EPA Public Access

Author manuscript

Environ Sci (Camb). Author manuscript; available in PMC 2021 November 01.

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Published in final edited form as:

Environ Sci (Camb). 2020 November 1; 6(11): 3142–3156. doi:10.1039/d0ew00361a.

The removal of ammonia, arsenic, iron and manganese by biological treatment from a small Iowa drinking water system†

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Abstract

Although not regulated in United States drinking water, ammonia has the potential to increase chlorine consumption and cause nitrification problems in the distribution system. Many groundwaters with elevated ammonia are also contaminated with other inorganic analytes such as arsenic, iron, and manganese, all of which have primary or secondary maximum contaminant levels (MCLs). The objective of this work was to demonstrate the effectiveness of an innovative biological treatment process to simultaneously remove ammonia (2.9 mg N per L), arsenic (23 $\mu\text{g L}^{-1}$), iron (2.9 mg L^{-1}) and manganese (80 $\mu\text{g L}^{-1}$) from a groundwater source in Iowa. The biological treatment system consisted of an “aeration contactor” followed by a conventional granular media filter. Orthophosphate was also added, as a biological nutrient, at 0.3 mg PO_4 per L. Ammonia, manganese, and iron were consistently reduced through the pilot system by 98 to 99%. Complete oxidation of ammonia to nitrate was observed (*i.e.*, no nitrite was released) and arsenic was consistently removed to below the 10 $\mu\text{g L}^{-1}$ MCL. Ammonia was oxidized by ammonia and nitrite oxidizing bacteria and arsenic by bacteria which converted As(III) in the source water to more readily removable As(V). Iron was presumably oxidized by oxygen during aeration although some biologically assisted oxidation could not be ruled out. As(V) bound iron particles were removed in the filter resulting in effective arsenic (and iron) reduction. A surprising treatment benefit was the effective manganese reduction, the mechanism of which was not so clear, but was attributed to biologically assisted oxidation of Mn(II). While some system acclimation time was necessary to achieve desired ammonia and manganese reductions, acceptable arsenic and iron reductions were observed shortly after start-up.

1. Introduction

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

†Electronic supplementary information (ESI) available. See DOI: [10.1039/d0ew00361a](https://doi.org/10.1039/d0ew00361a)

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Conflicts of interest

There are no conflicts to declare.

Protection Agency (USEPA) as a contaminant. However, the USEPA has issued a lifetime exposure advisory and taste threshold concentration of 30 mg L⁻¹ for ammonia.¹ Although ammonia may not pose a direct health concern, nitrification of significant levels of ammonia from the source water (or intentionally added ammonia to form monochloramine) in the drinking water treatment plant and/or distribution system may be a public health concern. Specifically, nitrification, which is the conversion of 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.²⁻⁶ A recommended nitrification control level for ammonia, of 0.12 mg NH₃ per L, has been referenced.⁷

Ammonia in water may also interfere 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.^{8,9} 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. For example, a system with 1 mg NH₃ per L would require a chlorine dose of 10 mg Cl₂ per L to achieve a free chlorine residual of 1 mg Cl₂ per L. In addition to chemical cost and added operational complexity issues, excessive chlorine addition may also result in disinfection by-product issues as well. However, the complete oxidation of source water ammonia prior to, or as part of, the water treatment process would eliminate these potential negative impacts on treatment effectiveness and nitrification on distribution system water quality.

Iowa has a widespread distribution of ammonia in groundwaters across the state that are largely associated with agriculture and other farming practices. Water quality testing of the source groundwater in one small Iowa community, Gilbert (population approximately 1082) showed that, on average, ammonia levels were 3.0 mg as nitrogen (N) per 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 mg N per L and 10 mg N per L, respectively, measured at the point of entry to the distribution system. The Iowa DNR 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 per L, where incomplete nitrification can lead to exceedances of the lower nitrite MCL.

Complicating matters in Gilbert, the source water also contained elevated levels of arsenic (0.027 mg L⁻¹), iron (4.25 mg L⁻¹) and manganese (0.16 mg L⁻¹), which were all at levels greater than their respective primary or secondary regulatory MCLs. In 2001, the USEPA reduced the arsenic MCL from 0.05 mg L⁻¹ to 0.010 mg L⁻¹ (ref. 10) based on 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. 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^{-1} , based on aesthetic issues. Specifically, iron in the water can cause a metallic taste, discoloration of the water, staining of faucet and fixtures, and sediment build-up. Similarly, manganese presents an aesthetic challenge associated with discoloured water, and staining of faucets and fixtures. As a result, a secondary MCL for manganese of 0.05 mg L^{-1} is in place.

The formation of monochloramine and breakpoint chlorination are commonly used water treatment options for addressing elevated ammonia in source waters. Breakpoint chlorination results in the removal of ammonia as nitrogen gas by a chemical reaction with chlorine added in the range of 8 to 11 times the mg N per L ammonia present. For a community with a water source such as the Gilbert, this would require an extremely high chlorine dose of approximately 29 mg L^{-1} to reach the breakpoint of ammonia and achieve a $1 \text{ mg Cl}_2 \text{ per L}$ free chlorine residual, and possible chemical feed equipment upgrades to achieve the target dose. In addition to chemical costs, such a chlorine dose raised the potential of forming large amounts of disinfection by-products. The formation of monochloramine is achieved by adding sufficient amounts of chlorine to effectively remove all free ammonia from source water. This too may require excessive levels of chlorine and is further challenged by balancing dose with seasonal ammonia level changes and or altering water sources. Inadequately adjusting chlorine dose can allow free ammonia to enter the distribution system, and as monochloramine decays and reacts with other materials in the distribution system, ammonia may be released. Other approaches including ion exchange with zeolites, reverse osmosis (RO), advanced oxidation, and air stripping, are capable of removing ammonia from water, but are relatively complex, expensive, or have limited applications, mainly when additional contaminants such as iron, manganese, and arsenic, are present.

