



Removing arsenic and co-occurring contaminants from drinking water by full-scale ion exchange and point-of-use/point-of-entry reverse osmosis systems

Abraham S.C. Chen^a, Lili Wang^{b,*}, Thomas J. Sorg^c, Darren A. Lytle^d

^a ALSA Tech, LLC, North Potomac, MD, 20878, USA

^b U.S. Environmental Protection Agency, Office of Water, Washington, DC, 20460, USA

^c U.S. Environmental Protection Agency, Retired, USA

^d U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati, OH, 45268, USA

ARTICLE INFO

Article history:

Received 30 August 2019

Received in revised form

10 December 2019

Accepted 30 December 2019

Available online 31 December 2019

Keywords:

Ion exchange

Reverse osmosis

Arsenic

Nitrate

Natural organic matter

Co-occurring contaminants

ABSTRACT

This study investigated the performance of two full-scale ion exchange (IX) systems, one point-of-entry (POE) reverse osmosis (RO) system and nine point-of-use (POU) RO units for simultaneous removal of arsenic and several co-occurring contaminants from drinking water. The study was performed as part of the U.S. Environmental Protection Agency's Arsenic Treatment Demonstration Program. The IX systems, with strong base anionic (SBA) resins, effectively removed arsenic (As), nitrate (NO₃⁻) and uranium (U) to below respective maximum contaminant levels and vanadium (V) and molybdenum (Mo) to below 2 µg/L. The useful run length, as determined by either 10-mg/L (as N) nitrate or 10-µg/L arsenic breakthrough, was approximately 400 bed volumes (BV) initially. However, it was decreased over time, e.g., by 15% in 13 months at one site and 33% in 7 months at another site, apparently caused by resin fouling due to the presence of 2-mg/L natural organic matter (NOM) in source waters. The use of dual resins – an acrylic SBA resin underlain by a polystyrene SBA resin – effectively removed NOM and allowed the system to perform at its baseline level through the 13-month study. Arsenic and nitrate peaking occurred when the resins were not regenerated timely. The removal of contaminants appeared to follow a selectivity sequence: U, Mo > V > SO₄²⁻ > HAsO₄²⁻ > NO₃⁻ > HCO₃⁻. RO effectively removed arsenic, nitrate, antimony, uranium and vanadium, mostly with a >99% rejection rate. The POE RO coupled with dual plumbing (only treating a fraction of water for potable use) and POU RO in individual homes could be used as low-cost alternatives to traditional RO treatment.

© 2019 Elsevier Ltd. All rights reserved.

1. Introduction

Arsenic (As) exposure has long been linked to bladder, lung and skin cancers, and more recent science shows that it can also increase risks of cardiovascular, developmental and birth problems (National Institute of Health, 2014). Arsenic affects the drinking water of millions of people worldwide (World Health Organization, 2011). The U.S. Environment Protection Agency (EPA) lowered the maximum contaminant level (MCL) for arsenic in drinking water from 50 to 10 µg/L in January 2001 (EPA, 2001). Since then, evidence has continued to mount concerning the health effects of its

exposure at levels <10 µg/L (such as Moon et al., 2018; Kuo et al., 2017; National Institute of Health, 2014). Currently, the EPA's Integrated Risk Information System Program is updating its 1988 toxicological review of inorganic arsenic (upon which the 10-µg/L MCL was based) to support EPA's regulatory activities and decisions to protect public health (EPA, 2019). In July 2019, New Hampshire became the second state in the U.S., after New Jersey, to set a more stringent arsenic drinking water standard at 5 µg/L, half of the federal MCL (New Hampshire Public Radio, 2019).

Arsenic levels in the U.S. tend to be higher in groundwater supplying rural small communities, most of which must install treatment systems to meet the federal and state arsenic standards. These small systems continue to seek innovative, cost-effective treatment technologies, especially those proven with full-scale, long-term performance data (Hering et al., 2017). A wealth of

* Corresponding author. U.S. Environmental Protection Agency, 1200 Pennsylvania Ave, NW, Washington, DC, 20460, USA.

