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Innovative Biological Treatment Process for the Removal of Ammonia, Arsenic, Iron and Manganese from a Small Drinking Water System in Gilbert, Iowa

Office of Research and Development
Water Systems Division

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Innovative Biological Treatment Process for the Removal of Ammonia, Arsenic, Iron and Manganese from a Small Drinking Water System in Gilbert, Iowa

Phase 1: Pilot Evaluation

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Notice

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1. Background

1.1 Ammonia in Drinking Water Sources

Many regions in the United States have excessive levels of ammonia in their drinking water sources (e.g., ground and surface waters) because of naturally occurring processes, agricultural and urban runoff, concentrated animal feeding operations, municipal wastewater treatment plants, and other sources. Ammonia is not regulated by the U.S. Environmental Protection Agency (EPA) as a contaminant. Based on a 2003 World Health Organization (WHO) assessment, ammonia levels in groundwater are typically below 0.2 milligrams per liter (mg/L), and ammonia does not pose a direct health concern at levels expected in drinking water (WHO 2003); however, it may pose a concern when nitrification of significant levels of ammonia from the source water occurs in the drinking water treatment plant and/or distribution system. Nitrification, which is the conversion of the ammonia to nitrite and nitrate by bacteria, leads to distribution system water quality issues, such as potential corrosion problems, oxidant demand, taste and odor complaints, and elevated nitrite levels (Bremer *et al.,*2001; Fleming *et al*., 2005; Lee *et al*., 1980; Odell *et al*., 1996; Rittman & Snoeyink, 1984; Suffet *et al*., 1996).

Ammonia in water may also pose problems with water treatment effectiveness. For example, in source waters containing both ammonia and arsenic, ammonia may negatively impact the removal of arsenic by creating a chlorine demand, therefore reducing the availability of chlorine needed to oxidize the arsenic (Lytle *et al.*, 2007). Lastly, water systems that have ammonia in their source water and desire to maintain a free chlorine residual will need to add additional chlorine to overcome the demand of ammonia. While chemical cost and added operational complexity are an issue, excessive chlorine addition can pose disinfection by-product issues as well. The complete oxidation of source water ammonia prior to or as part of the water treatment process would eliminate the potential negative impacts on treatment effectiveness and nitrification on distribution system water quality.

1.2 Community Water Source with Elevated Ammonia and Other Co-Occurring Contaminants (Arsenic, Iron and Manganese)

Many regions in the Midwest are particularly impacted by ammonia in their source waters from natural geology, agricultural runoff, and other farming practices. For example, the State of Iowa has a widespread distribution of ammonia in well waters across its communities (Figure 1). Water quality testing of the source groundwater in one small Iowa community, Gilbert (population approximately 1082) (Figure 1) showed that, on average, ammonia levels were 2.9 mg as nitrogen N)/L (Table 1). Although ammonia in water is not regulated, the State of Iowa Department of Natural Resources (IDNR) can require water systems in the state to

monitor nitrite and nitrate at their points of entry to the distribution system and in their distribution systems should they suspect that nitrification of the source water ammonia is occurring. Nitrite and nitrate have drinking water standards or maximum contaminant levels (MCLs) of 1 (in Iowa 1.0) and 10 mg N/L, respectively, measured at the point of entry to the distribution system. The Iowa IDNR extends the MCL sampling location definition to drinking water in the distribution when nitrification is a concern. Particularly worrisome are waters with ammonia levels greater than 1 mg N/L where incomplete nitrification can lead to exceedances of the lower nitrite MCL.

Complicating matters, the groundwater source in Gilbert also contains elevated levels of arsenic (0.023 mg/L), iron (2.9 mg/L) and manganese (0.08 mg/L), which are all at levels greater than their respective primary or secondary regulatory MCLs. The impact of arsenic on human health is well known. In 2001, the EPA reduced the MCL for arsenic from 0.05 mg/L to 0.010 mg/L (USEPA, 2001). The MCL reduction was prompted by new health effects research, which concluded that extended human exposure to this element can cause severe health-related illnesses, including various types of cancer, at much lower levels than previously believed (Hopenhayn-Rich *et al.*, 1996; 1998; Smith *et al.*, 1998). As with ammonia, iron in drinking water does not pose a direct health concern. However, there is an EPA recommended, non-enforceable iron secondary MCL of 0.3 mg/L, based on aesthetic issues, rather than health-based concerns. Iron in the water can cause a metallic taste, discoloration of the water, staining of faucet and fixtures, and sediment build-up. Similarly, manganese levels at this site do not pose health concerns but do present an aesthetic challenge associate with discolored water, and staining of faucets and fixtures. As a result, a secondary MCL (SMCL) for manganese of 0.05 mg/L is in place. The SMCL is based on staining and taste considerations. It is not a federally enforceable regulation, but is intended as a guideline for States.

Given the negative issues associated with high ammonia, iron and manganese concentrations in drinking water, and with the health risks associated with arsenic and nitrite, there was a clear need to identify an effective treatment approach to remove these contaminants from Gilbert's drinking water while considering constraints on the small water system. Treatment effectiveness as well as ease of operation, reduced operating costs, and reliability are important design considerations that must be evaluated when recommending a treatment approach.

1.3 Ammonia Treatment Options

The most commonly used water treatment options for addressing elevated ammonia in source waters are the formation of monochloramine and breakpoint chlorination. Breakpoint chlorination results in the removal of ammonia as nitrogen gas by a chemical reaction with chlorine; typically, in the range of 8 to 11 times the mg N/L ammonia present. For a community

with a water source such as the Gilbert, this would require a very high chlorine dose of approximately 29 mg/L to breakpoint ammonia and achieve a 1 mg/L free chlorine residual. The formation of monochloramine involves the addition of chlorine to concentrations where ammonia is not removed but rather bound to chlorine. Other approaches including ion exchange with zeolites, reverse osmosis (RO), advanced oxidation, and air stripping, can remove ammonia from water, but are relatively complex, expensive, or have limited applications, mainly when additional contaminants such as iron, manganese, and arsenic, are present.

Although often performed unintentionally, biological ammonia "removal"[1] is another treatment approach to reduce source water ammonia. The process relies on bacteria to convert ammonia to nitrate. As a result, a more biologically-stable water is produced, nitrification in the distribution system is not an issue because ammonia has already been converted to nitrate, and free chlorine residual is easily achieved. Biological conversion of ammonia (NH_3) to nitrate (NO_3^-) involves a two-step sequence of reactions mediated by two different genera of bacteria: *Nitrosomonas* and *Nitrospira*. These autotrophic bacteria derive energy for cellular functions from the oxidation of ammonia and nitrite, respectively. *Nitrosomonas* are responsible for the oxidation of ammonia, in the form of ammonium (NH_4^+), to nitrite (NO_2^-) according to the reaction:

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + H_2O + 2H^+ \quad (1)$$

Nitrospira subsequently oxidizes nitrite to nitrate, as follows:

$$NO_2^- + 0.5\ O_2 \rightarrow NO_3^- \quad (2)$$

By summing these equations, the overall nitrification reaction is obtained:

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + 2\ H^+ + H_2O$$

It should be noted that these equations are net reactions involving a complex series of enzyme-catalyzed intermediate steps. Nitrification produces free protons, H^+ which readily consume available bicarbonate ions (HCO_3^-), thereby reducing the buffering capacity of the water. In addition, nitrifying bacteria consume CO_2 to build new cells. The total consumption of alkalinity by nitrification is 7.1 mg as $CaCO_3$ per mg NH_4^+- N oxidized (US EPA, 1975). The oxygen demand of nitrification is also significant. For complete nitrification, 4.6 mg O_2 is required per mg NH_4^+-N oxidized (US EPA, 1975; US EPA 1993).

[1] The terms "removal" and "oxidation" are used interchangeably throughout this document. "Removal" is used to represent the *conversion* of ammonia to nitrate and/or nitrite by biological oxidation even though treatment does not *physically remove* ammonia-nitrogen but rather converts the form of nitrogen (i.e., total of ammonia, nitrite, and nitrate).

Other factors that affect nitrification include orthophosphate concentration, pH, and water temperature. All organisms including nitrifying bacteria require phosphorus to build cell mass, with approximately 3% of dry weight consisting of phosphorus. Microorganisms use phosphate as the source of phosphorus for the synthesis of structural and physiological biomolecules such as deoxyribonucleic acid (DNA), phospholipids (membranes), teichoic acid (cell walls), and most importantly, as inorganic phosphorus in adenosine triphosphate (ATP) synthesis. Without ATP, the cellular metabolism (i.e. nitrification) cannot proceed and the cells either become dormant or die. Some organisms are more sensitive to phosphate starvation than others, and in the case of nitrification, ammonia oxidizing bacteria are less sensitive than nitrite oxidizing bacteria (de Vet *et al.*, 2012; Scherrenberg *et al*., 2011; Scherrenberg *et al*., 2012).

Numerous laboratory studies have cited the optimum pH for complete nitrification is between 7.4 and 8.0; although in practice, the bulk water pH may deviate from this value while nitrification remains high (Shammas, 1986). Temperature can impact growth rate and metabolism by slowing or destroying necessary enzymes and proteins involved in physiological processes. Laboratory studies have demonstrated that the growth rate of nitrifying bacteria is negatively impacted by temperatures below 10°C, although adjustments to the treatment process can be made to enhance nitrification in colder climates (Andersson, *et al.*, 2001).

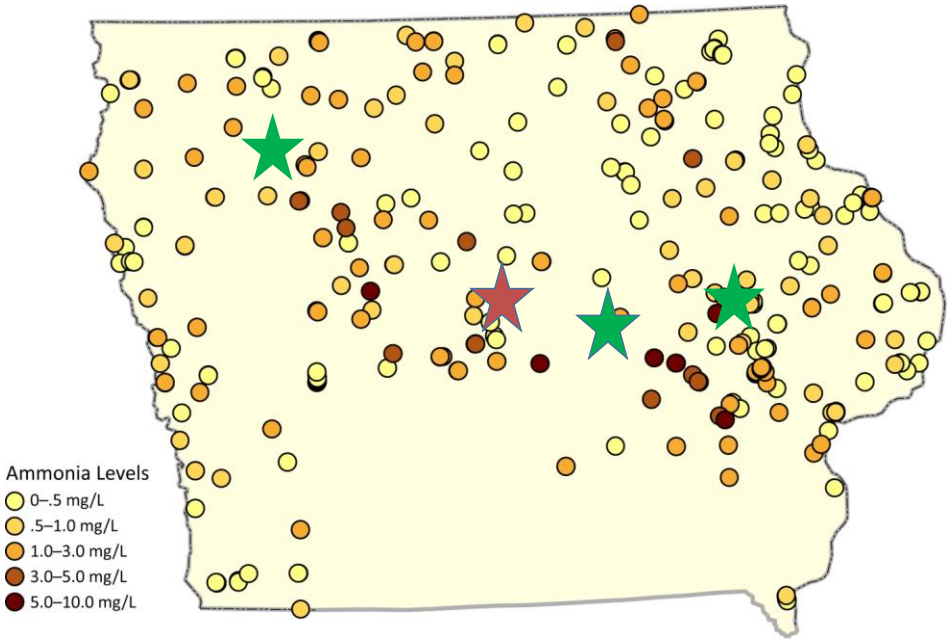

Figure 1. Map of ammonia levels in Iowa based on groundwater well analyses (1998–2012) provided by the State of Iowa (star represent locations of current and past EPA demonstration pilot studies) (Red star is location of Gilbert, Iowa).

Parameter	Raw
Arsenic	23 µg/L
Alkalinity	410 mg $CaCO_3$/L
Fe	2.94 mg/L
Mn	0.08 mg/L
P	0.32 mg/L
TOC	2.74 mg/L
S	0.12 mg/L
Cl^-	7.4 mg/L
Mg	26.30 mg/L
NH_4	2.91 mg-N/L
NO_2	0.01 mg-N/L
NO_3	0.02 mg-N/L
PO_4	0.43 mg PO_4/L
pH	7.63
Temp °C	13.3

Table 1. Source water quality in Gilbert, Iowa

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2. Biological Water Treatment Technology Pilot Study

2.1 Collaboration

The City of Gilbert, a small community in Iowa, and their Engineering firm, Fox Engineering, invited the EPA's Office of Research and Development (ORD) to conduct a pilot demonstration of an innovative biological treatment approach to address elevated source water ammonia concentrations and other co-contaminants. The City was interested in an EPA-patented biological treatment approach (Figure 2) to address elevated levels of ammonia as well as iron in the source water (Patent No. US 8, 029,674). This treatment approach has been demonstrated at the pilot-scale at several locations in Iowa and elsewhere, and in the case of Palo, Iowa, led to the construction of a full-scale implementation (US EPA, 2014).

EPA established a Cooperative Research and Development Agreement (CRADA, October 30, 2014) with AdEdge Water Technologies, LLC to develop a commercially available full-scale biological drinking water treatment system marketed by AdEdge as "NoMonia" based on the treatment approach and pilot study.

The treatment system relies on naturally occurring bacteria for the conversion of ammonia to nitrate; provided the raw ammonia levels are lower than the nitrate MCL of 10 mg

N/L, the approach can be effective and relatively simple. In addition, biological activity was expected to play a necessary role in the oxidation and removal of arsenic, iron, and manganese.