Biological ammonia “removal”[‡] is another treatment approach shown to reduce source water ammonia.^{8,11-14} The process relies on autotrophic bacteria to convert ammonia to nitrate, in the presence of oxygen, involving a two-step sequence of aerobic reactions generally mediated by two different genera of bacteria: *Nitrosomonas* and *Nitrospira*, although others may also be important. The oxygen demand of nitrification is significant. For complete nitrification, 4.6 mg O_2 is required per $\text{mg NH}_4^+\text{-N}$ oxidized.^{15,16} 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 $7.1 \text{ mg as CaCO}_3 \text{ per mg NH}_4^+\text{-N}$ oxidized.¹⁵ Other water quality factors that affect nitrification include phosphate concentration, pH, and water temperature.¹⁷⁻²¹

Gilbert's drinking water source, like many Midwest groundwaters, also contained significant levels of reduced arsenic, iron and manganese. The necessity to oxidize arsenite, As(III), to the arsenate, As(V), to facilitate effective removal is well known.²²⁻²⁴ Iron also has two primary valence states in water; the ferrous, Fe(II) and ferric, Fe(III), forms. Oxidation to the insoluble ferric iron form is necessary to achieve effective iron removal by filtration.

[‡]The terms “removal” and “oxidation” will be used interchangeably throughout this document. We use “removal” to represent the conversion of ammonia to nitrate and/or nitrite by biological oxidation. We recognize that treatment does not physically remove ammonia-nitrogen but rather converts the form of nitrogen (*i.e.*, total of ammonia, nitrite, and nitrate).

Manganese also has multiple oxidation states although Mn(II) and Mn(IV) are the most relevant forms in drinking water. Oxidation of Mn(II) is also necessary for effective removal by filtration although the resulting particle properties must also be considered. Effective chemical oxidation of iron can be achieved by oxygen and monochloramine while manganese oxidation requires stronger oxidants including chlorine, permanganate, or ozone. Alternatively, in the presence of oxygen, iron, manganese and arsenic can be oxidized by bacteria. Alternatively, in the presence of oxygen, iron, manganese and arsenic can be oxidized by bacteria and co-removed with biologically oxidized ammonia.^{9,11,25-28}

Given the negative issues associated with high ammonia, iron and manganese concentrations in drinking water, and the health risks directly 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 simultaneously considering practical constraints on the small water system. Therefore, the objective of this work was to evaluate the effectiveness of an innovative aerobic biological treatment approach to simultaneously reduce ammonia, iron, manganese and arsenic below their respective primary and secondary MCLs. In addition, operational engineering parameters will be presented, and ease of operation and reliability will be discussed.

2. Materials and methods

2.1 Pilot technology description

The ammonia biological removal treatment pilot system was based on an USEPA patented treatment process design (US8029674B2 awarded on 10/2/2011) (Fig. 1). The Gilbert pilot system consisted of a pair of 3 inch (7.62 cm) diameter columns by 6 foot tall configured in series built from clear schedule 40 polyvinyl chloride (PVC) and other common plumbing materials. The pair consisted of an "Aeration Contactor" column filled with 55 inches (139.7 cm) of medium gravel having a nominal 1/2 inch diameter (Fig. 2) followed in series with a "filter" column filled with anthracite (10 inches [25.4 cm] deep) over ADGS⁺ silica sand-based media (AdEdge Water Technologies, LLC) with a manganese dioxide coating (30 inches [76.2 cm] deep). The innovative treatment step, the aeration contactor, was aerated from the bottom, such that air bubbles flow upward co-current to the water flow (up-flow) (Fig. 1) using a diffuser (US9914654 awarded 3/13/2018) connected to a gas pump at a rate of 2.5 L min⁻¹ (0.66 gpm). Water exiting the top of the aeration contactor fed the top of the filter that was operated in the down-flow mode.

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 biological nitrification process, and iron, manganese and arsenic oxidation. The gravel in the contactor supported the growth of bacteria where nitrification and other biological oxidation processes occurred. Gravel supported bacteria attachment and growth while leaving a relatively large void space that greatly reduced any likelihood 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 occurred in the contactor, but minimal iron removal was expected. Contactor loading rates were adjusted during the pilot study (Table 2) to identify optimal performance. The filter was intended to remove arsenic-containing iron particles,

manganese and bacteria, and can also provide additional biological oxidation, if necessary. The filter served as a polishing step and safeguard against disruption in operation of the contactor. Effluent water from the filter was routed to a clear well that, when full, was either used to backwash the contactor and filter, or overflowed to the sanitary sewer.

2.2 Treatment approach

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 per mg to NH_4^+-N in the source water. The groundwater in the study community had low oxygen (1.3 mg O_2 per L) and elevated ammonia of 2.9 mg N per L as well as reduced iron, manganese and arsenic (Table 1), that also exert an oxygen demand. As a result, more than 13.5 mg O_2 per 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 engineering configuration of aeration followed by filtration (*e.g.*, iron removal) including biologically-active filtration was not sufficient to address the oxygen demand required to meet the treatment objectives of the community's water system.