E-mail address: wang.lili@epa.gov (L. Wang).

Nomenclature			
ADP	Arsenic Treatment Technology Demonstration Program	NOM	natural organic matter
AM	adsorptive media	NTNCWS	non-transient, non-community water system
As	arsenic	ORP	oxidation-reduction potential
BV	bed volumes	POE	point of entry
COCs	co-occurring contaminants	POU	point of use
CWS	community water system(s)	RO	reverse osmosis or effluent from RO modules
DO	dissolved oxygen	Sb	antimony
EBCT	empty bed contact time	SBA	strong base anionic
EPA	Environmental Protection Agency	SI	Supplementary Information
gpd	gal/day (gallons per day)	SO ₄ ²⁻	sulfate
gpm	gal/min (gallons per minute)	TA	effluent from Tank A
IN	raw water	TB	effluent from Tank B
IX	ion exchange	TDS	total dissolved solids
MCL	maximum contaminant level	TFC	thin-film composite
MDL	method detection limit	TOC	total organic carbon
Mo	molybdenum	TT	combined tank effluent
NO ₃ ⁻	nitrate	U	uranium
		V	vanadium
		WS	effluent from water softener

such data has been collected by EPA's Arsenic Treatment Technology Demonstration Program (ADP) that consisted of 50 full-scale, on-site demonstration projects in 26 states over a 10-year period (Sorg et al., 2015). Technologies evaluated included adsorptive media (AM), ion exchange (IX), point-of-entry (POE)/point-of-use (POU) reverse osmosis (RO), and others.

In addition to arsenic, one or more co-occurring contaminants (COCs) such as antimony (Sb), nitrate (NO₃⁻), uranium (U), vanadium (V) and molybdenum (Mo) were present in source waters of some ADP sites. Among these COCs, Sb, NO₃⁻ and U are regulated by EPA with an MCL of 6 µg/L, 10 mg/L (as N) and 30 µg/L, respectively (EPA, 2018). V and Mo are unregulated but were included in EPA's Contaminant Candidate Lists 3 and 4 for regulatory consideration (EPA, 2016; EPA, 2009). Some states have drinking water guidelines for vanadium with values ranging from 7 to 50 µg/L (Hazardous Substance Data Bank, 2006); EPA has developed a lifetime health advisory of 0.04 mg/L for molybdenum (EPA, 2018). Removal of these COCs by an arsenic treatment technology is generally lacking in the literature. Thus, the ADP provides a unique dataset on their removal. Also, using a treatment technology that can remove multiple COCs is likely more efficient and cost effective (EPA, 2007). This paper reports the removal of arsenic and COCs by IX and POE/POU RO; the removal by AM systems including an hybrid metal (hydr)oxide/anion exchanger, ArsenX^{np} (Sarkar et al., 2007; Sylvester et al., 2007; Cumbal and Sengupta, 2005), is discussed in a companion paper being prepared.

Strong base anionic (SBA) resins are the most studied and commonly used resins for arsenic removal (Clifford et al., 2011; Ilesan et al., 2004; Kim et al., 2003; Wang et al., 2002; Korngold et al., 2001; Vagliasindi and Benjamin, 1998). The resins' affinity for anionic species generally follows a selectivity sequence: uranium is much more preferred to sulfate, which, in turn, is more preferred to arsenate and then nitrate (Purolite, 2016; Clifford et al., 2011; Boodoo et al., 2008; Guter and Jensen, 2003). However, the resins' selectivity for vanadium and molybdenum is unknown. SBA resins are not effective for antimony removal (Arnold et al., 2019). Sulfate has a profound effect on arsenic and COC removal because of its higher selectivity and, often, orders of magnitude higher concentrations (Clifford et al., 2011). Therefore, for waters containing high sulfate (>150 mg/L) and total dissolved solids (TDS) (>500 mg/L), IX may not be an economical choice (Clifford et al., 2011). Furthermore, the

presence of natural organic matter (NOM) in source water can have adverse effects on IX treatment. It was reported that macroporous resins have strong affinities to NOM, such as polyvalent humate and fulvate anions, which could cause resin fouling and short run length (Purolite, 2016; Clifford et al., 2011; Boodoo et al., 2008).