An EPA patent-pending aeration pilot skid system (U.S. Application serial 14/459,277) was designed and built by EPA staff, and installed in Gilbert on August 2016 (Figure 3) to demonstrate the ammonia treatment approach. The City's plant operator, was trained on the system operation and maintenance, as well as water sample collection and analysis.

Lastly, IDNR and EPA Region 7 were stakeholders of this pilot in Gilbert. IDNR was provided periodic project updates, and commented on data and the draft project report.

2.2 Treatment Approach

The introduction of oxygen through an aeration treatment step is critical to the successful microbiological conversion of ammonia to nitrate. Nitrification is a two-step, microbiological process that requires oxygen (aerobic) to oxidize NH_4 to NO_2, and then to NO_3. The entire process requires approximately 4.5 mg of O_2/mg of NH_4-N in the source water. Because the groundwater in the study community has low oxygen (1.3 mg O_2/L) and elevated ammonia of 2.9 mg N/L as well as reduced forms of iron (Fe^{2+}), manganese (Mn^{2+}) and arsenic (As^{3+}) (Table 1) that also exerts an oxygen demand, more than 13.5 mg O_2/L (without considering oxygen gradients in a fixed bed reactor or kinetic constraints) would be necessary to address the demand. Aeration consisting of a continuous supply of adequate concentrations of dissolved oxygen is a necessary feature of the biological ammonia treatment system; however, the traditional configuration of aeration followed by filtration (e.g., iron removal) including biologically-active filtration is not sufficient to address the oxygen demand to meet the treatment objectives of the community's water system.

The amount of oxygen that can be added to the water is controlled by the saturation limit of oxygen in water, which in most drinking waters including the study community's, is well below the total oxygen requirements of treatment. The EPA's experience with microbiological systems that do not provide sufficient oxygen to a nitrifying system has shown that the result is incomplete nitrification or the production of elevated nitrite levels in the finished water. Given the drinking water standard for nitrite is only 1 mg N/L (1.0 in Iowa), concerns for potential exceedances exist where source water ammonia levels are greater than 1 mg N/L. Therefore, an innovative approach to introducing oxygen to the treatment system was necessary to meet the treatment objectives. Aerating with pure oxygen could provide super saturated oxygen conditions and sufficient oxygen, however there are safety issues associated with flammable gases and filter binding associated with gas bubbles can also be an issue.

2.3 Pilot Technology Description

The ammonia biological removal treatment pilot system is based on the EPA patented design (US 8,029,674 B2 awarded on 10/2/2011) seen in Figure 2. The Gilbert pilot study varied slightly using one pair of 3-inch (7.62 cm) diameter columns in series built from clear PVC and other common plumbing materials (Figure 3). Each pair consisted of one column or "Aerated Contactor" filled with 55 inches (139.7 cm) of medium gravel having a nominal 1/2" diameter (Figure 4) in series with a second column or "filter" filled with anthracite (10 inches [25.4 cm] deep) over ADGS^{+} silica sand-based media with a manganese dioxide coating (30 inches [76.2 cm] deep). The contactor was aerated from the bottom, such that air bubbles flow upward co-current to the water flow (up-flow) using a diffuser (U.S. Patent Application Serial 14/459,277) connected to a gas pump at a rate of 2.5 L/min (0.66 gpm).

In this configuration, water in the aerated contactor was always saturated with respect to dissolved oxygen throughout the gravel media bed despite the demand from the nitrification process, and iron, manganese and arsenic oxidation. The gravel in the contactor served to support growth of nitrifying (and other important oxidizing) bacteria where nitrification and other biological oxidation processes occur. Gravel allowed bacteria attachment and growth yet eliminated the potential for "clogging" of the media, reduced backwashing frequency, and allowed air bubbles to move through the contactor. Oxidation of ferrous iron in the source water also occurs in the contactor, but minimal iron removal is expected to occur. Contactor loading rates were adjusted during the pilot study (Table 2). The filter was intended to remove arsenic-containing iron particles, manganese and bacteria, and can also provide biological oxidation of excess ammonia and/or nitrite that exit the contactor because of incomplete nitrification. The filter serves as a polishing step and back-up against disruption in the operation of the contactor. Non-chlorinated effluent water from the filter is routed to a clear well, that when full, can be used to backwash the contactor and filter, or overflow to the sanitary sewer.

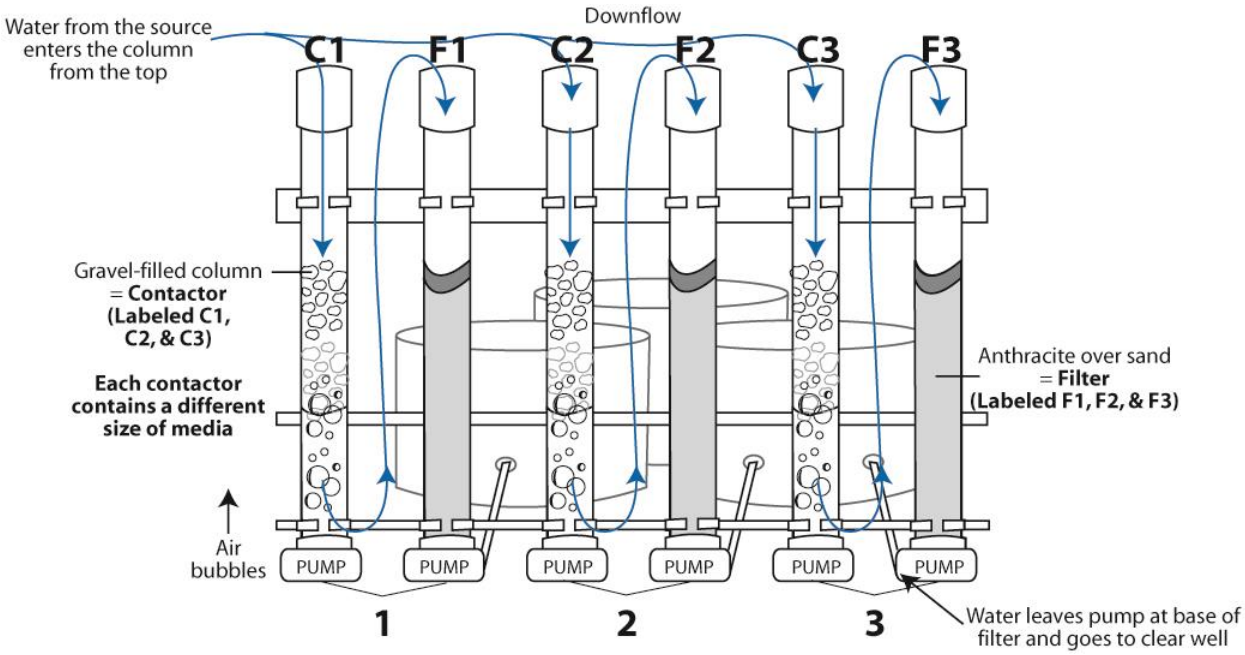

Figure 2. Schematic of a “down-flow” (or counter-current to air) three pilot biological ammonia, iron, manganese and arsenic removal treatment technology system ("NoMonia"). In this study source water was pumped into the bottom of contactor “up-flow” (or co-current to air).

Figure 3. Pilot biological water treatment system used to evaluate ammonia, arsenic, iron and manganese removal in Gilbert, Iowa.

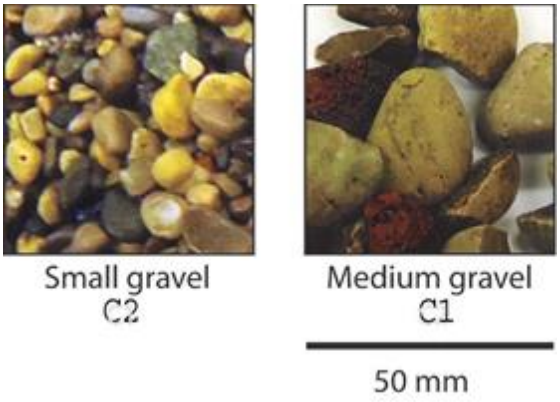

Figure 4. Column granular media for pilot biological water treatment system used to evaluate ammonia, arsenic, iron and manganese removal in Gilbert, Iowa.

Table 2. Timeline of operational changes for contactor 1 and 2, and filter 1.

Date	Elapsed Days	Description
8/17/2016	0	Pilot Start up
8/17/2016	0	Contactor 1 loading rate average 2.7 gpm/ft^2
8/17/2016	0	Filter 1 loading rate 2.15 gpm/ ft^2
8/19/2016	2	Needle valve removed from raw feed
8/31/2016	14	Filter 1 ran dry
9/2/2016	16	Possible mud ball formation top of filter
9/9/2016	23	Air flow increased in contactor (low DO)
9/13/2016	22	Start acclimation
10/13/16	54	Changed loading rate of filter to 1.8 gpm/ ft^2, contactor to 2.3gpm/ ft^2
11/28/16	100	Backwash of contactor
12/12/2016	114	Air flow increased in contactor (low DO)
1/10/2016	143	Filter 1 ran dry
01/20/17	153	Backwash of contactor
2/14/2017	178	Contactor flow rate was 370 ml/min (2.0 gpm/ ft^2)
2/21/2017	185	Contactor was at 430 ml/min (2.3 gpm/ ft^2)
2/28/2017	192	Filter 1 ran dry
3/1/2017	193	Filter 1 ran dry
4/10/2017	230	Changed contactor flow rate to 375 ml/min (~2.0 gpm/ ft^2)
4/17/2017	243	Contactor 2 startup 450 ml/min (~2.4 gpm/ft^2)
5/06/2017	262	Challenge test #1: Contactor flow doubled 820 ml/min (4.4 gpm/ ft^2) ortho-PO_4 feed adjusted accordingly. Filter 1 shut off for weekend
5/9/2017	265	Filter 1 back online loading rate of 1.8 gpm/ft2
5/11/2017	267	Filter 1 ran dry
5/19/2017	275	Filter 1 ran dry
5/30/2017	286	Contactor flow back to 400 ml/min (~2.15 gpm/ ft^2)
6/01/2017	288	Backwash Contactor 1
6/14/2017	301	Challenge test #2: Contactor 1 and Filter 1 shutdown (air was shut off)
6/23/2017	310	Contactor 1 and Filter 1 back on-line with air
7/12/2017	329	Backwash Contactor 1
7/26/2017	343	Inter stage pH adjustment started
8/8/2017	356	Backwash Contactor 1 weekly samples collected 60 minutes after backwash (C1/F1)

3. Operations, Materials, and Methods

3.1 Pilot System Operation

The pilot system (Figure 3) contactor (contactor 1, C1) was operated approximately 7 hours a day, 7 days per week for nearly a year beginning on August 17, 2016. Raw water from the Gilbert's existing well was not chlorinated or treated in any way prior to supplying the pilot system. Treated water and excess filter backwash water was routed to the on-site sanitary sewer.

Field operating and water quality measurements were collected by the Gilbert's water plant operator and included flowrates, temperature, dissolved oxygen, and pH. Dissolved oxygen, pH, and temperature were measured using an HQ40d meter with an LD101 dissolved oxygen probe and PHC281 pH probe (Hach Company, Loveland, CO). Gilbert's water plant operator also conducted field tests to determine the concentrations of iron, manganese, arsenic, ammonia, nitrate, and nitrite in addition to water samples that were collected and sent to the EPA on a weekly basis. The filter was backwashed using filter effluent water approximately every 24 hours of operation although longer frequency was evaluated successfully (up to 110 hours). Backwashing was achieved by expanding the bed by 50% for 15 minutes. The contactor was first backwashed at 100 days, then again at 153 days using raw water. In following months of the pilot study, the contactor was placed on a monthly backwash cycle. Contactor gravel did not expand during backwashing. A total volume of 12.5 gallons (47.3 L) was used to backwash the contactor for approximately 5 minutes at rate of 2.5 gallon/min (gpm) (9.45 L/min).

Many parameters were varied to optimize nitrification; these included changes to increase dissolved oxygen levels and reduce loading rate. A second contactor (contactor 2, C2) was brought online April 17, 2017 to evaluate the impact of smaller gravel or increased contactor surface area on ammonia levels. Changes to pilot system operation, water quality, and other notable conditions are summarized in Table 2. Filter loading rate changes were made by adjusting the flowrate through the pilot columns by valve adjustment. For example, contactors began the study with a loading rate of 2.4 gpm/ft^2 (5.87 m/hr) and ended the study at 2.2 gpm/ft^2 (5.38 m/hr). Filters averaged 1.8 gpm/ ft^2 (3.67 m/hr) over the duration of the study.

Since nitrifying bacteria require phosphorus to build cell mass, a phosphate chemical feed with a target dose of 0.3 mg orthophosphate PO_4/L based on previous pilot studies was installed in-line from initial startup of study. Microorganisms use phosphate as the source of phosphorus for the synthesis of structural and physiological biomolecules such as

deoxyribonucleic acid (DNA), phospholipids (membranes), teichoic acid (cell walls), and most importantly, as inorganic phosphorus in adenosine triphosphate (ATP) synthesis. Without ATP, the cellular metabolism (i.e. nitrification) cannot proceed and the cells either become dormant or die. Some organisms are more sensitive to phosphate starvation than others, and in the case of nitrification, ammonia oxidizing bacteria are less sensitive than nitrite oxidizing bacteria (de Vet *et al.*, 2012; Scherrenberg *et al*., 2011; Scherrenberg *et al*., 2012). Orthophosphate was provided by the EPA in the form of technical grade $Na_3PO_4 \cdot 12H_2O$ (Fisher Scientific) dissolved in deionized water. This solution was added to 20 L of deionized water in a carboy and injected into contactor 1 (and later contactor 2) at 2 mL/min via a peristaltic pump.