The amount of oxygen that can be added to 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 treatment requirements. Therefore, an innovative approach to introducing oxygen to the treatment system in the small community was necessary to meet the treatment objectives. Aerating with pure oxygen could provide super saturated oxygen conditions and sufficient oxygen, however, storage and handling issues including safety concerns might be limiting.

2.3 Pilot system operation

The pilot system (Fig. 2) 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 small community's existing well and drinking water 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.

On-site operating and water quality measurements were performed by the city's water plant operator and included, flow rates, temperature, dissolved oxygen, and pH. Dissolved oxygen, pH, and temperature were measured using a 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 USEPA on a weekly basis. The filter was backwashed using filter effluent water approximately every 24 hours of operation although longer frequencies were also evaluated successfully (up to 110 days). 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 a rate of 2.5 gallon per min (gpm) (9.45 L min^{-1}).

Several parameters were adjusted to optimize nitrification, including changing dissolved oxygen levels and filter loading rates. 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 condition changes are summarized in Table 2. Filter loading rate changes were made by adjusting the flow rate through the pilot columns by valve adjustment. For example, the study began with contactors at a loading rate of 2.4 gpm ft^{-2} (5.87 m h^{-1}) and ended at a rate of 2.2 gpm ft^{-2} (5.38 m h^{-1}). Filters averaged 1.8 gpm ft^{-2} (3.67 m h^{-1}) over the duration of the study.

A phosphate chemical feed, with a target dose of orthophosphate at 0.3 mg PO_4 per L, was installed in-line from initial startup of study. Orthophosphate was provided by the USEPA in the form of technical grade $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (Fisher Scientific) dissolved and suspended 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^{-1} via a peristaltic pump.

2.4 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 USEPA 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]), and 60 mL for arsenic speciation w/EDTA added as a preservative. Upon arriving at USEPA, 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 (within approximately 24 hours of sampling). Soluble arsenic speciation, As(III) and As(V), was performed modifying a reversed phase-high performance liquid chromatography-inductively coupled-mass spectrometry (RP-HPLC-ICP-MS) method.²⁹ 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 detection and quantification using USEPA Method 200.8. Arsenic samples were preserved with EDTA (ethylenediaminetetraacetic acid) upon collection and filtered using a $0.2 \mu\text{m}$ nylon syringe filter prior to analysis. All water analyses were performed according to USEPA methods^{30,31} or Standard Methods³² (Table S1†).

†Electronic supplementary information (ESI) available. See DOI: [10.1039/d0ew00361a](https://doi.org/10.1039/d0ew00361a)

3. Results and discussion

3.1 General water chemistry

Extensive source water chemistry data, as well as the pilot contactor and filter effluent water quality data over the entire pilot study, are summarized in Table 3. The source water was a very hard, high alkalinity groundwater with calcium and magnesium levels averaging 69 and 26 mg L⁻¹, respectively, total hardness of 280 mg CaCO₃ per L, and a total alkalinity of 410 mg CaCO₃ per L. The pH averaged 7.68 and chloride was 1.1 mg Cl⁻ per L. Iron and manganese levels averaged 2.9 and 0.08 mg L⁻¹, respectively, and ammonia averaged 2.9 mg N per L. Orthophosphate averaged 0.44 mg PO₄ per L and nitrite (average 0.04 mg N per L) and nitrate (average 0.01 mg N per L) were at or near the respective method detection limits and total organic carbon (TOC) averaged 2.7 mg C per L.

3.2 Removal of ammonia in source water

3.2.1 Contactor 1.—Ammonia levels in contactor 1 decreased over the first 20 days of operation from nearly 3 mg N per L to approximately 2.2 mg N per L where levels remained for the following 50 days (Fig. 3). During this time, levels of nitrite increased peaking at 0.4 mg N per L on day 20 then dropped back to near non-detectable levels as the contactor acclimated with nitrite oxidizing bacteria. Nitrate levels steadily increased during this same time eventually stabilizing 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 per 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.^{8,11} 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 this study, the pilot operated 7 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 treatment progression, other parameters necessary for nitrification were closely examined. The importance of oxygen has been stressed in past work^{8,11,12} so dissolved oxygen (DO) levels during the initial 70 days of operation were closely monitored.

Oxygen levels in the raw water were typically less than 2 mg O₂ per L over the entire study (Fig. 4). Oxygen levels in the contactor started at approximately 8.4 mg O₂ per L, but the concentration steadily decreased over the initial 20 days of operation corresponding to the onset of nitrification. Oxygen levels remained relatively steady between 20 and 70 days at approximately 7.2 mg O₂ per L (Fig. 4). During this time ammonia levels leaving the contactor also remained steady. Problems with the air-feed system were encountered between 70 and 80 days that resulted in reduced oxygen levels in the contactor reducing oxygen levels to 3.6 mg O₂ per L. The rapid decrease in oxygen directly corresponded to the sudden increase in ammonia. Adjustments to the oxygen feed rate were made at 114 days resulting in a dissolved oxygen increase to 9.6 mg O₂ per L that was maintained, roughly, 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 per L within 14 days after the oxygen adjustment. Nitrate produced in the contactor before

DO increase was an average of 0.25 mg N per L and was increased to an average of 1.32 mg N per 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 based on the continued downward trend in ammonia levels. With constant elevated dissolved oxygen levels, acclimation continued and by 220 days (approximately 105 days after contactor improvement), ammonia levels were below 1 mg N per L and eventually reached steady-state at a low of 0.5 to 0.6 mg N per L (or approximately 60% reduction) nitrite levels remained consistently below 0.4 mg N per L during this time and nitrate was the predominant nitrogen species present, accounting for the remaining nitrogen mass around the contactor. Nitrite never spiked above the 1.0 mg N per L MCL at any point of time after complete acclimation.