RO is well known for removing ionic species and a variety of solutes from water. For drinking water applications, cellulose acetate or polyamide thin-film composite (TFC) membranes are mostly used (Duranceau and Taylor, 2011; EPA, 2003). RO can remove 80–99% of As(V) (Hou, 2017; Schmidt et al., 2016; Elcik et al., 2015; Akin et al., 2011; Walker et al., 2008; Uddin et al., 2007; EPA, 2006; EPA, 2003; Ning, 2002; Waypa et al., 1997). However, the reported removal efficiencies (or rejection) for As(III) varied from as low as 5% (Amy et al., 2000) to surprisingly high levels similar to those of As(V) (Pawlak et al., 2006; Kang et al., 2000; Brandhuber and Amy, 1998). Other factors affecting RO performance include arsenic concentration of feed water, membrane type, operating pressure and membrane fouling (Schmidt et al., 2016; Walker et al., 2008; George et al., 2006; Persinger and Woolard, 2005; Lin et al., 2002).

Most reported IX and RO studies on arsenic removal were on a bench- or pilot-scale; only a few on full-scale under real world settings (Sorlinia et al., 2014; Boodoo et al., 2008; Walker et al., 2008; EPA, 2006; George et al., 2006; Persinger and Woolard, 2005; Guter and Jensen, 2003; Wang et al., 2002). Even fewer studies reported on long-term performance, such as the ones by Pawlak et al., 2006 and Wang et al. (2002). Data on the simultaneous removal of COCs are also lacking. The objective of this paper is to evaluate the long-term performance of two full-scale IX systems, one POE/RO system and nine POU RO units for the removal of arsenic and COCs. In addition, the ability of these systems to remove arsenic to a lower level such as 5 µg/L as required in New Jersey and New Hampshire is also assessed. Results of the studies can help small system operators, consultants and state personnel select appropriate technologies, identify operational issues and optimize system performance.

2. Materials and methods

2.1. Site descriptions

Table 1 summarizes key information of the four ADP sites where

Table 1
Key ADP Site information.

	Site 1	Site 2	Site 3	Site 4
Location	Fruitland, Idaho	Vale, Oregon	Carmel, Maine	Homedale, Idaho
Type of System	Municipal CWS	Municipal CWS	School NTNCWS	Subdivision CWS
Total No. of Wells	11	7	2	1
Population Served	4000	2000	200	9 Homes
No. of Well(s) Used for ADP	1	7	2	1
Available Flowrate for ADP (gal/min; L/min)	200; 757	525; 1987	30; 114	20; 76
Average Daily Demand (gal/day; m ³ /day)	NA	263,000; 996	1750; 6.6	NA
Co-Occurring Contaminants	NO ₃ ⁻ , U, V, Mo	NO ₃ ⁻ , V, U	Sb	NO ₃ ⁻ , U, V
Technology Selected	IX	IX	POE RO	POU RO

ADP = arsenic treatment technology demonstration program; CWS = community water system; IX = ion exchange.

NA = not available; NTNCWS = non-transient, non-community water system; POE = point of entry; POU = point of use; RO = reverse osmosis.

IX and RO technologies were demonstrated. Table 2 presents IX system design parameters and resin properties whereas Table 3 presents RO system design and operational parameters. Sites 1 and 2 are municipal community water systems (CWS) serving a population of approximately 4000 and 2,000, respectively (Table 1). Site 1 used one of its 11 production wells for the study. Site 2 used all seven wells with water blended to minimize nitrate concentration (note that up to 18.9 mg/L of nitrate was measured historically in two wells [Wang et al., 2011a]). Due to the presence of elevated nitrate in source waters, IX was selected by both sites. Each IX system consisted of sediment filters, IX resin vessels, salt saturators, brine day tanks, and associated pumps, valves, pressure gauges and flow elements/controls for fully-automated system operations. The spent resin was regenerated with a brine solution. The wastewater was discharged to the city sewer at Site 1 and an evaporation pond at Site 2.