3.2 Water Quality Analysis

Gilbert's water plant operator collected weekly water quality samples, while making routine measurements and shipped them on ice overnight to the EPA Office of Research and Development (ORD) in Cincinnati for analysis. Water samples were collected from the raw water and effluent of contactor and filter. The following water samples were collected on a weekly basis:

- 250 mL for inorganic analysis
- 60 mL for metals analysis
- 40 mL for organic carbon analysis
- 250 mL for bacteria analysis (heterotrophic plate counts [HPC's])
- 60 mL for arsenic speciation (i.e., As^{3+} and As^{5+}) w/EDTA

Upon arriving at EPA, the samples along with the chain of custody, were removed from the cooler, preserved accordingly, and submitted for analysis. Ammonia, nitrite, and nitrate analysis were typically performed on the same day the cooler arrived (approximately 24 hours after sampling). All water analyses were performed according to EPA or Standard Methods (Table 3).

Table 3. Water quality analyses methods

Analysis	Method	Method #	Reference
Total Alkalinity	Potentiometric Titration	2320 B.4.6	Std. Methods[1]
Ammonia (as N)	Automated Colorimetric	350.1	EPA Methods[2]
Chloride	Potentiometric Titration	4500-Cl D	Std. Methods[1]
Nitrate & Nitrite (as N)	Automated Colorimetric	353.2	EPA Methods[2]
Orthophosphate	Automated Colorimetric	365.1	EPA Methods[2]
As, Pb, U, Se, Bi	ICP-MS	200.8	EPA Methods[2]
Al, As, Ba, Be, Bi, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Sb, Sulfate, Si, Silica, Sn, Zn	ICP-AES	200.7	EPA Methods[2]
TOC	Combustion	5310 C	Std. Methods[1]
Temperature	Thermocouple	17.1	EPA Methods[2]
HPC	Culture	9215 C	Std. Methods[1]

[1] Standard Methods for the Examination of Water and Wastewater," 21st Edition (2005).

[2] USEPA, "Methods for the Determination of Metals in Environmental Samples," EPA-600/14-91-010 (1994).

4. Results of the Pilot Study

4.1 Important Dates

There are many operating changes and other events that occurred over the course of the pilot study that are worth noting because they had a direct impact on the results and proceeding discussions. Events including changes in contactor dissolved oxygen, flowrates (loading rates), backwash events, have been documented (listed in Table 2) and will be referred to when appropriate.

4.2 General Water Chemistry

Extensive water quality analysis of the site's source water, as well as the pilot contactor and filter effluent over the entire pilot study, is summarized in Table 4. The source water was a very hard, high alkalinity groundwater with calcium and magnesium levels averaging 69 and 26 mg/L, respectively, total hardness of 280 mg $CaCO_3$/L, and a total alkalinity of 410 mg $CaCO_3$/L. The pH averaged 7.68, and sulfate, chloride, and silica averaged 94 mg SO_4/L, 5 mg/L and 7.1 mg SiO_2 /L, respectively. Iron and manganese levels averaged 2.9 mg/L and 0.079 mg/L, respectively, and ammonia averaged 2.9 mg N/L. Orthophosphate was on average 0.395 mg PO_4/L, and total phosphorus was 0.316 mg P/L. Nitrite (average 0.009 mg N/L) and nitrate (0.021 mg N/L) were at or near the respective method detection limits and total organic carbon (TOC) averaged 2.74 mg C/L.

4.3 Removal of Ammonia in Source Water

Contactor 1. Ammonia levels in contactor 1 decreased over the first 20 days of operation from nearly 3 mg N/L to approximately 2.2 mg N/L where levels remained for the following 50 days (Figure 5). During this period, nitrite peaked early to 0.4 mg N/L on day 20 then dropped back to near non-detectable levels as the contactor acclimated with nitrite oxidizing bacteria. Nitrite peaked for a short period of time due to the lag in acclimation of nitrite oxidizing bacteria (i.e., no nitrite was available prior to encourage activity). Nitrate levels steadily increased during this same time eventually to a concentration that nearly equaled the amount of oxidized ammonia. Between 65 and 70 days, ammonia levels unexpectedly increased back to 2.7 mg N/L while nitrate levels decreased by a similar amount. Based on past work, biological ammonia oxidizing contactors operated under similar conditions and water chemistries totally acclimated (achieved complete oxidation of ammonia) within 30 days when operated 24 hours per day (Lytle. *et al.*, 2007). When operated for a fraction of a day, the acclimation time can be approximated by multiplying 30 days by the reciprocal of the fraction of operation. In the Gilbert pilot, the pilot operated 8 hours (1/3) of 24-hour day so the

contactor was anticipated to be totally acclimated by 90 days. Given the observed slow rate of acclimation and reversal in progress, other parameters necessary for nitrification were closely examined. Oxygen is a critically important parameter identified in past work so dissolved oxygen (DO) levels during the first 70 days of operations were closely examined.

Analyte	Detection Limit (mg/L)	Raw	Contactor 1	Contactor 2	Filter 1
As	0.4 μg/L	22.8 ± 2.0 (50)	14.0 ± 3.0 (60)	15.0 ± 3.0 (48)	8.0 ± 3.0 (67)
Ca	0.01	69.1 ± 1.5 (50)	68.6 ± 1.6 (60)	68.7 ± 1.5 (48)	68.2 ± 1.6 (67)
Cl	5	7.4 ± 6.1 (41)	7.8 ± 1.9 (46)	na	8.6 ± 4.7 (46)
Fe	0.001	2.9 ± 0.3 (50)	1.2 ± 0.6 (60)	1.1 ± 0.3 (48)	0.02 ± 0.1 (67)
K	0.3	4.4 ± 0.1 (50)	4.4 ± 0.1 (51)	4.4 ± 0.2 (48)	4.4 ± 0.2 (67)
Mg	0.005	26.3 ± 0.6 (50)	26.3 ± 0.7 (60)	26.2 ± 0.5 (48)	26.2 ± 0.7 (67)
Mn	0.001	0.08 ± 0.003 (50)	0.05 ± 0.02 (60)	0.06 ± 0.02 (48)	0.01 ± 0.01 (67)
Na	0.03	39.4 ± 1.1 (50)	39.3 ± 1.1 (60)	39.3 ± 0.7 (48)	39.3 ± 1.2 (67)
NH_3	0.03 (mg-N/L)	2.9 ± 0.1 (50)	1.6 ± 0.7 (47)	1.6 ± 1.0 (48)	0.4 ± 0.7 (47)
NO_2	0.01 (mg-N/L)	0.01 ± 0.0 (46)	0.2 ± 0.1 (47)	0.2 ± 0.1 (48)	0.23 ± 0.4 (47)
NO_3	0.02 (mg-N/L)	0.04 ± 0.03 (43)	1.3 ± 0.7 (46)	1.1 ± 0.9 (48)	2.3 ± 0.9 (46)
o-PO_4	0.025 (mg PO_4/L)	0.4 ± 0.2 (46)	0.4 ± 0.7 (46)	0.4 ± 0.08 (42)	0.2 ± 0.1 (46)
P	0.005 (mg P/L)	0.3 ± 0.03 (50)	0.2 ± 0.08 (60)	0.2 ± 0.05 (48)	0.1 ± 0.02 (67)
S	0.003	0.12 ± 0.1 (50)	0.09 ± 0.01 (60)	0.1 ± 0.01 (48)	0.09 ± 0.02 (67)
Sr	0.001	0.9 ± 0.03 (50)	0.9 ± 0.02 (60)	0.9 ± 0.01 (48)	0.9 ± 0.03 (67)
Total Alkalinity	1 (mg-$CaCO_3$/L)	410.7 ± 2.3 (49)	398.7 ± 7.3 (50)	397.5 ± 7.4 (48)	389.8 ± 8.7 (50)
TOC	0.1 (mg-C/L)	2.74 ± 0.2 (42)	2.80 ± 0.12 (41)	2.84 ± 0.14 (48)	2.78 ± 0.11 (39)
pH	0.1	7.68 ± 0.17 (50)	8.07 ± 0.29 (55)	8.16 ± 0.13 (14)	8.03 ± 0.28 (55)
DO	0.01 (mg-O_2/L)	1.1 ± 0.4 (50)	8.94 ± 2.21 (55)	9.38 ± 0.4 (14)	8.83 ± 1.29 (55)
Temperature	0.1˚C	14.2 ± 2.3 (50)	15.9 ± 2.2 (55)	16.6 ± 1.7 (14)	16.3 ± 2.5 (55)

Table 4: Water quality summary [average ± standard deviation (n)].

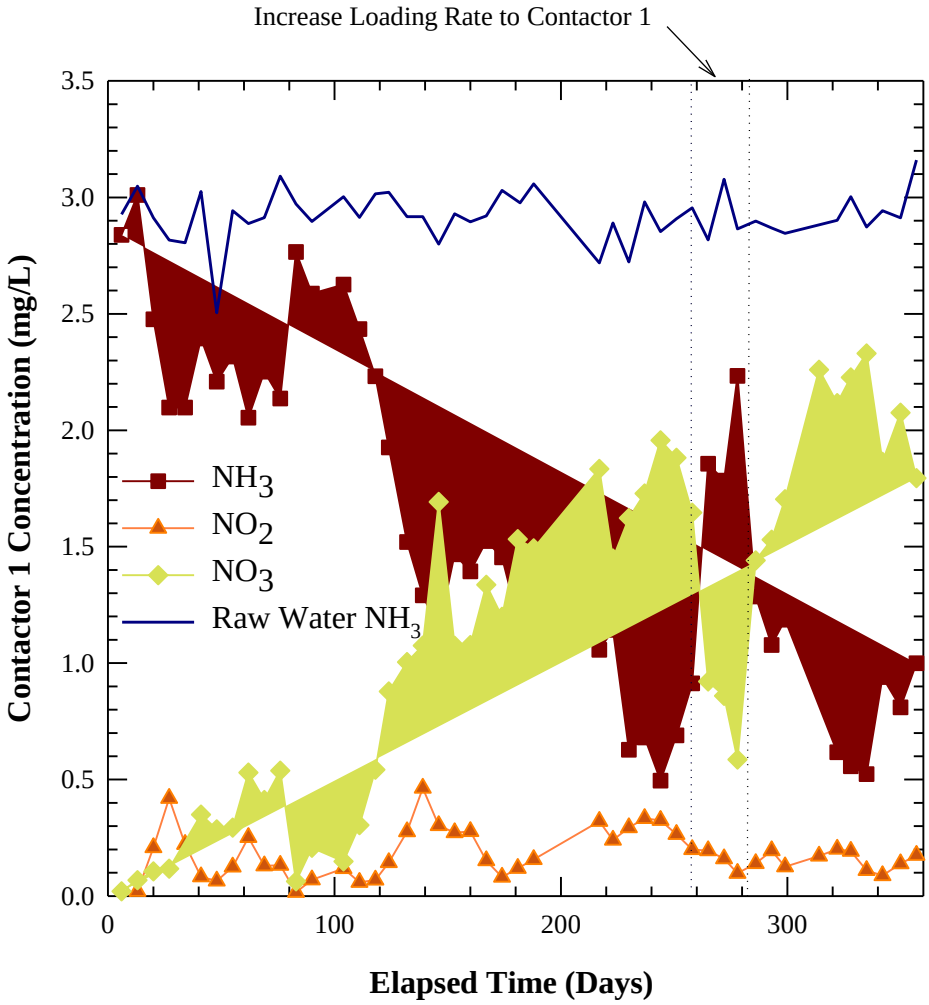

Figure 5. Nitrogen content of treated water from contactor 1.

Oxygen is a critical parameter in the nitrification process, where 4.6 mg O_2/L is necessary to microbiologically oxidize 1 mg N/L ammonia to nitrate. Further, there is also a connection between oxygen levels and kinetic limitations associated with molecular diffusion. Oxygen levels in the raw water were generally less than 2 mg/L over the course of the entire study (Figure 6). The contactor oxygen level was increased to 8.4 mg/L at the contactor start-up, after which it steadily dropped over the initial 20 days of operation that corresponded to the initiation of nitrification. Oxygen levels remained relatively steady between 20 and 70 days at approximately 7.2 mg/L (Figure 6). During this time ammonia levels leaving the contactor also remained steady. Problems with the air-feed system between 70 and 80 days resulted in a large drop in oxygen to 3.6 mg/L leaving the contactor. The drop directly corresponded to the

sudden observed increase in ammonia. Adjustments to the oxygen feed rate were made at 114 days resulting in a dissolved oxygen increase to 9.6 mg/L where the level roughly stayed for the remainder of the study. The increase in dissolved oxygen resulted in an immediate decrease in ammonia levels (and corresponding nitrate increase) dropping to nearly 1.2 mg N/L within 14 days after the oxygen adjustment. Nitrate produced in the contactor before DO increase was an average of 0.249 mg N/L and was increased to an average of 1.32 mg N/L after the DO increase. Although significant and rapid improvement was observed (i.e., more ammonia was oxidized), bacterial acclimation progress was still not totally complete. With constant and elevated dissolved oxygen levels, acclimation continued and by 220 days, ammonia levels were below 1 mg N/L and reached an eventual low of 0.5 to 0.6 mg N/L. Nitrite levels remained consistently below 0.4 mg N/L and nitrate made up the concentration difference between the raw water ammonia and contactor effluent ammonia and nitrite levels. The contactor took approximately 105 days to fully stabilize in regard to reaching maximum ammonia removal after dissolved oxygen levels were controlled and optimally maintained. Under these conditions contactor 1 reached steady levels of about 60% reduction in ammonia concentration. It is worth noting that Nitrite spiking above the 1.0 mg/L MCL was not observed at any point of time after acclimation.

