exceeding regulated DBP values.

5.3 Recommendations

Further research should be conducted on additional manganese oxide coated media for manganese removal, both in the laboratory and at the pilot plant. Also, extended testing of high performing media, such as anthracite # 2 and Macrolite, should occur both in the laboratory and at the pilot plant to observe how manganese removal performance changes over time. Additionally, this extended testing would allow for determination of operational parameters, such as head losses over time and the frequency of backwashes.

In addition to more experiments, an effort should be made to further develop existing second-stage contactor performance models. These models incorporate manganese concentrations, chlorine residuals, and media bed depths and can predict effluent conditions. These models should be calibrated with numerous data sets to increase the accuracy of simulations. As these models become more developed, industry will be able to use them as a valuable design tool in the water treatment process.

Lastly, once the construction of the two-stage Lantern Hill facility upgrade is complete, start-up and monitoring assessments should be conducted. These assessments can be used to document the facility performance and identify any problems with the treatment process. Water quality should be characterized across the full-scale facility and treatment should be optimized accordingly.

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APPENDIX

Table A-1: Averaged Mn removal data for each set of test runs in the laboratory for the permanganate conditioned anthracite column. (anthracite # 1) (HLR/Cl Res.)

Anthracite	depth of media (in.)	10/0.2		10/1.0		10/4.0		15/0.2		15/1.0		15/4.0		20/0.2		20/1.0		20/4.0	
		conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i
influent	0.0	0.20	1.00	0.20	1.00	0.19	1.00	0.21	1.00	0.21	1.00	0.22	1.00	0.19	1.00	0.20	1.00	0.19	1.00
port 0	1.5	0.19	0.95	0.18	0.92	0.16	0.89	0.20	0.94	0.19	0.90	0.19	0.85	0.18	0.93	0.18	0.90	0.16	0.85
port 1	4.5	0.16	0.80	0.14	0.68	0.11	0.59	0.17	0.79	0.15	0.73	0.13	0.58	0.17	0.90	0.13	0.64	0.12	0.63
port 2	7.5	0.13	0.65	0.10	0.52	0.07	0.38	0.15	0.70	0.13	0.63	0.10	0.45	0.15	0.79	0.11	0.52	0.10	0.54
port 3	10.5	0.10	0.46	0.07	0.33	0.03	0.18	0.13	0.63	0.10	0.49	0.07	0.28	0.13	0.65	0.08	0.39	0.07	0.37
port 4	13.5	0.09	0.41	0.05	0.25	0.03	0.16	0.12	0.55	0.08	0.39	0.05	0.24	0.10	0.54	0.05	0.27	0.04	0.24
port 5	19.5	0.05	0.25	0.03	0.17	0.01	0.06	0.08	0.38	0.05	0.22	0.03	0.11	0.08	0.43	0.04	0.20	0.02	0.12
port 6	24.5	0.03	0.14	0.02	0.11	0.01	0.07	0.06	0.27	0.03	0.16	0.02	0.09	0.05	0.30	0.02	0.10	0.02	0.13
effluent	27.5	0.02	0.11	0.01	0.06	0.00	0.01	0.05	0.25	0.02	0.11	0.01	0.05	0.04	0.19	0.02	0.10	0.01	0.08

Table A-2: Averaged Mn removal data for each set of test runs in the laboratory for the Siemens conditioned anthracite column. (anthracite # 2) (HLR/Cl Res.)