Supplied by two wells, Site 3 is a non-transient, non-community water system (NTNCWS) serving nearly 200 students and teachers with an average daily demand of 1750 gal (Table 1). Source water contained elevated arsenic and antimony. A pre-demonstration pilot study was conducted using a 600-gal/day (gpd) RO system, which effectively removed arsenic and antimony from source water to well below their respective MCLs (Wang et al., 2011b). A 9600-gpd POE RO system was initially proposed to treat the entire water supply for the school. Due to high costs associated with expanding the building to house the RO system and constructing a new leach field to receive RO reject water, an innovative dual plumbing approach was developed to treat only a portion of the water for potable use. As a result, a smaller, 1200-gpd RO system was selected to treat only potable water. Installed downstream of a preexisting 600-gal storage tank, the POE RO system consisted of a sediment filter, two TFC RO membrane modules (along with a booster pump and a TDS monitor), a calcite pH adjustment tank, two storage tanks and a re-pressurization system (Table 3). The reject water was discharged to an existing septic system.

Site 4 was a nine-home subdivision supplied by a 20-gal/min (gpm) well (Table 1). The well water contained elevated As, NO₃⁻, U and V. Under the ADP, an NSF Standard 58-listed POU RO unit was installed under-the-sink in the kitchen of each home to treat softened intake water. Each RO unit consisted of a pre-filter cartridge, a TFC RO element, a storage tank and a granular activated carbon post filter (Table 3). The RO unit was also equipped with a TDS monitor and a 500-gal automatic shut-off valve which discontinued water production after 500 gal of water had been processed. The reject water was discharged directly to individual home septic systems.

2.2. Sample collection and handling

Table 4 summarizes sampling activities at the four ADP sites.

During the initial site visit, the EPA contractor (Battelle, Columbus, OH) collected source water samples at either wellheads or combined headers after purging the well(s) for at least 10 min. Upon collection, samples were filtered using 0.45- μ m syringe filters and the filtrate speciated for soluble As(III) and soluble As(V) using a speciation method described in (Sorg et al., 2014). Water quality parameters, including pH, temperature, dissolved oxygen (DO) and oxidation-reduction potential (ORP), were measured onsite. All sample bottles were packed with wet ice and shipped overnight to Battelle for analyses.

During the long-term performance evaluation studies, trained treatment plant operators recorded daily system operational data, such as pressure, flowrate, throughput, hour meter, etc., and collected water samples from the treatment processes, including raw water (designated as IN); effluent from IX tanks A and B (TA and TB) and/or combined tank effluent (TT); and effluent from water softeners (WS) and/or RO modules (RO). The operators also performed onsite arsenic speciation and measured water quality parameters. Sampling schedules generally followed a four-week cycle, with speciation and onsite measurements performed only in the first week. At Site 4, sampling events took place monthly at all nine homes and speciation quarterly only at one home. All samples were packed with wet ice and shipped overnight to Battelle for analyses. Table 5 shows a complete list of analytes.

2.3. IX run length and elution studies

Run length studies were performed multiple times at Sites 1 and 2 to construct breakthrough curves for arsenic and other anions and determine a useful run length to 10- μ g/L arsenic or 10-mg/L (as N) nitrate breakthrough, whichever happened earlier. For each study, a series of grab samples were collected from the IX tank effluent throughout a complete service cycle. The results were used to assess IX system performance and adjust regeneration throughput setpoints.

Elution studies were also performed multiple times at both IX sites to evaluate the effectiveness of a regeneration process and characterize regeneration wastes. During each study, a side stream of the regeneration waste discharge was directed via a piece of Tygon tubing to an 800-mL plastic beaker, which was used as a flow-through cell. A Hanna HI 9635 conductivity/TDS probe and a VWR pH probe were placed inside the beaker to continuously monitor conductivity/TDS, pH and temperature of the water. The water overflowing the flow-through cell was collected in a 32-gal plastic container. Upon completion of the brine draw step, the flow-through cell was immediately transferred to another 32-gal plastic container for continuous measurements and this process continued until the slow and fast rinse steps were completed. A

Table 2
Key IX system design parameters and resin properties.