Contactor loading rate is also a very important parameter with respect to contactor and filter performance. To somewhat complicate the interpretation, loading rate (flowrate through contactor) was adjusted particularly over the first 80 days of operation from as high as 3 gpm/ft^2 to 1.5 gpm/ft^2 (Figure 7) in effort to improve the performance of contactor 1 prior to becoming aware of the reduction in DO. Since oxygen levels were being adjusted to accelerate acclimation at the same time, it was difficult to clearly quantify the relative impact of loading rate on performance, although clearly, increasing DO had the most dramatic impact on ammonia removal. After 80 days, the loading rate settled in at approximately 2.2 gpm/ft^2 until approximately 220 days to 250 days where it decreased to nearly 2.0 gpm/ft^2 (4.8 m/hr) (Figure 7). The loading rate decrease resulted increase ammonia oxidation on average of 0.5 mg N/L coming out of contactor between 230 days and end of pilot. During this time, ammonia levels in the contactor effluent did appear correspondingly decrease as bacteria were given more time in the contactor to accomplish ammonia oxidation.

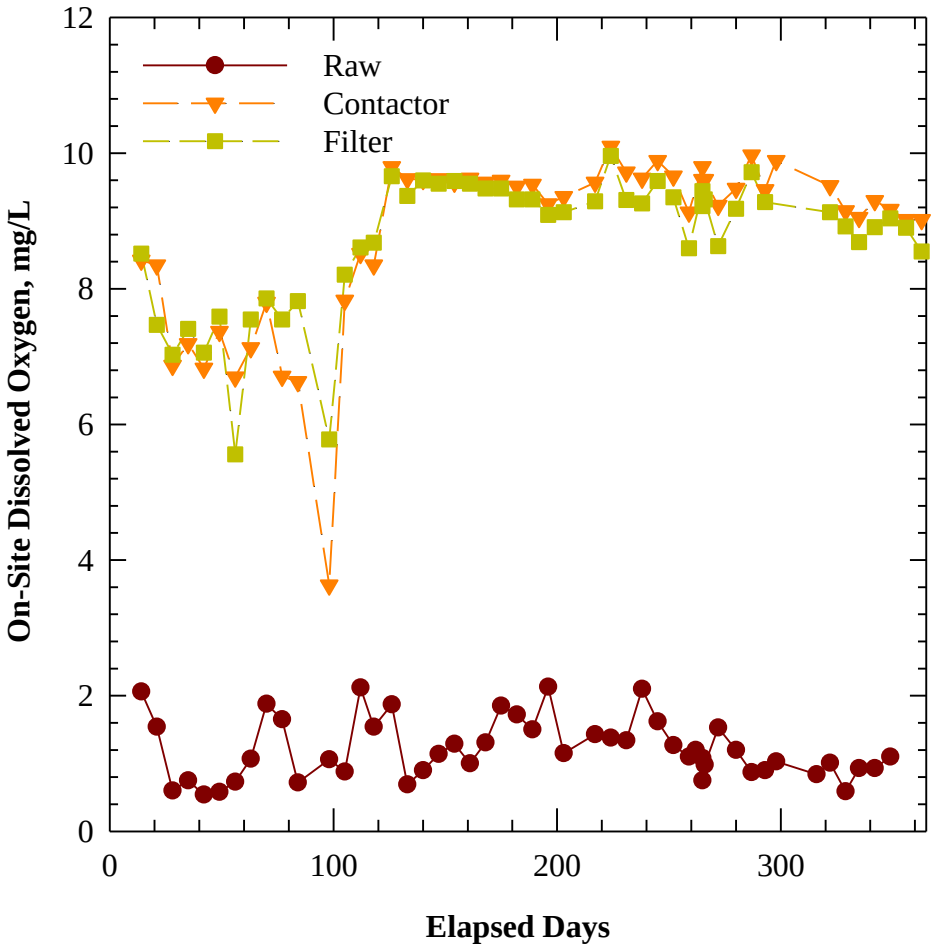

Figure 6. Dissolved oxygen levels through pilot system.

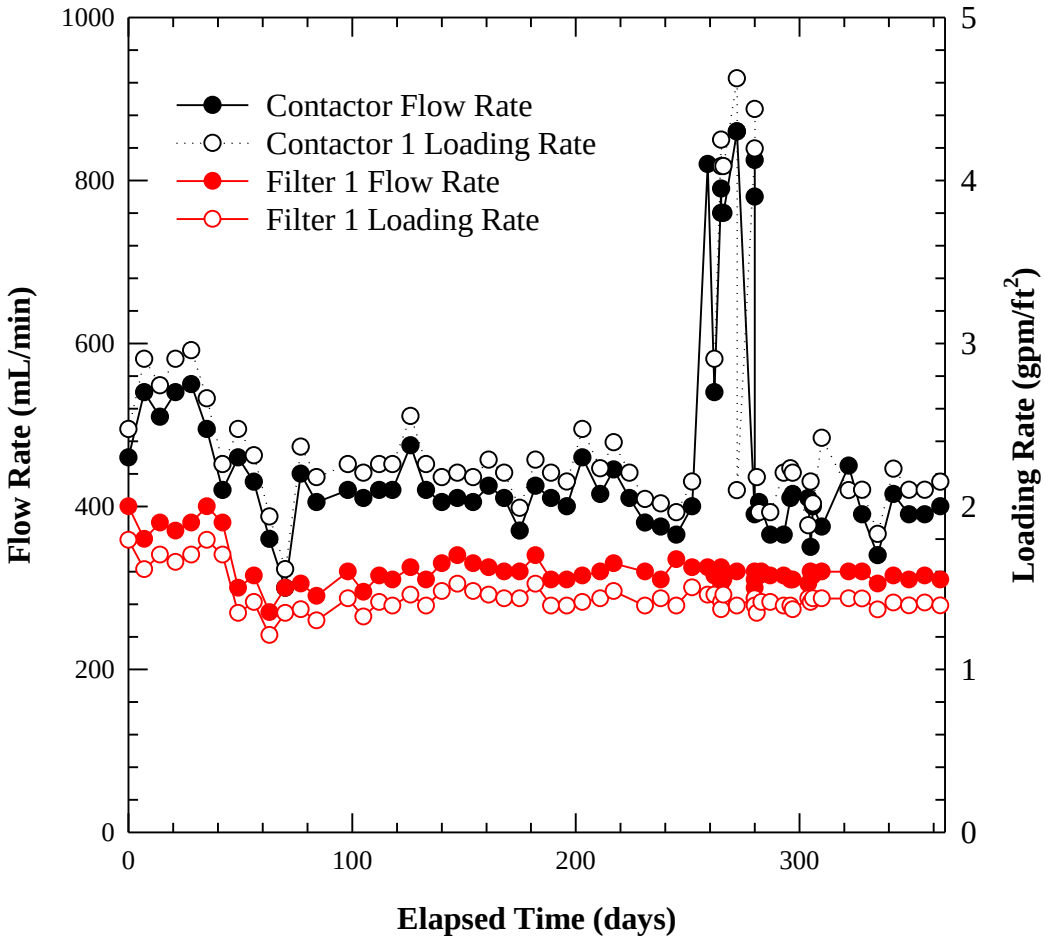

Figure 7. Contactor and filter flow and hydraulic loading rates.

Previous work (Lytle et al., 2007) indicated that the complete oxidation of ammonia to nitrate, or complete acclimation of bacteria after start-up of a new biologically active nitrifying filter could take as little as 30 days for a system operated 24 hours per day, seven days a week for a system with similar ammonia levels as Gilbert. It was also reported in subsequent work that the acclimation time (time required to reach optimized ammonia oxidation) was proportional to the daily hours of operation (i.e., a system operated 12 hours per day would take twice as long to fully acclimate or 60 days). Gilbert's pilot operated 7 hours per day suggesting a period of more than 90-days to reach steady state. The Gilbert pilot was in operation for approximately 105 days between the time when oxygen levels were corrected and ammonia levels approached a stable low value which is in agreement with past observations.

Filter. The primary intent of the filter that followed the contactors was to remove iron particles that contained arsenic and manganese that formed in the contactor. The filter was also biologically-active, and served as a secondary back-up barrier by oxidizing any excess ammonia and nitrite that may have passed through the contactor. Ammonia, nitrite, and nitrate levels entering Filter 1 were those exiting Contactor 1 (Figure 5). Ammonia oxidation to nitrite began shortly after the pilot was initiated and rapidly increased to a peak of 2.3 mg N/L by 20 days and dropped off by 40 days (Figure 8). Such a spike is typical as there is a lag in the growth of nitrite oxidizing bacteria until significant nitrite levels are present to trigger their activity. The peak must be watched closely as it can briefly increase above the nitrite MCL of 1 mg N/L. Fortunately the peak is short-lived and nitrite can be oxidized with chlorine if needed. Considering that DO concentrations were not optimized at the beginning of the pilot (only ~ 7.5 mg/L), this peak would be expected to be even shorter under adequate DO concentrations. Between 40 and 80 days (the time when oxygen levels were relatively low), nitrite varied but never exceeded 0.6 mg N/L, illustrating that oxygen levels leaving the contactor impact the filter as well. After 114 days, nitrite levels were very low and never were greater than 0.3 mg N/L (Figure 8). Nitrate corresponded to changes in ammonia and nitrite to complete mass balance. After 114 days, nitrate accounted for 96% of the total nitrogen leaving the filters. The filter loading rate at the beginning of the study up to 42 days was 2.1 gpm/ft^2 (5.0 m/hr), and 1.8 gpm/ft^2 (4.1 m/hr) for the remainder of the study (Figure 7). It is worth noting that the filter functioned successfully as a polishing stage by completing the removal of ammonia that was not removed in the contactor.

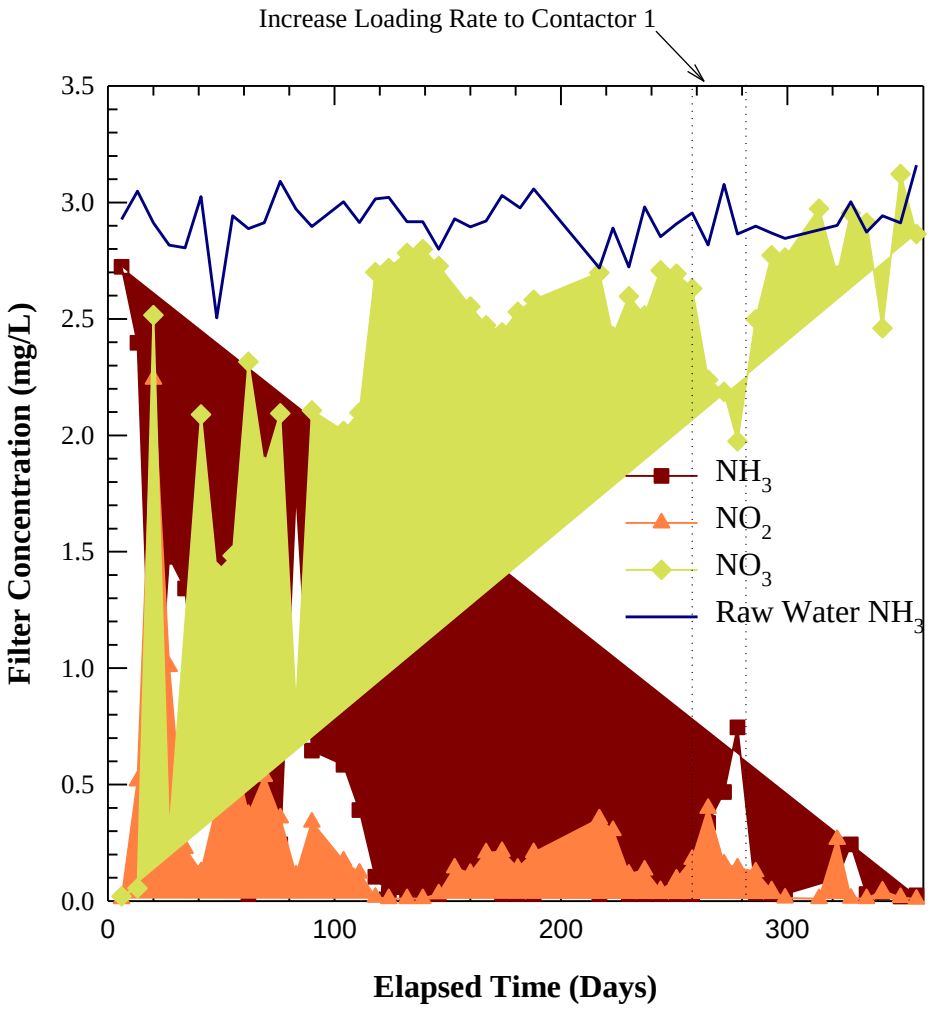

Figure 8: Nitrogen content of filter 1

Contactor 2. A second contactor installed on 4/17/2017 was constructed to the same design (diameter bed depth, etc.,) and received the same raw water as Contactor 1. However, it had two sample ports located within the gravel media bed, and was loaded with smaller nominal ¼ inch diameter gravel with a 55" gravel bed depth (including support layers consisting of 4" of large-sized gravel and 4" of medium-sized gravel). The water sample taps were positioned on the side of contactor 2 protruding 1" into the media bed to facilitate a true media bed sample and to provide diagnostic performance are various depths if desired. The lowest contactor tap (25") was located at an elevation equivalent to the depth where the surface area of the ¼" gravel was equal to the surface area of 55" of ½" gravel (designated tap C1) in the Contactor 1. The second tap was located (37.5") at half the depth between C1 and the media surface. A contactor effluent sample (C3) was also collected.