Contactor loading rate is also a very important parameter with respect to contactor and filter performance.^{8,11,12} Considering past research efforts as an initial guide, loading rates were adjusted throughout the study to optimize system performance. Contactor loading rate was adjusted during the first 80 days of pilot operation from a high of 2.7 gpm ft⁻² (6.6 m h⁻¹) to 1.5 gpm ft⁻² (3.8 m h⁻¹) (Fig. 5) to improve the performance of contactor 1 while the contactor was experiencing low DO levels. Since oxygen levels were adjusted while also making loading rate changes, there was some difficulty separating the relative impacts of each change, although increasing DO concentration had the greatest impact on ammonia reduction. After 80 days, the loading rate settled in at approximately 2.2 gpm ft⁻² (5.4 m h⁻¹) until approximately 220 to 230 days when it was decreased to nearly 2.0 gpm ft⁻² (4.9 m h⁻¹) (Fig. 5). The final loading rate change increased ammonia oxidation by approximately 0.5 mg N per L.

Previous work^{8,11} reported the role of system operation during start-up and time to achieve complete acclimation of bacteria 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 90 days to reach steady state. The Gilbert pilot was in operation for approximately 105 days between the time when oxygen levels were adjusted, and ammonia levels approached a stable low value which is in line with past observations.

3.2.2 Filter.—The primary role of the filter was to remove iron particles that contained arsenic and manganese that developed in the contactor. The filter was also biologically active and provided additional oxidation of any ammonia and nitrite that may have passed through the contactor. Ammonia, nitrite, and nitrate levels entering filter 1 were those exiting contactor 1. Ammonia oxidation to nitrite began shortly after the pilot was initiated and rapidly increased to a peak of 2.3 mg N per L by 20 days and dropped off as quickly as it appeared by 40 days (Fig. 6). A spike in nitrite is typically observed in such systems 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 per L as the system acclimates. Fortunately, the elevated nitrite spike was short-lived and nitrite was oxidized by free chlorine. Considering DO concentrations

were not optimized at the beginning of the pilot (only ~ 7.5 mg O₂ per L), the nitrite peak may have been shorter than observed with optimal DO concentration. Between 40 and 80 days (period when oxygen levels were relatively low), nitrite concentrations varied, but never exceeded 0.6 mg N per L, indicating that oxygen levels leaving the contactor impacted biological oxidation within the filter, as well. After 114 days, nitrite levels remained very low and were never greater than 0.3 mg N per L. 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 h⁻¹) and 1.8 gpm ft⁻² (4.1 m h⁻¹) for the remainder of the study (Fig. 5). The filter successfully “polished” the water by oxidizing any ammonia that was not removed in the contactor.

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

Contactor 2 was started on 4/17/2017 (day 0) which corresponded to 243 days into operation of contactor 1. Results from both contactors were plot together despite different start-up dates for comparison since they both received the same source water. Decrease of ammonia levels was relatively constant through contactor 2 (C3 location) from 3 mg N per L to non-detectable levels by 110 days (Fig. 7). During this time, nitrite levels remained low and never exceeded 0.45 mg N per 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.

Over time, 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 illustrated the benefit of added surface area using smaller gravel *versus* medium gravel. Although the acclimation rate did not change, treated ammonia levels were greatly improved.

3.2.4 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 (Fig. 8). The elevated oxygen concentration and pH in the contactor likely resulted in rapid oxidation of Fe(II) to Fe(III) particles likely before the water entered the contactor gravel. Although Fe(II) oxidation kinetics are rapid under the pilot conditions, it can't be completely excluded that some biological iron oxidation may have taken place in the contactor.

Iron in the source water, averaged 2.94 mg L^{-1} (± 0.30 standard deviation) (Table 3) and was relatively consistent across the entire evaluation period (Fig. 8). Interestingly, the contactor removed considerable levels of iron (approximately 59%) with the effluent iron averaging 1.20 mg L^{-1} (± 0.6 standard deviation) (Table 3). The contactor effluent iron levels were variable within a wide range of approximately 0.5 mg L^{-1} to 2 mg L^{-1} . 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 ever observed. Nonetheless, the contactor was backwashed routinely, more frequently than 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^{-1} (± 0.1 standard deviation) (Table 3). Regardless of the iron content in the contactor effluent, iron levels in filter effluent waters were at or below the detection limit (Fig. 8). Outstanding and consistent removal of iron was observed through the system from the very start-up of the pilot.

Iron removal through the filters was not impacted by filter loading rates (Fig. 5 and 8). Filters were operated between 1.6 gpm ft^{-2} (3.8 m h^{-1}) and 2.1 gpm ft^{-2} (5.1 m h^{-1}). Filter flow rates had to be lower than contactor flow rate only due to limitations in pilot design. This observation will be taken into consideration when the design of the full-scale system is finalized. At the completion of the study, the filter was operated at a loading rate of approximately 1.8 gpm ft^{-2} (4.2 m h^{-1}).