	Site 1	Site 2	
		Study Period I	Study Period II
Pre-treatment			
Bag Filter Pore Size (μm)	20	20	5
IX Vessels/Resins			
No. of Vessels and Size (in; cm)	2 \times (48 D \times 72 H); 2 \times (122 D \times 183 H)	2 \times (63 D \times 86 H); 2 \times (160 D \times 218 H)	2 \times (63 D \times 86 H); 2 \times (160 D \times 218 H)
Vessel Configuration/Construction	Parallel/FRP	Parallel/FRP	Parallel/FRP
Resin Volume ($\text{ft}^3/\text{vessel}$; m^3/vessel)	50; 1.42	93; 2.63	16/82; 0.45/2.32
Resin Products ^(a)	A300E	Arsenex II	A850END/PFA300 ^(b)
Resin Polymer Structure	STY-DVB	STY-DVB	ACR-DVB/STY-DVB
Resin Functional Group	DMEA	DMEA	TMA/DMEA
Resin Type	SBA Type II	SBA Type II	SBA Type I/SBA Type II
Service			
Design Flowrate (gal/min; L/min)	250; 946	540; 2044	540; 2044
Hydraulic Loading Rate (gal/min/ft ² ; L/min/m ²)	10; 407	12.5; 509	12.5; 509
EBCT (min)	3.0	2.6	2.8
Resin Capacity for NO ₃ ⁻ and As (BV) ^(c)	700 & 880	740 & 680	600 & 700 ^(d)
Regeneration			
Regeneration Mode	Co-current Downflow	Co-current Downflow	Co-current Downflow
Regeneration Level (lb salt/ft ³ ; kg salt/m ³)	10; 160	12; 192	10; 160
Brine Concentration (%)	4	10	8
Brine Draw Duration (min)/Flowrate (gal/min; L/min)	64/23; 87	17/50; 189	21/64; 242
Slow Rinse Duration (min)/Flowrate (gal/min; L/min)	64/23; 87	30/50; 189	45/44; 167
Fast Rinse Duration (min)/Flowrate (gal/min; L/min)	30/75; 284	15/220; 833	15/260; 984
Average Wastewater Produced per Cycle (gal; L)	7100; 26,900	14,500; 54,900	14,500; 54,900
Post-treatment			
Target Chlorine Residual (mg/L [as Cl ₂])	None	0.025	0.025

(a) All supplied by Purolite in chloride form.

(b) Similar to A300E but having a more uniform particle size distribution.

(c) Purolite's computerized simulation.

(d) PFA300 resin.

ACR = polyacrylic; DMEA = dimethyl ethanol amine; DVB = divinylbenzene; EBCT = empty bed contact time; FRP = fiber reinforced plastic; IX = ion exchange; SBA = strong base anionic; STY = polystyrene; TMA = trimethylamine.

series of grab samples was collected from each regeneration step for measurements of As (total), COCs, competing anions and/or total organic carbon (TOC). These analytes also were measured for composite samples taken directly from the respective 32-gal containers after contents in the containers had been well-mixed. A stopwatch was used to measure time elapsed.

2.4. Analytical methods

Water pH, temperature, DO and ORP were measured onsite using a WTW Multi 340i handheld meter after calibration. The ORP probe was checked for accuracy using a standard solution with known ORP value. Analytical methods used for other analytes were all EPA-approved as described in an EPA-endorsed Quality Assurance Project Plan (Battelle, 2003). EPA Method 200.8 with inductively coupled plasma-mass spectrometry was used for metal analyses. Data quality in terms of precision, accuracy, method detection limit (MDL) and completeness met the criteria established in the QAPP.