Ammonia levels decreased relatively constantly through contactor 2 (C3 location) from 3 mg N/L to non-detectable levels by 110 days (Figure 9). During this time, nitrite levels remained low and never exceeded 0.45 mg N/L. Nitrification at location C3 reflected biological activity through the entire contactor. The time necessary for complete acclimation was on target to the estimated 90 days based on the hours of daily operation.

As time went on, the contactor became fully acclimated with bacteria as reflected by the progression of nitrification through Contactor 2. Nitrification progression through contactor locations 2 and 1 lagged shortly behind contactor effluent (C3). Interestingly, more than 90% of the ammonia was oxidized at location C1 (first 25 inches of gravel) by 110 days. The results clearly illustrate the benefits of added surface area for smaller gravel versus medium gravel. Although acclimation rate was not impacted, treated ammonia levels were improved. Contactor 2 performance rivaled Fe, Mn removal with no backwashing required as of 110 days.

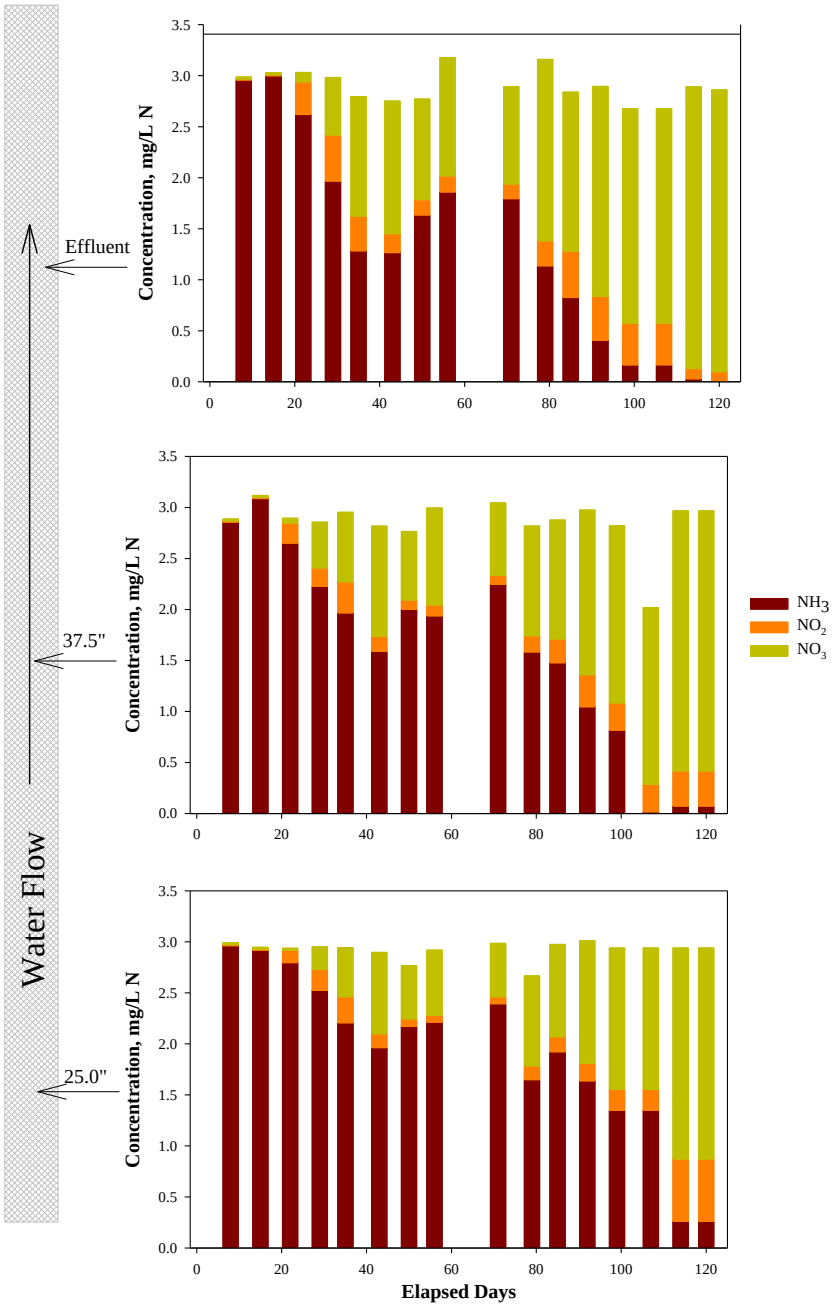

Figure 9: Nitrogen content of treated water from contactor 2 as a function of depth into contactor.

4.4 Removal of Iron from Source Water

The contactor was designed to be a main point where nitrification occurred, and iron, arsenic and manganese could be oxidized. The contactor was not intended to remove particles, such as iron particles, from the source water. The oxidation state of iron in the source water

was not determined, but it is reasonable to assume that the reduced Fe (II) form was prevalent based on water chemistry, low dissolved oxygen, and local geology (Figure 10). The elevated oxygen concentration and pH in the contactor likely resulted in rapid oxidation of Fe(II) to Fe(III) particles before the water entered the contactor gravel. Although Fe(II) oxidation kinetics are rapid under the pilot conditions, it is possible that some biological iron oxidation took place in the contactor. Iron particles that exit the contactor should be readily removed by the polishing filter which are commonly designed for such purposes.

Iron in the source water averaged 2.91 mg/L (±0.20 standard deviation) (Table 4) and was relatively consistent across the entire evaluation (Figure 10). Interestingly, the contactor removed considerable levels of iron (approximately 59%) with the effluent iron averaging 1.2 mg/L (±0.6 standard deviation) (Table 4). The contactor effluent iron levels were variable but stayed within a wide range of approximately 0.5 mg/L to 2 mg/L (Figure 10). Although iron was trapped in the gravel and likely became incorporated into the biofilm structure, no degradation in contactor performance, flow restriction, or any obvious negative impact was observed. Nonetheless, the contactor was backwashed routinely more frequently the past pilots to removed accumulated iron. Specifically, the contactor was backwashed monthly at a rate of 2.5 gpm for 5 minutes.

The filter iron effluent averaged 0.02 mg/L (±0.1 standard deviation) (Table 4). Regardless of the iron content in the contactor effluent, iron levels in filter effluent waters were at or below the detection limit (Figure 10). Outstanding and consistent removal of iron was observed through the system from the very start-up.

Iron removal through the filters was not impacted by filter loading rates (Figures 7 and 10). Filters were operated between 1.6 gpm/ft^2 (3.8 m/hr) and 2.1 gpm/ft^2 (5.1 m/hr). Filter flowrates had to be lower than contactor flowrate only due to limitations in pilot design and this observation will be taken into consideration when the design of the full-scale system is finalized. At the completion of the study, Filter 1 was operated at a loading rate of approximately 1.8 gpm/ft^2 (4.2m/hr).

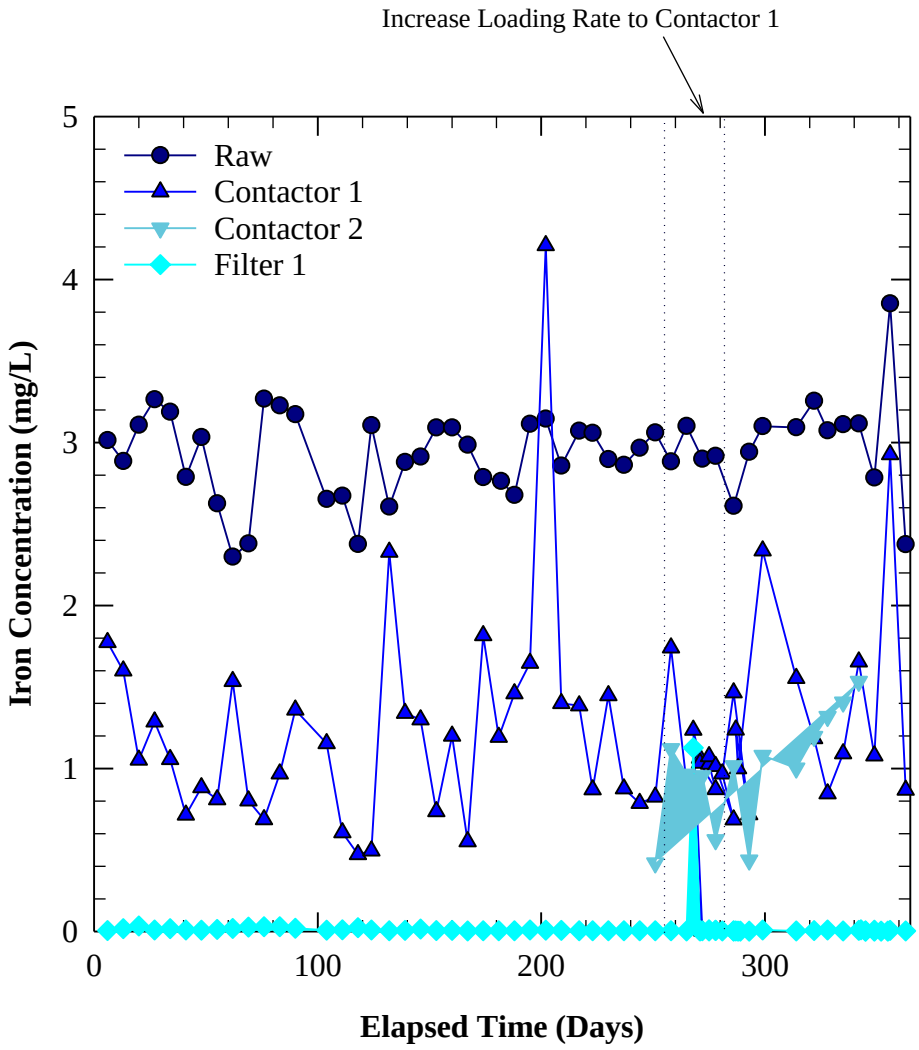

Figure 10. Iron in raw water and treated water through contactor 1, contactor 2 and filter 1

4.5 Removal of Manganese from Source Water

The oxidation state of manganese in the source water was not determined, but it is reasonable to assume that the reduced Mn(II) form was prevalent based on water chemistry, low dissolved oxygen, and local geology (Figure 11). Manganese oxidation to Mn(IV) and solid MnO_2 is not feasible without the addition of permanganate, chlorine or other strong oxidation or through biological oxidation processes. Unlike iron, elevated oxygen concentration alone will not oxidize soluble Mn(II).

Manganese in the source water averaged 0.080 mg/L (±0.003 standard deviation) (Table 4) and was relatively consistent across the entire study period (Figure 11). Interestingly, the contactor removed considerable levels of manganese (approximately 36% on average) with the effluent manganese averaging 0.05 mg/L (±0.01 standard deviation) (Table 4). The contactor effluent manganese levels were very variable, however, and corresponded closely with

dissolved oxygen concentration (Figure 11). Manganese levels dropped steadily to 0.06 mg/L over the first 80 days while a relatively stable dissolved oxygen level was maintained (Figure 6). Although manganese is assumed to be trapped in the gravel and likely became incorporated into the biofilm structure, no degradation in contactor performance, flow restriction, or any obvious negative impact was observed. Nonetheless, the contactor was backwashed routinely more frequently than past pilots to removed accumulated manganese (the contactor was backwashed monthly at a rate of 2.5 gpm for 5 minutes). The sudden drop in dissolved oxygen experienced at 80 days resulted in an immediate increase in manganese (Figure 11).

The filter manganese effluent concentration averaged 0.01 mg/L (±0.01 standard deviation) (Table 4). The filter reduced manganese levels beyond the contactor throughout the study except for the time when oxygen control was lost (day 80). Reestablishment of oxygen levels resulted in an improvement of manganese levels. After oxygen levels were increased (115 days), manganese levels decreased to near the detection limit for the remainder of the evaluation. Outstanding and consistent removal of manganese was observed but oxygen control is critical.