3.2.5 Removal of manganese from source water.—The oxidation state of manganese in the source water was not directly 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 (Fig. 9). Manganese oxidation to Mn(IV) and solid MnO_2 is not feasible without the addition of permanganate, chlorine or other strong oxidant or through biological oxidation processes. Unlike iron, elevated oxygen concentrations will not be effective and rapidly oxidize soluble Mn(II) particularly at pH values below 9.0 to 9.3.³³⁻³⁵

Manganese in the source water, averaged 0.08 mg L^{-1} (± 0.003 standard deviation) (Table 3) and were relatively consistent across the entire study period (Fig. 9). Interestingly, the contactor also removed considerable levels of manganese (approximately 36% on average) with the effluent manganese averaging 0.05 mg L^{-1} (± 0.01 standard deviation) (Table 3). The contactor effluent manganese levels were variable and corresponded with dissolved oxygen concentration (Fig. 4 and 9). Manganese levels dropped steadily to 0.06 mg L^{-1} over the first 80 days while a relatively stable dissolved oxygen level was maintained. Although manganese was assumed to be trapped in the gravel and incorporated into the biofilm structure, no degradation in contactor performance, flow restriction, or any obvious negative

impact was observed. The sudden drop in dissolved oxygen experienced at 80 days resulted in an immediate increase in manganese (Fig. 9).

The filter manganese effluent concentration averaged 0.01 mg L^{-1} (± 0.02 standard deviation) (Table 3). The filter reduced manganese levels beyond the contactor throughout the study except the time period when oxygen levels dropped (day 80). Re-establishment of oxygen resulted in a rapid improvement of manganese levels. After oxygen levels were increased (115 days), manganese levels decreased consistently to near the detection limit for the remainder of the evaluation. Outstanding and consistent removal of manganese iron was observed although maintaining oxygen control was clearly critical.

3.2.6 Removal of arsenic from source water.—Studies have demonstrated the effectiveness of removing arsenite, As(III) from aqueous systems with iron.²²⁻²⁴ However, most of those studies required a strong oxidant such as chlorine, potassium permanganate or iron-based, chemical coagulation treatment (adsorptive media) to remove the arsenic. The oxidant is necessary to convert As(III) to the more easily adsorbed arsenate, As(V) form, and oxygen is not strong enough to do so. The sorption of arsenic to naturally present iron is also affected by many factors such as pH, water quality and the amount and form of iron present.^{22-24,36} In this pilot study, air pumped into the contactor supporting bacterial growth was the likely source of arsenic oxidation as reported in past work.^{8,11,37}

Source water arsenic levels were dominantly in the As(III) (Fig. 10) oxidation state. As oxygen was introduced into the contactor, arsenic oxidizing bacteria acclimated within the gravel and began to convert As(III) to the pentavalent, and more easily removed oxidized, form of As(V). Oxygen is not a strong enough oxidant to effectively and rapidly oxidize As(III) to As(V).^{38,39} Arsenic 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 time correspond to lowering of the hydraulic loading rate. All the arsenic leaving the filter was in As(V) (Fig. 10) indicating effective biological arsenic oxidation. Combined arsenic (soluble and particulate As[III] and As[V]) in the source water, averaged $22.8 \text{ } \mu\text{g L}^{-1}$ ($\pm 2.4 \text{ } \mu\text{g}$ standard deviation) (Table 3 and Fig. 11). The contactor removed large concentrations of arsenic (approximately 60% on average) with the effluent arsenic averaging $14.0 \text{ } \mu\text{g L}^{-1}$ ($\pm 2.9 \text{ } \mu\text{g}$ standard deviation) (Table 3) through coprecipitation with oxidized iron. At 100 days the contactor was backwashed and at 114 days the contactor oxygen concentration increased resulting in a higher pH (8.7). Thus, a slight increase in arsenic levels (Fig. 10) was observed as predicted (*i.e.* arsenic reduction associated with iron particles decreases with increasing pH).^{22-24,36} Reduction of pH by acid addition could improve arsenic reduction if desired.

The filter arsenic effluent concentration averaged $8.0 \text{ } \mu\text{g L}^{-1}$ ($\pm 2.9 \text{ } \mu\text{g L}^{-1}$ standard deviation) (Table 3). The filter arsenic levels were at or below the arsenic MCL of $10 \text{ } \mu\text{g L}^{-1}$ over nearly the entire study with the exception of only a few samples. In most cases, filter arsenic levels greater than the MCL were attributed to pilot operational issues (Fig. 12). For example, at 200 days the contactor air concentration was increased which released large

amounts of floc particulates onto the filter. On day 267 the filter ran dry just prior to sample collection. And on day 285, the filter run time was extended beyond the designated backwash time.

Slight variances when comparing these values were attributed to the differences in each method. The arsenic speciation method only detects soluble arsenic because the method required sample filtration before injecting samples onto the HPLC column. However, total arsenic by ICP-AES detects both soluble and particulate arsenic because the samples were not filtered.

3.2.7 Contactor redundancy evaluation.—The loading rate of contactor 1 was doubled to over 4.4 gpm ft⁻² after 260 days (Fig. 5) for 25 days to simulate the scenario where one of two operating contactors failed or needed to be taken offline. Ammonia immediately increased by approximately 1.5 mg N per L to nearly 2 mg N per L and nitrate decreased by an equivalent amount (Fig. 3), while nitrite did not change. Although the loading rate through the filters did not change during the evaluation, both the ammonia and nitrite levels leaving the filters increased by nearly 1 mg N per L while nitrate decreased by an equivalent amount. The filters could not address the additional ammonia loading.