3. Results and discussion

3.1. Source water quality

Table 5 presents analytical results of the source water samples collected prior to system installation at all four ADP sites. The results were generally representative of the data obtained during the long-

term performance evaluation studies (provided in the Supplementary Information [SI]), except when noted. The four source waters contained 16.7–51.6 $\mu\text{g/L}$ of total As, existing predominantly as As(V). Only a trace amount of As(III) existed; this, along with the elevated DO and ORP readings, suggests that all four source waters were oxidizing in nature. Particulate As concentration at Site 1 was 9.8 $\mu\text{g/L}$, which was unusually high compared with the average concentration of 3.5 $\mu\text{g/L}$ obtained during the performance evaluation study (see Table S1a in SI). Given the low particulate As and As(III) concentrations, total As data were discussed in lieu of As(V) data in this paper. For Site 2, due to water blending from multiple wells, arsenic concentrations varied from 16.0 to 31.8 $\mu\text{g/L}$ (averaged 21.1 $\mu\text{g/L}$) and nitrate from 1.4 to 7.6 (averaged 5.5 mg/L) (see Table S2a in SI); both were significantly lower than those of the Site 1 water. Approximately 2 mg/L of TOC was measured at both IX sites, which led to severe resin fouling at Site 2 (Section 3.2.3). Sites 1 and 2 had relatively low sulfate (<150 mg/L) but high TDS (close to or above 500 mg/L). Very little iron or manganese was present in all source waters, as desired by the IX and RO treatment. Source waters also contained U, V, Sb and/or Mo with all present in soluble form. Vanadium at Site 2 and antimony at Site 3 had concentrations exceeding the applicable state guideline and antimony MCL, respectively.

3.2. IX systems

The performance evaluation studies at Sites 1 and 2 lasted 13 and 29 months, respectively (Table 4). Table 6 summarizes key

Table 3
Key RO system design and operational parameters.

	Site 3	Site 4
System Components		
Sediment Filter Dimension (in, <i>cm</i>)	2.75 D × 10 H; 6.99 D × 25.4 H	NA
Sediment Filter Pore Size (μm)	5	20
No. of RO Membrane Elements	2	1
RO Membrane Construction	TFC	TFC
Membrane Element Dimensions (in, <i>cm</i>)	2.5 D × 40 H; 6.35 D × 102 H	1.7 D × 11 H; 4.3 D × 27.9 H
Booster Pump Size (hp; <i>kw</i>)	½; 0.37	NA
Post Treatment (in; <i>cm</i>)	Calcite Tank (10 D × 44 H; 25.4 D × 112 H)	GAC Cartridge
Storage Tanks Volume (gal; <i>L</i>)	300; 1,136 ^(a)	3; 11.4
Repressurization Pump Size (hp; <i>kw</i>)	1; 0.74	NA
Design Specifications		
Max. Operating Pressure (psi; <i>kPa</i>)	300; 2069	100; 699
pH (S.U.)	2–11	3–11
Daily Production Rate (gal/day; <i>m³/day</i>)	1200; 4.5	35.5; 0.13
Recovery (%)	40	37%
System Shutdown Volume (gal; <i>L</i>)	NA	500; 1893
Flowrate to Distribution System (gal/min; <i>L/min</i>)	16; 61	NA
Operational Parameters		
Average Daily Run Time (hr/day)	11.7 (in session) 1.9 (out of session)	NA
Average Permeate Water Flowrate (gal/min; <i>L/min</i>)	0.8; 3.0	NA
Average Reject Water Flowrate (gal/min; <i>L/min</i>)	1.2; 4.5	NA
Average Feed Water Pressure (psi; <i>kPa</i>)	37; 255	NA
Average Δp across Sediment Filter (psi; <i>kPa</i>)	0.3; 2.1	NA
Average Permeate Discharge Pressure (psi; <i>kPa</i>)	145; 1000	NA
Average Reject Water Discharge Pressure (psi; <i>kPa</i>)	141; 972	NA

(a) Two 300-gal (1136-L) storage tanks.