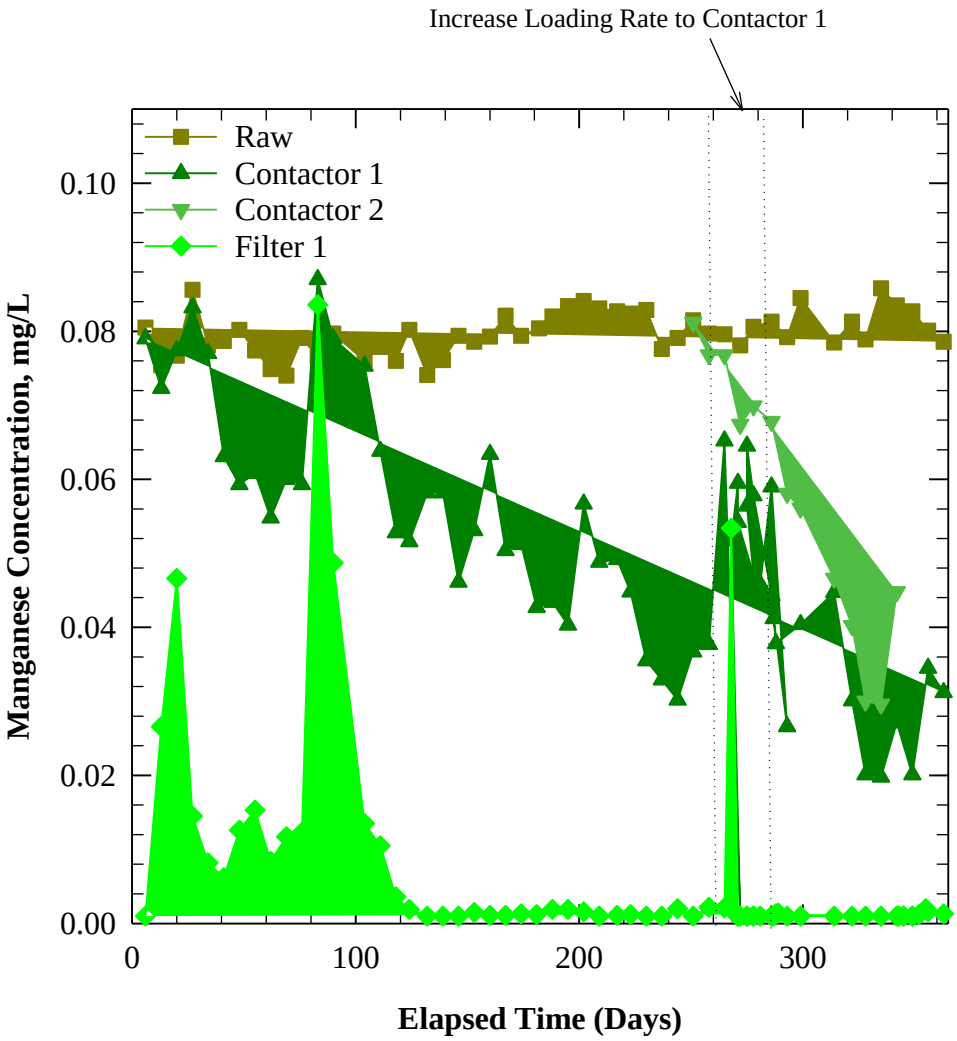

Figure 11. Manganese in raw water and treated water through contactor 1, contactor 2 and filter 1.

4.6 Removal of Arsenic from Source Water

Studies have demonstrated the effectiveness of removing arsenic from aqueous systems with natural iron. However, most of those studies required a strong oxidant such as chlorine, potassium permanganate or iron-based, chemical coagulation treatment (adsorptive media) to remove arsenic. In addition, those studies have shown that the sorption of arsenic is affected by many factors such as pH, water quality, amount and form of iron. In this pilot study, air pumped into the contactor supporting bacterial growth was the source of arsenic oxidation, although some bacterial oxidation cannot be ruled out.

Typically, the oxidation state of inorganic arsenic in groundwater is in the form of arsenite, As(III), and arsenate, As(V), in surface water. Speciation of As(III) and As(V) was performed by varying a Reversed Phase-High Performance Liquid Chromatography-Inductively Coupled-Mass Spectrometry (RP-HPLC-ICP-MS) method published by Almassalkhi, (2009). Separation of As(III) and As(V) was achieved using an Agilent 1260 Infinity Series (HPLC) outfitted with an Agilent Zorbax Eclipse XDB C-18 analytical column. The HPLC was coupled to an Agilent 7700x Inductively Coupled Plasma Mass Spectrometer (ICP-MS) for arsenic^{75} mass detection and quantification using EPA Method 200.8. All arsenic speciation solutions and samples were prepared daily in HPLC ammonium phosphate ($(NH_4)H_2PO_4$), tetrabutyl-ammonium hydroxide (TBAH) mobile phase (pH 6.0). Calibration standards were prepared at concentrations of 1, 10, 25, 50, 75, 100 and 150 $\mu g \cdot L^{-1}$ and As(III/V) samples were diluted to ~ 75 $\mu g \cdot L^{-1}$ in $(NH_4)H_2PO_4$, TBAH (pH 6.0) mobile. The Detection Limit (MDL) calculated for the HPLC-ICP-MS As (III/V) speciation method was 0.148 and 0.155 $\mu g \cdot L^{-1}$, respectively, for As(III) and As(V). Samples where preserved with EDTA (Ethylenediaminetetraacetic acid) at time of collection. Samples were also filtered using a nylon 0.2 µm nylon syringe filter prior to loading into spectrometer.

Source water arsenic levels were dominantly in the As(III) (Figure 12) oxidation state. As oxygen was introduced into the contactor, arsenic oxidizing bacteria acclimated the gravel and began to convert As (III) to the pentavalent form As(V) and more easily removed oxidation state (Figure 13). Oxidation was evident shortly after start-up, suggesting arsenic oxidizing bacteria were rapid growers. As(V) accounted for as much as 65% of the arsenic that passed the contactor during the first 50 days of operation. Just after 50 days, a rapid shift in arsenic speciation was noted that resulted in as much as 93% of the arsenic in the oxidized As(V) form. The shift occurred at the same time as the hydraulic loading rate was lowered. All the arsenic leaving the filter was in As(V) (Figure 14), indicating effective biological arsenic oxidation.

Total arsenic (soluble and particulate As[III] and As[V]) as determined by ICP-AES are shown in Figure 15. Total arsenic in the source water, averaged 23 µg/L (±2.4 µg standard deviation) (Table 4) (Figure 15). The contactor removed considerable levels of arsenic (approximately 60% on average) with the effluent arsenic averaging 14.0 ug/L (±3.0 ug standard deviation) (Table 4). At 100 days, the contactor oxygen concentration was increased resulting in a higher pH (8.7); thus, a slight increase in arsenic levels (Figure 15) was observed.

The filter arsenic effluent concentration averaged 8.0 ug/L (±3.0 ug/L standard deviation) (Table 4). The filter arsenic levels were at or below the arsenic MCL of 10 ug/L for most of the study with the exception of a few sample collections. It is possible that some of the higher arsenic valves can be attributed to operational issues. At 200 days, the contactor air concentration was increased which released large amounts of floc particulates onto the filter.

On day 268, the filter ran dry just prior to sample collection. Extending the filter run time may have resulted in higher arsenic values (day 285).

It is important to note the difference between arsenic speciation (Figures 12,13,14) and total arsenic (Figure 15) levels. Slight variances when comparing these values are attributed to the differences in each analytical method. The arsenic speciation method only detects soluble arsenic because the method requires sample filtration before loading onto the mass spectrophotometer. However, total arsenic by ICP-AES detects both soluble and particulate arsenic because the sample is not filtered.

To reduce filter effluent arsenic concentrations, filter influent water (contactor 1 effluent) was pH adjusted (day 343). pH adjustment consisted of installing a chemical injection and inline mixer prior to entering the top of filter. Muriatic acid (31.5%, Sun Belt Chemical, Palm Coast, FL.) was used to adjust pH from 8.21 to approximately 7.5. Results indicated that adjusting pH after the contactor did not decrease filter arsenic concentrations (Figure 15). The more beneficial location to adjust pH to benefit arsenic removal is before the contactor, and iron and arsenic are oxidized with the understanding that aeration will counter to some degree pH reduction. Optimal pH adjustment to 7.0 to 7.2 before the contactor would potentially increase arsenic attachment to iron particles thus increasing removal efficiency through the contactor and onto the polishing filter. However, the pilot study ended before the acid feed location (pH adjustment) before contactor could be evaluated.

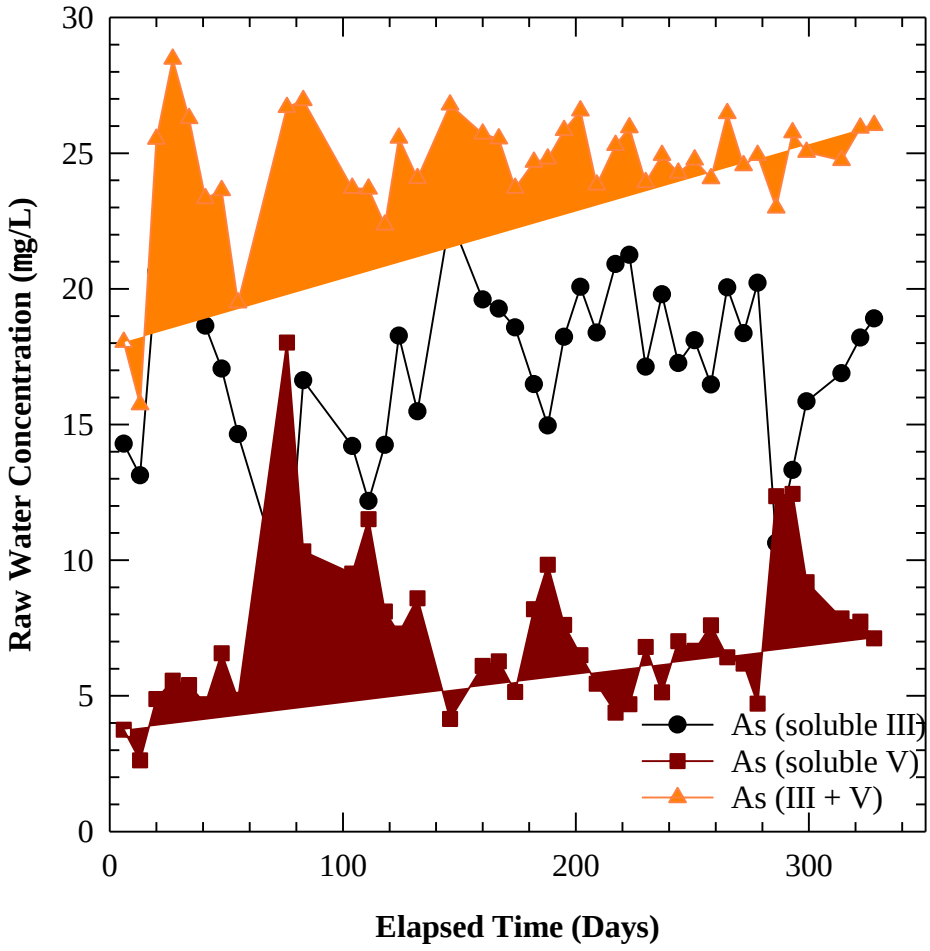

Figure 12. Raw water arsenic speciation.

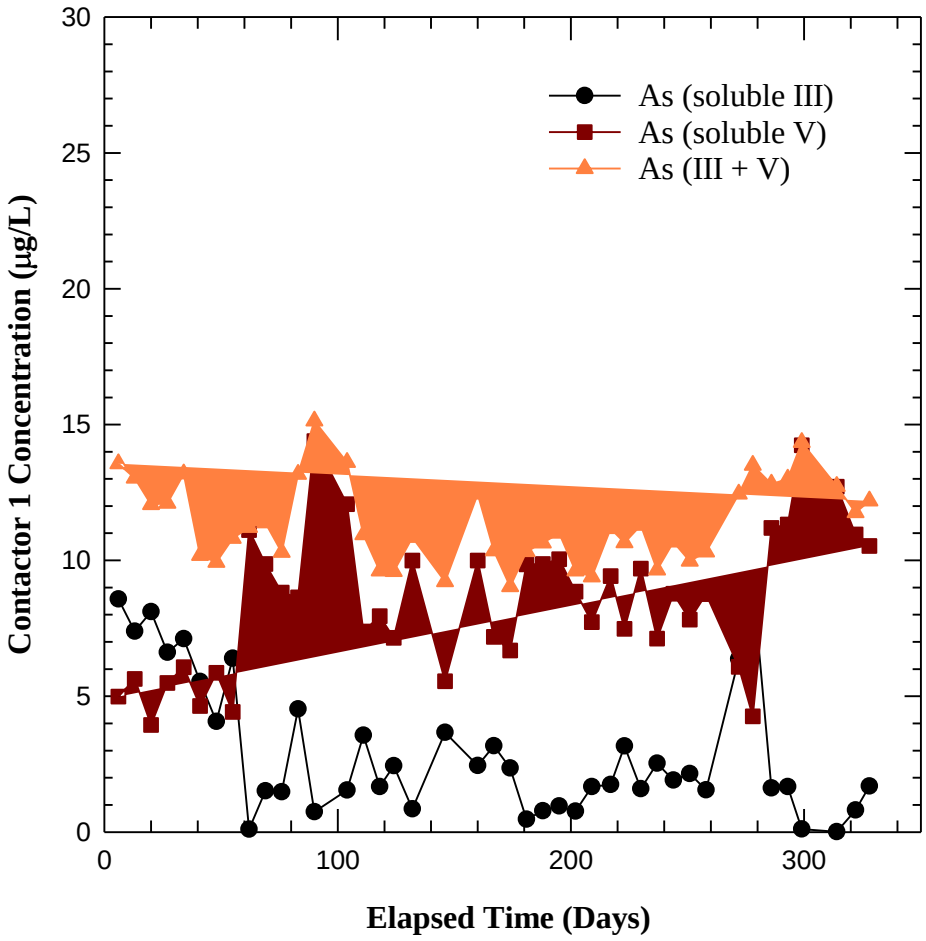

Figure 13. Arsenic speciation through contactor 1.