Siemens Anthracite	depth of media (in.)	10/0.2		10/1.0		10/4.0		15/0.2		15/1.0		15/4.0		20/0.2		20/1.0		20/4.0	
		conc.	c/ci	conc.	c/ci	conc.	c/ci	conc.	c/ci	conc.	c/ci	conc.	c/ci	conc.	c/ci	conc.	c/ci	conc.	c/ci
influent	0	0.22	1.00	0.24	1.00	0.20	1.00	0.24	1.00	0.23	1.00	0.23	1.00	0.20	1.00	0.20	1.00	0.21	1.00
port 1	2.5	0.18	0.84	0.18	0.77	0.13	0.63	0.23	0.96	0.20	0.86	0.16	0.69	0.19	0.95	0.18	0.89	0.14	0.66
port 2	8.5	0.13	0.62	0.09	0.38	0.04	0.19	0.18	0.75	0.12	0.52	0.06	0.28	0.16	0.78	0.14	0.69	0.06	0.26
port 3	14.5	0.05	0.22	0.03	0.14	0.01	0.04	0.14	0.59	0.09	0.37	0.02	0.10	0.14	0.69	0.11	0.54	0.04	0.16
port 4	17.5	0.03	0.13	0.02	0.10	0.00	0.00	0.12	0.50	0.03	0.13	0.01	0.04	0.12	0.59	0.07	0.33	0.02	0.10
port 5	20.5	0.01	0.06	0.02	0.08	0.00	0.00	0.11	0.45	0.02	0.09	0.01	0.03	0.10	0.49	0.05	0.24	0.01	0.04
port 6	23.5	0.01	0.05	0.01	0.04	0.00	0.00	0.10	0.43	0.02	0.06	0.00	0.02	0.10	0.47	0.04	0.17	0.00	0.01
port 7	26.5	0.01	0.04	0.01	0.03	0.00	0.00	0.10	0.41	0.01	0.03	0.00	0.02	0.10	0.48	0.03	0.16	0.00	0.00
port 8	32.5	0.01	0.04	0.01	0.03	0.00	0.00	0.09	0.38	0.00	0.01	0.00	0.02	0.09	0.43	0.01	0.03	0.00	0.00
port 9	37.5	0.01	0.03	0.00	0.02	0.00	0.00	0.08	0.34	0.00	0.00	0.00	0.02	0.09	0.43	0.00	0.00	0.00	0.00
effluent	40.5	0.00	0.02	0.00	0.02	0.00	0.00	0.08	0.32	0.00	0.00	0.00	0.01	0.08	0.37	0.00	0.00	0.00	0.00

Table A-3: Averaged Mn removal data for each set of test runs in the laboratory for the UMass Macrolite column. (UMass Macrolite) (HLR/CI Res.)

Anthracite	depth of media (in.)	10/0.2		10/1.0		10/4.0		15/0.2		15/1.0		15/4.0		20/0.2		20/1.0		20/4.0	
		conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i
influent	0.0	0.18	1.00	0.18	1.00	0.18	1.00	0.18	1.00	0.18	1.00	0.18	1.00	0.18	1.00	0.18	1.00	0.18	1.00
port 0	1.5	0.19	1.06	0.19	1.06	0.19	1.06	0.19	1.06	0.19	1.06	0.19	1.06	0.19	1.06	0.19	1.06	0.19	1.06
port 1	4.5	0.14	0.81	0.14	0.81	0.14	0.81	0.14	0.81	0.14	0.81	0.14	0.81	0.14	0.81	0.14	0.81	0.14	0.81
port 2	7.5	0.11	0.60	0.11	0.60	0.11	0.60	0.11	0.60	0.11	0.60	0.11	0.60	0.11	0.60	0.11	0.60	0.11	0.60
port 3	10.5	0.09	0.50	0.09	0.50	0.09	0.50	0.09	0.50	0.09	0.50	0.09	0.50	0.09	0.50	0.09	0.50	0.09	0.50
port 4	13.5	0.06	0.34	0.06	0.34	0.06	0.34	0.06	0.34	0.06	0.34	0.06	0.34	0.06	0.34	0.06	0.34	0.06	0.34
port 5	19.5	0.04	0.21	0.04	0.21	0.04	0.21	0.04	0.21	0.04	0.21	0.04	0.21	0.04	0.21	0.04	0.21	0.04	0.21
port 6	24.5	0.05	0.30	0.05	0.30	0.05	0.30	0.05	0.30	0.05	0.30	0.05	0.30	0.05	0.30	0.05	0.30	0.05	0.30
effluent	27.5	0.03	0.16	0.03	0.16	0.03	0.16	0.03	0.16	0.03	0.16	0.03	0.16	0.03	0.16	0.03	0.16	0.03	0.16

Table A-4: Averaged Mn removal data for each set of test runs in the laboratory for the Macrolite column. (HLR/CI Res.)