GAC = granular activated carbon; NA = not applicable or not available; RO = reverse osmosis; TFC = thin film composite.

Table 4
Summary of demonstration study sampling activities.

	Site 1	Site 2		Site 3	Site 4
		Study Period I	Study Period II		
Technology Demonstrated	IX	IX		POE RO	POU RO
Initial Source Water Sampling ^(a)	07/13/04	12/02/04		03/07/06	12/01/04
Study Duration (month)	13	16	13	8	12
Sampling Duration (month)	13	7	11	8	12
Total No. of Sampling Events	49 ^(b)	28 ^(b)	32	21 ^(b)	12 at 8 homes 16 ^(b) at 1 home
No. of Speciation Sampling Events	14	8	0	8	4 ^(c)

(a) See analytical results on Table 5.

(b) Including speciation sampling events.

(c) Taking place quarterly at one home.

IX = ion exchange; NA = not applicable; POE = point of entry; POU = point of use; RO = reverse osmosis.

operational parameters based on daily field logs. With a design value of 3 min, the actual empty bed contact times (EBCT) at Sites 1 and 2 averaged 4.8 and 2.6 (or 2.8) min, respectively, well within the range typical for such systems (Sorlinia et al., 2014; Clifford et al., 2011; Wang et al., 2002). The Site 1 system operated for a total of 13 months uninterrupted. The Site 2 system, however, experienced a variety of water quality (e.g., TOC fouling) and mechanical-related issues (Wang et al., 2011a) during the first 16 months of operation (Study Period I). Upon completion of an investigation into the resin fouling and cleaning, a dual resin approach was adopted; the system operation then resumed for additional 13 months (Study Period II).

3.2.1. Baseline run length determination

Shortly after the two IX systems were placed online, run length

studies were conducted to determine the systems' baseline run lengths and throughput setpoints for resin regeneration. Fig. 1 presents the arsenic and nitrate breakthrough curves from one such study at Site 1. Nitrate had reached its MCL (10 mg/L as N) earlier than arsenic (10 μg/L), which is consistent with the selectivity sequence where the monovalent nitrate ion is less preferred by the SBA resin than the divalent arsenate ion. Thus, the resin useful run length was determined by the nitrate breakthrough at approximately 316,000 gal (422 bed volumes [BV], 1 BV = 748 gal).

At Site 2, however, the useful run length was determined by the 10-μg/L arsenic breakthrough at 562,300 gal (404 BV, 1 BV = 1392 gal); nitrate did not reach 10 mg/L (as N) in the effluent (see Fig. S1 in SI) due to its rather low source water concentration (e.g., 4.1 mg/L as N) Fig. S1.

These baseline run length values were about 60% of the vendor's

Table 5
Source water quality parameters for four selected ADP Sites^(a) and McCook, NE.