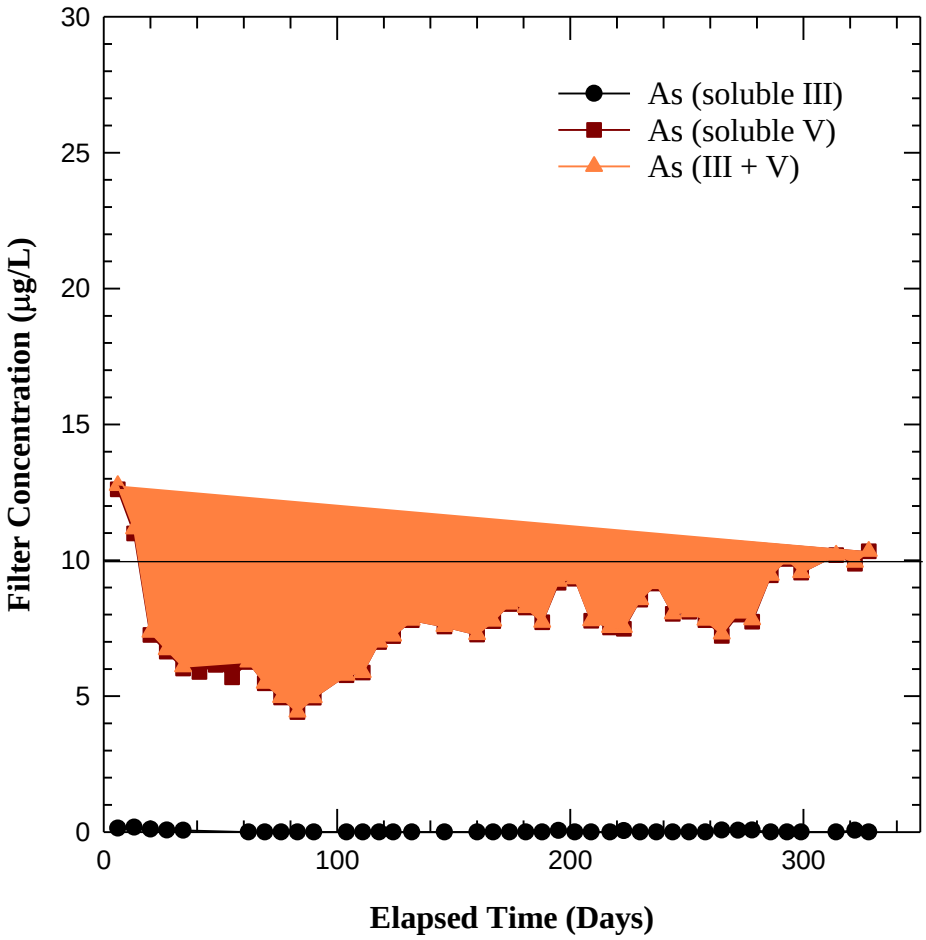

Figure 14. Arsenic speciation through filter.

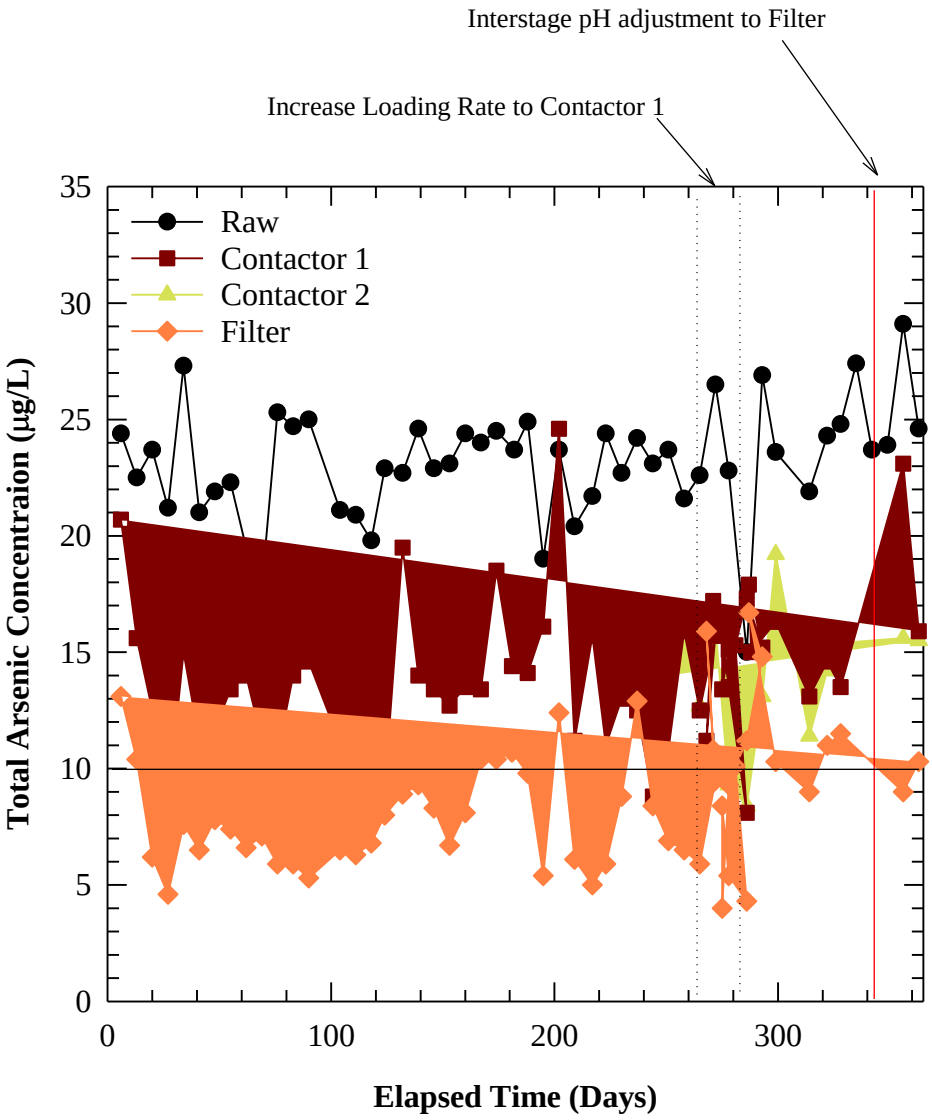

Figure 15. Total arsenic in raw, contactor 1, contactor 2 and filtered waters.

4.7 Test Challenges: Redundancy Evaluation and Long-Term Shutdown

Challenge test #1 - failure of one contactor: The loading rate of Contactor 1 was doubled to over 4.4 gpm/ft^2 after 260 days (Figure 7) for 25 days to simulate the scenario in which one of two operating contactors fails (i.e., treatment redundancy). During this time, ammonia immediately increased by approximately 1.5 mg N/L to nearly 2 mg N/L and nitrate decreased by an equivalent amount (Figure 5). Nitrite did not change. Although the filter's loading rate did not change, ammonia and nitrite levels combined increased by a total of nearly 1 mg N/L while nitrate decreased by an equivalent amount.

Iron levels through the contactor and filter were not impacted by the loading rate increase (Figure 10) with the exception of an iron spike on the first day of the change. Manganese levels increased by approximately 0.02 mg/L out of the contactor during the change in loading rate (Figure 11). Manganese removal through the filter were also not negatively impacted by the loading rate change except for a spike with iron on the first day of the loading rate increase. Total arsenic through the contactor did not noticeably change (Figure 15). Two of the three arsenic levels through the filter during this time, however, were above the MCL. The results reflect the reduced contact time in the contactor. Upon returning to the original loading rate, all water quality parameters rapidly returned to previous levels.

Challenge Test #2 - intermittent operation: Contactor 1 and Filter 1 were shut down for 9 days (day 301) to simulate a scenario in which both contactor and filter were out of service for an extended amount of time. During this time, the air pump supplying oxygen to contactor 1 was also turned off. The results indicated no negative impact on contactor ammonia oxidation performance, ammonia (0.565 mg/L), nitrite (0.172 mg/L), and nitrate (2.261 mg/L) were observed. Filter 1 also showed very little impact from the shutdown. Oxidation levels observed were ammonia (0.035 mg/L), nitrite (0.004 mg/L), and nitrate (2.967 mg/L).

4.8 Other Water Quality Parameters

Source water dissolved oxygen levels averaged 1.1 ± 0.4 mg/L over the course of the study (Figure 16 and Table 4). The source water temperature averaged 14.2 ± 2.3˚ C and did experience some seasonal variability ranging between 11^{o}C to 21^{o}C over the course of the pilot. Although the expectation would be that the biological system would perform better in the warmer months of the year, it was not evident that temperature during the pilot influenced performance. The pilot study demonstrated that biological treatment will work in colder regions, provided groundwater is the source of drinking water and the facility is adequately heated. TOC as was not removed throughout the pilot study. TOC in the source water averaged 2.7± 0.2 mg C/L and 2.8 mg C/L in the contactor and filter. .

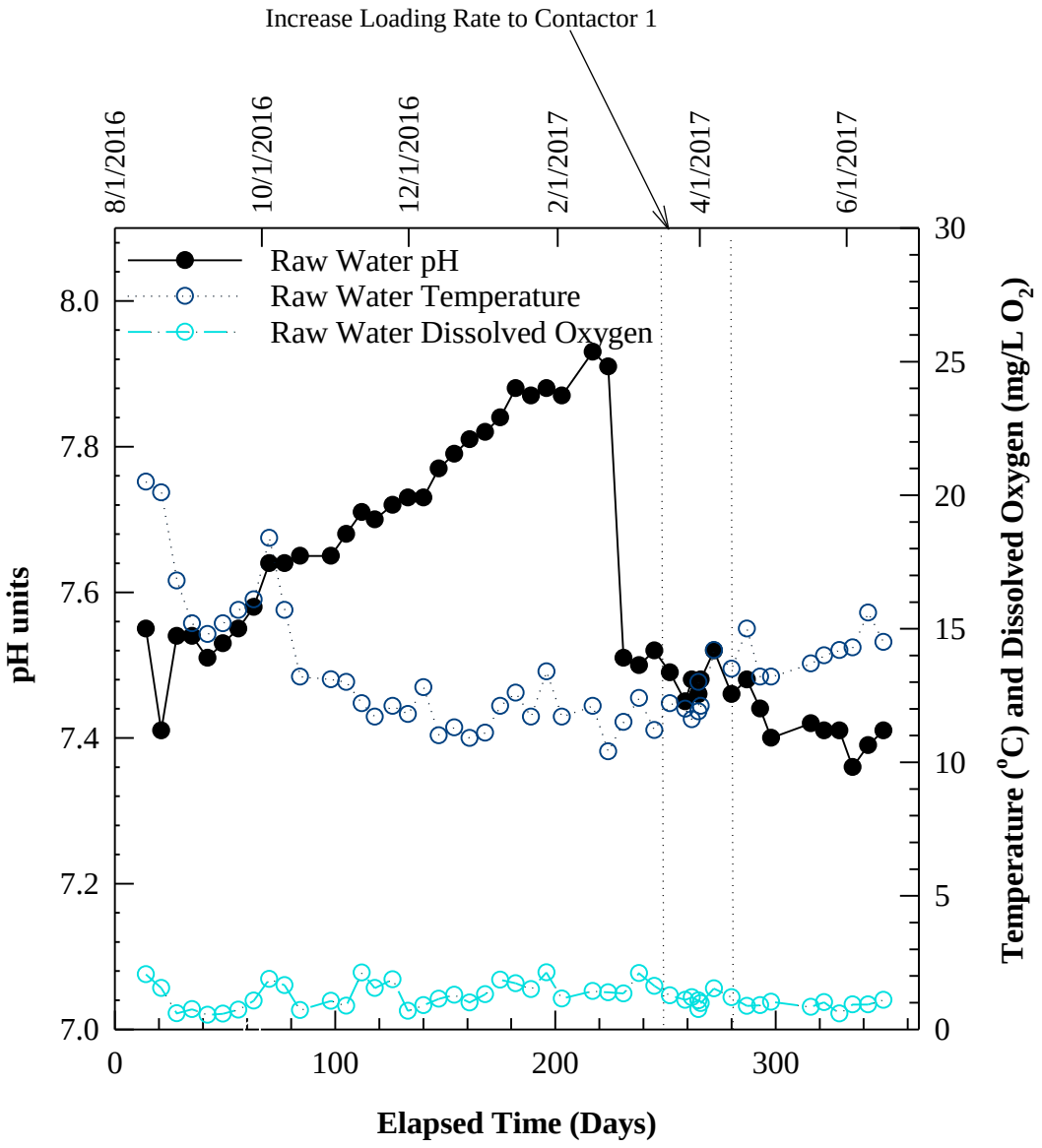

Figure 16. Raw water pH, temperature and dissolved oxygen.