Iron levels through contactor 1 and the filter were not impacted by the loading rate increase (Fig. 8) with the exception of a spike in iron on the first day of the change. Manganese levels increased by approximately 0.02 mg L⁻¹ out of the contactor during the change in loading rate (Fig. 9). Manganese removal recovered through the filter except for a spike, with iron, on the first day of the loading rate increase. Total arsenic through contactor did not noticeably change (Fig. 11). 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.

3.2.8 Long-term shutdown.—Contactor 1 and filter 1 were shut down for 9 days (day 301) to simulate a scenario where both contactor and filter were out of service for an extended amount of time. During this period the air pump supplying oxygen to contactor 1 was also turned off. Results indicated no negative impact on contactor ammonia oxidation performance, with levels of ammonia (0.57 mg N per L), nitrite (0.17 mg N per L), and nitrate (2.26 mg N per L) observed. Filter 1 also showed very little impact from the shutdown. Oxidation levels observed were ammonia (0.04 mg N per L), nitrite (0.004 mg N per L), and nitrate (2.97 mg N per L).

3.2.9 Other water quality parameters.—Source water dissolved oxygen levels averaged 1.1 ± 0.5 mg L⁻¹ over the course of the study (Fig. 13 and Table 3). The pH increased from an average of 7.68 in the raw water to 8.03 in the filtered water. Although biological nitrification produces a pH drop, the net pH change through the system (an increase) is dependent on other factors such as iron oxidation, iron precipitation and carbon dioxide stripping which are more influential. The source water temperature averaged 14.2 ± 2.5 °C experiencing some seasonal variability ranging between 11 °C to 21 °C over the course of the pilot (Fig. 13). 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 affected 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. Total organic carbon (TOC) in the source water averaged 2.7 ± 1.7 mg C per L during the pilot study, and did not change passing through the contactor and filter, both measured at 2.8 mg C per L.

Alkalinity in the source water averaged a steady and very high 410 ± 2.3 mg CaCO_3 per L (Table 3 and Fig. 14). Average alkalinity after passing through the contactor and filter fell to an average of 399 ± 7 mg CaCO_3 per L and 390 ± 5 mg CaCO_3 per L. The change in alkalinity was directly attributed to nitrification since nitrifying bacteria use inorganic carbon as a carbon source and therefore, closer examination of alkalinity trends would be worthwhile. Differences in alkalinity in the contactor and filter effluents reflected changes and progress of nitrification, and therefore closely paralleled ammonia trends (Fig. 3, 6 and 7). Toward the end of the study when the system was running optimally (days 200 to 250), approximately 20 mg CaCO_3 per L dropped through the pilot system. This decrease was precisely what was theoretically predicted to drop (7.1 mg CaCO_3 per L per 1 mg N per L ammonia oxidized) for Gilbert's source water after complete oxidation of ammonia (2.9 mg N per L) was achieved.

3.2.10 Microbiological parameters.—Microbiological analyses were limited to heterotrophic plate counts (HPCs) due to resources constraints. 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 HPC does not directly reflect nitrifying bacteria. Raw water HPCs generally fell between 500 and 9500 CFU mL^{-1} (Fig. 15). During the same period, 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 which was most apparent after 250 days of operation and might suggest a stabilization of the system. There also appeared to be a temperature trend, where 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.

Microbiological community structure analysis of biofilm in the contactor and filter at different stages of operation would have provided interesting information had resources been available. Previous studies have considered microbiological characterization of biological water treatment systems including where ammonia and manganese removal was considered.⁴⁰⁻⁴⁴ In this study, such information would have provided an understanding of which microorganism(s) were responsible for the oxidation of each contaminant, competitive

interactions amongst microbiological populations, impact of seasonal change in microbiological community structure, and strategies for optimizing contaminant removal.

Conclusions

The biological treatment pilot study demonstrated the ability of a biological drinking water treatment approach to simultaneously remove ammonia, arsenic, iron and manganese. Several important findings that will aid in the design of a full-scale water treatment plant include:

- An innovative biological treatment system effectively reduced the levels of ammonia (2.9 mg N per L), iron (2.9 mg L⁻¹), manganese (0.08 mg L⁻¹) and arsenic (0.023 mg L⁻¹) to below the desired level or primary and secondary MCLs.
- The development of biological activity and subsequent complete oxidation of ammonia to nitrate in the system was near the anticipated time once the oxygen and loading rate parameters were optimized for a system only operating 8 hours a day.
- Once optimized, contactor 1 achieved approximately 83% ammonia reduction (to levels as low as 0.5 mg N per L) using medium (1/2 inch diameter) gravel. Contactor 2 using small (1/4 inch diameter) gravel achieved nearly 100% ammonia reduction, theoretically resulting from the additional 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.
- Engineering and design criteria for full-scale implementation of the biological treatment systems were defined (Table S2†). For example, the need to maintain saturated dissolved oxygen concentration throughout the contactor was supported, design loading rate targets were identified, monthly backwash of contactor was established, and orthophosphate feed requirements were described.
- The reduction of ammonia was compromised when the loading rate through the contactor was doubled to simulate the failure of a two-contactor system. Iron, manganese and arsenic, however, were not impacted. Long-term pilot shutdown (9 days) did not negatively impact system performance upon return to normal operation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