Macrolite	depth of media (in.)	10/0.2		10/1.0		10/4.0		15/0.2		15/1.0		15/4.0		20/0.2		20/1.0		20/4.0	
		conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i
influent	0.0	0.21	1.00	0.22	1.00	0.21	1.00	0.22	1.00	0.22	1.00	0.23	1.00	0.22	1.00	0.25	1.00	0.19	1.00
port 0	4.0	0.14	0.69	0.12	0.57	0.13	0.62	0.17	0.78	0.17	0.76	0.16	0.68	0.15	0.70	0.17	0.68	0.14	0.72
port 1	10.0	0.07	0.34	0.06	0.26	0.06	0.27	0.10	0.45	0.10	0.42	0.09	0.38	0.09	0.42	0.09	0.38	0.07	0.34
port 2	16.0	0.06	0.29	0.01	0.03	0.05	0.24	0.06	0.26	0.04	0.15	0.04	0.18	0.06	0.25	0.03	0.12	0.04	0.19
port 3	22.0	0.04	0.17	0.00	0.01	0.03	0.13	0.04	0.17	0.01	0.05	0.02	0.09	0.03	0.13	0.01	0.02	0.01	0.06
port 4	28.0	0.02	0.11	0.02	0.07	0.01	0.06	0.03	0.12	0.02	0.07	0.01	0.03	0.02	0.06	0.01	0.04	0.02	0.07
port 5	34.0	0.01	0.05	0.01	0.02	0.01	0.05	0.01	0.06	0.00	0.00	0.02	0.06	0.02	0.07	0.01	0.02	0.00	0.01
effluent	40.0	0.01	0.03	0.01	0.02	0.00	0.01	0.01	0.06	0.00	0.00	0.02	0.07	0.00	0.00	0.00	0.00	0.00	0.00

Table A-5: Averaged Mn removal data for each set of test runs in the laboratory for the pyrolusite column. (HLR/CI Res.)

Pyrolusite	depth of media (in.)	10/0.2		10/1.0		10/4.0		15/0.2		15/1.0		15/4.0		20/0.2		20/1.0		20/4.0	
		conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i	conc.	c/c _i
influent	0.0	0.22	1.00	0.21	1.00	0.18	1.00	0.21	1.00	0.19	1.00	0.19	1.00	0.19	1.00	0.19	1.00	0.20	1.00
port 0	1.5	0.21	0.94	0.21	1.02	0.20	1.09	0.21	0.99	0.20	1.06	0.20	1.05	0.18	0.95	0.20	1.03	0.20	1.01
port 1	4.5	0.14	0.65	0.13	0.64	0.13	0.71	0.15	0.74	0.14	0.73	0.13	0.67	0.14	0.74	0.16	0.85	0.15	0.75
port 2	7.5	0.09	0.39	0.08	0.38	0.06	0.35	0.10	0.49	0.08	0.40	0.07	0.38	0.09	0.48	0.11	0.57	0.10	0.49
port 3	10.5	0.07	0.31	0.06	0.27	0.06	0.31	0.09	0.45	0.07	0.37	0.07	0.35	0.08	0.41	0.10	0.52	0.09	0.44
port 4	13.5	0.06	0.26	0.04	0.18	0.04	0.21	0.08	0.37	0.05	0.25	0.05	0.25	0.07	0.34	0.08	0.43	0.07	0.35
port 5	19.5	0.01	0.05	0.01	0.05	0.00	0.01	0.03	0.14	0.00	0.01	0.00	0.00	0.03	0.15	0.04	0.20	0.02	0.12
port 6	24.5	0.02	0.08	0.02	0.09	0.01	0.06	0.03	0.15	0.00	0.02	0.00	0.03	0.03	0.13	0.03	0.13	0.03	0.15
effluent	26.5	0.01	0.05	0.01	0.03	0.01	0.03	0.02	0.10	0.00	0.00	0.00	0.00	0.02	0.11	0.03	0.14	0.02	0.09