Alkalinity in the source water averaged a steady and very high 410 ± 2.3 mg $CaCO_3$/L (Table 4 and Figure 17). Average alkalinity after passing through the contactor and filter fell to an average of 399 ± 7 and 390 ± 9 mg $CaCO_3$/L. Alkalinity change is directly related to nitrification since nitrifying bacteria use inorganic carbon as a carbon source and therefore, closer examination of alkalinity trends is worthwhile. Alkalinity differences in the contactor and filter effluents reflected changes and progress of nitrification, and therefore closely paralleled ammonia trends (Figures 5,8,9). Toward the end of the study when the system was running optimally (days 200 to 250), approximately 20 mg $CaCO_3$/L dropped through the pilot system. This decrease is precisely what is theoretically predicted to drop (7.1 mg $CaCO_3$/L per 1 mg N/L

ammonia oxidized) for Gilbert's source water after complete oxidation of ammonia (2.9 mg N/L) is achieved.

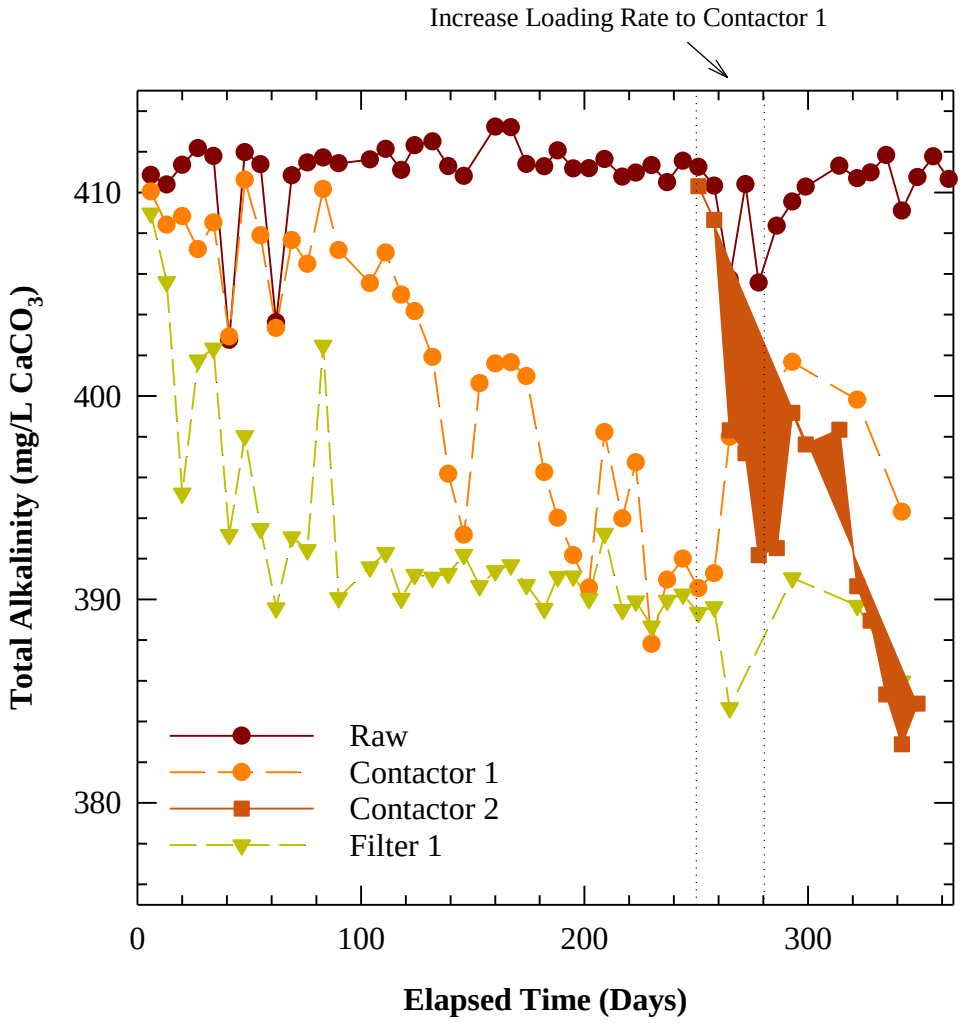

Figure 17. Total alkalinity of raw, contactor 1, contactor 2 and filter 1 effluent.

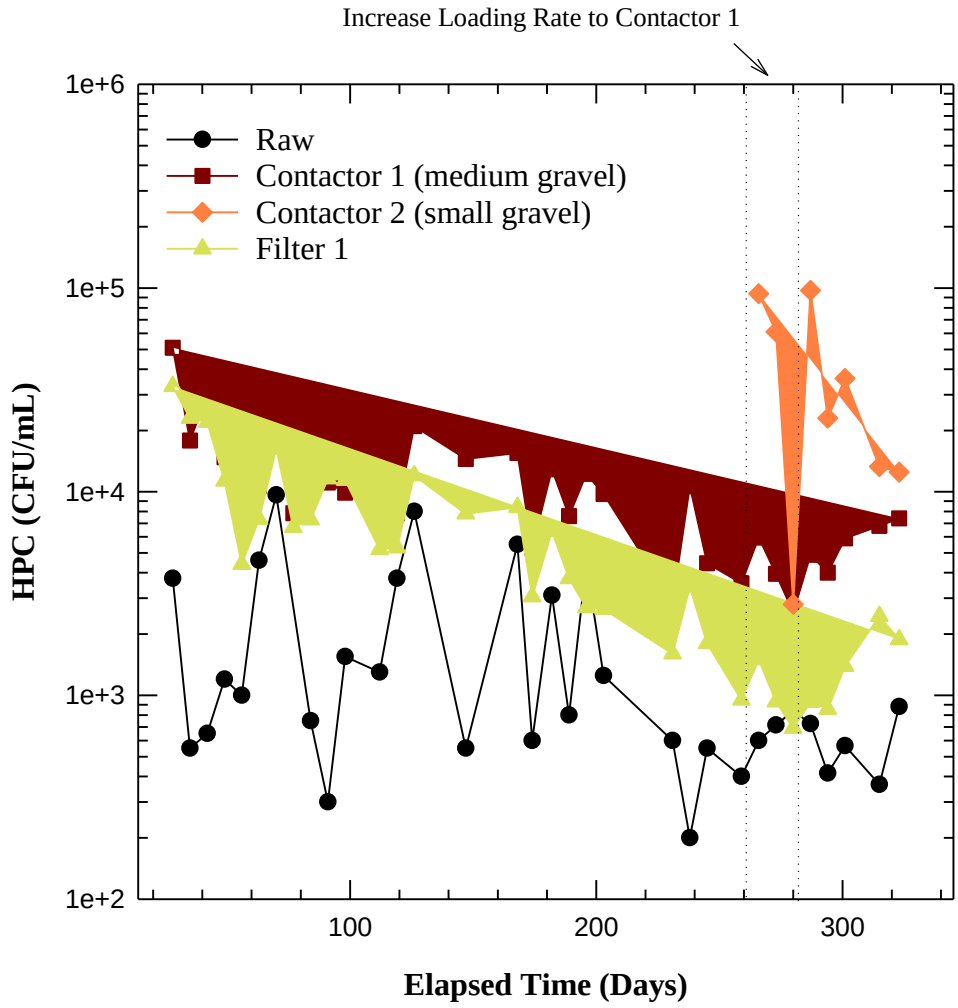

Figure 18. Heterotrophic plate counts (HPCs) in raw, contactor 1 effluent and filter 1 effluent.

4.9 Assessment of Bacterial Population Based on HPCs

Heterotrophic plate count (HPC) measurements in the raw source water, contactor, and filter effluent waters were performed on a routine basis as an indicator of microbial activity although they do not directly reflect nitrifying bacteria. Raw water HPCs generally fell between 500 and 9500 CFU/mL (Figure 18). During the same time, HPCs in both the contactor and filter were approximately an order of magnitude greater in concentrations indicating biological activity (although not necessarily associated with nitrifying bacteria) within both systems. HPC levels leaving the contactor and filter were very similar for the first 250 days of operation. Beyond 250 days, filtered HPC levels were lower than contactor effluent levels. There did not appear to be any important trends from the HPC data particularly as it relates to operational

considerations. The random variability of HPC measurements tended to decrease with time (most apparent after 250 days of operation) and might suggest a stabilization of the system. There also appeared to be a trend with temperature in which greater HPC levels were observed when the water was warmer.

The release of bacteria from the system will occur with any biological treatment approach. Appropriate and effective disinfection must be in place to adequately inactivate the microbiological community shed from the system.

5. Discussion and Summary

The biological treatment pilot study demonstrated the ability of biological treatment to effectively reduce ammonia, iron, manganese and arsenic from the source water to concentrations below their primary and secondary MCLs. The development of biological activity, and subsequent complete oxidation of ammonia to nitrate in the system, was established in the expected time based on past work once the oxygen and loading rate parameters were optimized for a system only operating 8 hours a day. Although the site's water quality was challenging because it included high ammonia, iron, manganese and arsenic levels, the pilot study proved to be valuable in identifying engineering and design criteria in support of future full-scale implementation. For example, dissolved oxygen throughout the contactor, loading rate targets, monthly backwash of contactor, and phosphate feed were all identified as important factors affecting performance.

Table 5. Final Design and Operating Parameters

Parameter	Contactor	Filter
Filter loading rate		
m/hr	5.4 (1.2 - 10.5)	4.9 (1.22 - 5.4)
gpm/ft^2	2.2 (0.5 - 4.3)	1.8 (0.5 - 2.2)
Air flowrate		
L/min	2.5	--
cfm/ft^2	2.86	--
Backwash conditions		
duration, min	5	15
bed expansion, %	0	50
m/hr	124	41.5

gpm/ft^2	51	17
Contactor		
depth, cm	139.7	--
depth, inches	55	--
effective size, mm	12.7 (6.35 - 31.8)	--
effective size, inches	0.5 (0.25 - 1.25)	--
Filter		
anthracite depth, cm		25.4
anthracite depth, inches		10
Anthracite, mm	--	0.97
anthracite, inches	--	0.04
ADGS$^+$ silica sand depth, cm		76.2
ADGS$^+$ silica sand depth, inches		30
ADGS$^+$ silica sand, mm	--	(0.30-.35)
ADGS$^+$ silica sand, inches	--	(0.012-0.014)

By the end of the pilot study, complete oxidation of the source water ammonia (2.9 mg N/L) to nitrate was achieved in Filter 1 and removal of arsenic (22.8 mg As/L), iron (2.9 mg Fe/L) and manganese (0.08 mg Mn/L) through the anthracite/ ADGS$^+$ silica sand filter followed. Other operating and maintenance parameters are summarized in Table 5.

5.1 Summary of Key Findings

The biological treatment pilot study produced several very important findings that will aid in the design and installation of a full-scale water treatment plant. The following findings are highlighted:

- The innovative biological treatment system effectively reduced the levels of ammonia, iron, manganese and arsenic to below the desired level of primary and secondary MCLs. Although arsenic was consistently removed below the MCL of 10 µg/L, further optimization could be explored such as pH adjustment (lowering of pH) before the contactor to enhance arsenic adsorption to iron oxy-hydroxides.
- Biological acclimation of contactor and filter can vary depending on pilot run time, DO, and other key parameters and is defined as the time once nitrogen species equilibrium is reached.

- Once optimized, contactor 1 achieved approximately 83% ammonia reduction (to levels as low as 0.5 mg N/L) using medium (1/2-inch diameter) gravel. Contactor 2 using small (1/4-inch diameter) gravel achieved nearly 100% ammonia reduction because of added surface area for biological attachment and growth. Despite relatively high iron and manganese levels in the source water, and the unexpected reduction of iron and manganese in the contactors, no clogging, flow restriction or short circuiting were observed in the contactors. Nonetheless, a monthly routine contactor backwash regime was followed.
- A dual media (10 inches [25.4 cm] anthracite/30 inches [76.2 cm] ADGS^{+} silica sand) filter after contactor 1 provided additional ammonia/nitrite oxidation, and achieved excellent and consistent iron, arsenic and manganese removal once the system was fully acclimated and optimized.
- Orthophosphate is an important biological nutrient and was necessary to for microbial acclimation, particularly with regards to nitrite oxidizing bacteria. A dose of 0.3 mg PO_4/L onto the contactor was used in the pilot.
- Maintaining saturated dissolved oxygen levels in the contactor was critical to the pilot's operation and effectiveness at achieving desired ammonia oxidation and iron removal. A drop in dissolved oxygen levels resulted in delayed oxidation of ammonia in the contactor and release of nitrite. Dissolved oxygen monitoring was a good process measurement tool and must be incorporated into full-scale operation. Diffuser design will also be very important engineering aspect of the full-scale system.
- Contactor and filter loading rates were important operating variables, although the pilot system was more sensitive to oxygen concentration. The pilot demonstrated that a contactor and filter operated in series at loading rates of 2.2 gpm/ft^2 (5.03 m/hr) and 1.8 gpm/ft^2 (4.14 m/hr), respectively, met desired finished water quality objectives. The contactor performance was affected with respect to ammonia reduction when the loading rate was doubled to evaluate redundancy considerations, yet, ammonia increase was not significant, and more even more important, there was no spiking on NO2 above the MCL which implies that in case of failure or maintenance, the system can still generate safe drinking water.
- The system was robust in that it recovered rapidly after long-term (1 week) and short-term (18 hours per day) shutdown periods, and changes in loading rates and minor seasonal water changes.
- Alkalinity decrease following nitrification in the systems was predicted by theoretical considerations and could be used as an additional process monitoring tool.

- The Filter was backwashed on average of 24 hours of run time by achieving 50% bed expansion.

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