The USEPA would like to acknowledge: Julie Sievers, Taroon Bidar and Tara Naber of the Iowa Department of Natural Resources Maria Lucente and John Arduini with the Ohio EPA for reviewing this document; the City of Gilbert, Iowa, for supporting this project; Tad Stupp with the City of Gilbert for operating and maintaining the pilot system, Steve Van Dyke with Fox Engineering for his valuable suggestions; Ronit Erlitzki, Greg Gilles, Chris Clark, Victor Miller, and Rich Cavagnaro of AdEdge Water Technologies for their important contributions to the project and support with the development of the study; USEPA Region 7 staff Brenda Groskinsky (retired) and Amy Shields for supporting much of this research effort under USEPA's Regional Applied Research Effort (RARE) program as well as the USEPA team responsible for administering the RARE program; Carolyn Carter and Mathew Pinelli of USEPA's Oak Ridge Associated Universities (ORAU) program. The U.S. Environmental Protection Agency, through its Office of Research and Development, funded, managed, and collaborated in, the research described herein. It has been subjected to the Agency's administrative review and has been approved for external publication. Any opinions expressed in this paper are those of the author (s) and do not necessarily reflect the views of the Agency, therefore, no official endorsement should be inferred. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Water impact

Many groundwaters contain multiple contaminants that can make treatment challenging. This research demonstrated an aerobic biological treatment approach combined with granular media filtration to reduce ammonia, arsenic, iron and manganese from a natural groundwater. The treatment process effectively reduced all contaminants below levels of concern, was simple and required minimal attention, making it appealing to small systems.

Fig. 1.
The pilot system schematic of an “up-flow” diagram.

Fig. 2.
A photograph of the pilot system at the test location and the granular media used in the aeration contractor of the system.

Fig. 3.
Nitrogen species in effluent water from contactor 1.

Fig. 4.
Field measurements of dissolved oxygen through pilot system.

Fig. 5.
Flow and hydraulic loading rates through contactor 1 and filter 1.

Fig. 6.
Nitrogen species in effluent water from filter 1.

Fig. 7. Nitrogen content of treated water from contactor 2 as a function of depth into contactor.

Fig. 8.
Concentrations of iron in raw and treated water through contactors and filter 1.

Fig. 9.
Concentrations of manganese in raw and treated water through contactors and filter 1.

Fig. 10.
Arsenic speciation in raw, contactor 1 effluent, and filter 1 effluent.

Fig. 11.
Comparison of total arsenic in raw, contactor 1, contactor 2, and filter 1 effluents waters.

Total Arsenic, µg/L	Elapsed Time, Days	Operational Outliers Description
13.1	6	Pilot start up transition
10.4	13	Pilot start up transition
10.4	167	Extended filter run without backwash
10.4	174	Extended filter run without backwash
15.9	268	C1 double loading rate
10.8	271	C1 double loading rate
10.1	281	C1 double loading rate
11.2	286	C1 double loading rate
16.7	287	C1 double loading rate
14.8	293	C1 double loading rate
11.0	322	115 hour filter run
	342	ph adjustment made after sample collection
10.1	355	C1 & F1 backwashed 1 hour prior to collection
10.3	363	1 week filter run between backwash

Fig. 12.
Operation upset occurrences associated with filter 1 total arsenic.

Fig. 13.
pH, temperature and dissolved oxygen of raw water.

Fig. 14.
Total alkalinity of raw, contactor 1, contactor 2 and filter 1 effluent waters.

Fig. 15.
Heterotrophic plate counts of raw, contactor 1, contactor 2 and filter 1 effluent waters.

Table 1

Source water quality in Gilbert, Iowa

Parameter	Well
Total arsenic	27 mg L ⁻¹
Alkalinity	410 mg CaCO ₃ per L
Fe	4.25 mg L ⁻¹
Mn	0.16 mg L ⁻¹
TOC	3.00 mg L ⁻¹
F ⁻	0.50 mg L ⁻¹
Ca	82.0 mg L ⁻¹
Mg	31.0 mg L ⁻¹
NH ₄	3.00 mg N per L
NO ₃	<1.00 mg N per L
NO ₂	<0.10 mg N per L
Temperature, °C	18.0
pH	7.55

Table 2

Timeline of operational changes associated with contactor 1 and 2, and filter 1

Date	Elapsed days	Description
8/17/2016	0	Pilot start up
8/17/2016	0	Contactor 1 flow (loading) rate average 500 mL min ⁻¹ (2.7 gpm ft ⁻²)
8/17/2016	0	Filter 1 flow (loading) rate 400 mL min ⁻¹ (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, 6.9 mg O ₂ per L)
9/13/2016	22	Start acclimation
10/13/16	54	Changed flow (loading) rate of filter to 334 mL min ⁻¹ (1.8 gpm ft ⁻²), contactor to 430 mL min ⁻¹ (2.3 gpm ft ⁻²)
11/1/2016	70	Drop in DO levels in contactor, air flow issues
11/28/2016	100	Backwash of contactor
12/12/2016	114	Air flow increased in contactor (low DO, 3.6 mg O ₂ per L)
1/10/2016	143	Filter 1 ran dry
01/20/17	153	Backwash of contactor
2/14/2017	178	Contactor flow (loading) rate was 370 mL min ⁻¹ (2.0 gpm ft ⁻²)
2/21/2017	185	Contactor flow (loading) rate was at 430 mL min ⁻¹ (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 (loading) rate to 375 mL min ⁻¹ (~2.0 gpm ft ⁻²)
4/17/2017	243	Contactor 2 startup flow (loading) rate 450 mL min ⁻¹ (~2.4 gpm ft ⁻²)
5/06/2017	262	Challenge test #1: contactor flow doubled flow (loading) rate 820 mL min ⁻¹ (4.4 gpm ft ⁻²) <i>ortho</i> -PO ₄ feed adjusted accordingly, Filter 1 shut off for weekend
5/9/2017	265	Filter 1 back online flow (loading) rate of 334 mL min ⁻¹ (1.8 gpm ft ⁻²)
5/11/2017	267	Filter 1 ran dry
5/19/2017	275	Filter 1 ran dry
5/30/2017	286	Contactor flow back to flow (loading) rate of 400 mL min ⁻¹ (~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)

Date	Elapsed days	Description
6/23/2017	310	Contact 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)

Table 3

Water quality summary [average $\pm$ standard deviation (*n*)] during study period

Analyte	Detection limit (mg L ⁻¹)	Raw	Contactor 1	Contactor 2	Filter 1
As	0.40 mg L ⁻¹	22.8 $\pm$ 2.0 (50)	14.0 $\pm$ 3.0 (60)	15.0 $\pm$ 3.0 (48)	8.00 $\pm$ 3.0 (67)
Ca	0.01	69.1 $\pm$ 1.5 (50)	68.6 $\pm$ 1.6 (60)	68.7 $\pm$ 1.5 (48)	68.2 $\pm$ 1.6 (67)
Cl	5.00	1.13 $\pm$ 3.7 (46)	0.51 $\pm$ 1.9 (46)	na	1.96 $\pm$ 4.7 (46)
Fe	0.001	2.94 $\pm$ 0.3 (50)	1.20 $\pm$ 0.6 (60)	1.15 $\pm$ 0.3 (48)	0.02 $\pm$ 0.1 (67)
K	0.3	4.37 $\pm$ 0.1 (50)	4.36 $\pm$ 0.1 (51)	4.39 $\pm$ 0.2 (48)	4.38 $\pm$ 0.2 (67)
Mg	0.005	26.3 $\pm$ 0.6 (50)	26.3 $\pm$ 0.7 (60)	26.2 $\pm$ 0.5 (48)	26.2 $\pm$ 0.7 (67)
Mn	0.001	0.08 $\pm$ 0.003 (50)	0.05 $\pm$ 0.02 (60)	0.05 $\pm$ 0.02 (48)	0.01 $\pm$ 0.01 (67)
Na	0.03	39.4 $\pm$ 1.1 (50)	39.3 $\pm$ 1.1 (60)	39.3 $\pm$ 0.7 (48)	39.3 $\pm$ 1.2 (67)
NH ₃	0.03 (mg-N per L)	2.92 $\pm$ 0.1 (50)	1.57 $\pm$ 0.7 (47)	1.59 $\pm$ 1.0 (48)	0.36 $\pm$ 0.7 (47)
NO ₂	0.01 (mg-N per L)	0.01 $\pm$ 0.0 (46)	0.18 $\pm$ 0.1 (47)	0.20 $\pm$ 0.1 (48)	0.23 $\pm$ 0.4 (47)
NO ₃	0.02 (mg-N per L)	0.04 $\pm$ 0.03 (43)	1.13 $\pm$ 0.7 (46)	1.12 $\pm$ 0.9 (48)	2.35 $\pm$ 0.9 (46)
<i>o</i> -PO ₄	0.025 (mg PO ₄ per L)	0.44 $\pm$ 0.2 (46)	0.36 $\pm$ 0.7 (46)	0.38 $\pm$ 0.08 (42)	0.21 $\pm$ 0.1 (46)
S	0.003	0.12 $\pm$ 0.1 (50)	0.01 $\pm$ 0.01 (60)	0.10 $\pm$ 0.01 (48)	0.09 $\pm$ 0.02 (67)
Sr	0.001	0.90 $\pm$ 0.03 (50)	0.89 $\pm$ 0.02 (60)	0.88 $\pm$ 0.01 (48)	0.89 $\pm$ 0.03 (67)
Total alkalinity	1.00 (mg-CaCO ₃ per L)	410 $\pm$ 2.3 (49)	399 $\pm$ 7.3 (50)	397 $\pm$ 7.4 (48)	390 $\pm$ 8.7 (50)
TOC	0.1 (mg-C per L)	2.74 $\pm$ 0.2 (42)	2.80 $\pm$ 0.12 (41)	2.84 $\pm$ 0.14 (48)	2.78 $\pm$ 0.11 (39)
pH	0.1	7.68 $\pm$ 0.17 (50)	8.07 $\pm$ 0.29 (55)	8.16 $\pm$ 0.13 (14)	8.03 $\pm$ 0.28 (55)
DO	0.01 (mg-O ₂ per L)	1.10 $\pm$ 0.4 (50)	8.94 $\pm$ 2.21 (55)	9.38 $\pm$ 0.4 (14)	8.83 $\pm$ 1.29 (55)
Temperature	0.10 °C	14.2 $\pm$ 2.3 (50)	15.9 $\pm$ 2.2 (55)	16.6 $\pm$ 1.7 (14)	16.3 $\pm$ 2.5 (55)