Analyte	Site 1	Site 2	Site 3	Site 4	McCook, NE ^(b)
Sampling Date	07/13/04 ^(c)	12/02/04 ^(d)	03/07/06 ^(e)	12/01/04 ^(d)	
pH ^(f) (S.U.)	7.4	7.5	7.9	7.5	7.2
DO ^(f) (mg/L)	2.7 ^(g)	4.8	4.3 ^(g)	5.4	NA
ORP ^(f) (mV)	244 ^(g)	236	351 ^(g)	249	NA
As, total (µg/L)	49.7	16.7	21.1	51.6	12.5 ^(h)
As, particulate (µg/L)	9.8	0.2	0.8	1.9	NA
As(III) (µg/L)	1.0	1.9	0.5	2.9	NA
As(V) (µg/L)	39.0	14.6	19.8	46.8	NA
F ⁻ (mg/L)	0.6	0.5	<0.1	0.9	NA
NO ₃ ⁻ -N (mg/L)	14.0	4.1	NA	8.9	13.0
U, total (µg/L)	19.4 ^(g)	6.1	NA	29.3	31.1
U, soluble (µg/L)	18.6 ^(g)	6.3	NA	30.1	NA
V, total (µg/L)	34.0	46.8	0.5	30.3	NA
V, soluble (µg/L)	33.7	50.4	0.6	31.2	NA
Sb, total (µg/L)	<0.1	NA	12.6	NA	NA
Sb, soluble (µg/L)	<0.1	NA	12.4	NA	NA
Mo, total (µg/L)	6.2	NA	NA	NA	NA
Mo, soluble (µg/L)	6.6	NA	NA	NA	NA
Alkalinity (as CaCO ₃) (mg/L)	379	158	216	305	382
TDS (mg/L)	580 ^(g)	446	246	698	850
SO ₄ ²⁻ (mg/L)	53.0	75.0	11.2	210	226
SiO ₂ (mg/L)	57.4	56.7	9.6	65.5	NA
PO ₄ ³⁻ -P (mg/L)	<0.1	0.3	NA	NA	NA
Fe, total (µg/L)	268	<25	<25	134	NA
Fe, soluble (µg/L)	<25	<25	<25	<25	NA
Mn, total (µg/L)	28.3	1.1	2.0	2.1	NA
Mn, soluble (µg/L)	18.0	0.8	1.9	1.5	NA
Hardness (as CaCO ₃) (mg/L)	240	181	226	310	525
TOC (mg/L)	2.2	2.1	NA	1.8	3.5

(a) Analytes listed in this table also analyzed for samples taken during performance evaluation studies.

(b) Not an EPA ADP site.

(c) Sampled after the designated well was replaced with a newly installed well at a nearby location.

(d) Sampled during initial site visits.

(e) Sampled during a pre-demonstration pilot study.

(f) Measured onsite.

(g) Average concentration/value from treatment plant performance evaluation studies.

(h) Existing predominately as As(V).

DO = dissolved oxygen; NA = not available; ORP = oxidation-reduction potential; TDS = total dissolved solids;

TOC = total organic carbon.

Table 6
Key IX system operational parameters.

	Site 1	Site 2	
		Study Period I	Study Period II
Average Daily Operating Time (hr/day)	17.4	9.5	9.5
Average Daily Production (gal/day; m ³ /day)	167,000; 630	274,000; 1040	277,653; 1050
Peak Daily Use (gal/day; m ³ /day)	255,000; 970	498,000; 1890	524,000; 1980
Average Service Flowrate (gal/min; L/min)	157; 594	534; 2021	536; 2029
Average EBCT (min)	4.8	2.6	2.8
Hydraulic Loading Rate (gal/min/ft ² ; L/min/m ²)	6.2; 253	12.3; 501	12.4; 505
Pressure Loss Across Each Vessel (psi; kPa)	4–13; 28–90	11; 76 ^(a)	11; 76 ^(a)
No. of Regeneration Cycles	202	278	144
Regeneration Frequency (day/regeneration)	2.0	1.7	2.3

(a) Average value.

EBCT = empty bed contact time.

computer simulated values (Table 2) and were used, most of the time, to trigger automatic resin regeneration at Site 1 and Site 2 (Study Period I).

3.2.2. Removal of arsenic and COCs at Site 1

During the 13-month study at Site 1, a total of 49 sets of weekly water samples were collected (Table 4), representing discrete breakthrough points of multiple service runs. To delineate breakthrough patterns for As, NO₃⁻ and V, Fig. 2 presents concentration data as a function of volume throughput values at which water samples were taken. The data clearly showed that the A300E resin

was effective in removing all three anions during the extended study period. However, seven samples collected after approximately 269,000 gal (360 BV) of water treated showed effluent nitrate concentrations exceeding the corresponding influent levels and its 10-mg/L (as N) MCL, indicating chromatographic peaking (Kim et al., 2003). Based on the sampling dates associated with these samples, the resin run length appeared to have decreased gradually from the baseline level to 269,000 gal (360 BV), representing a 15% reduction.

In addition to As, NO₃⁻ and V, other COCs and competing anions were also similarly plotted (see Figs. S2–S5 in SI). Alkalinity, a weakly

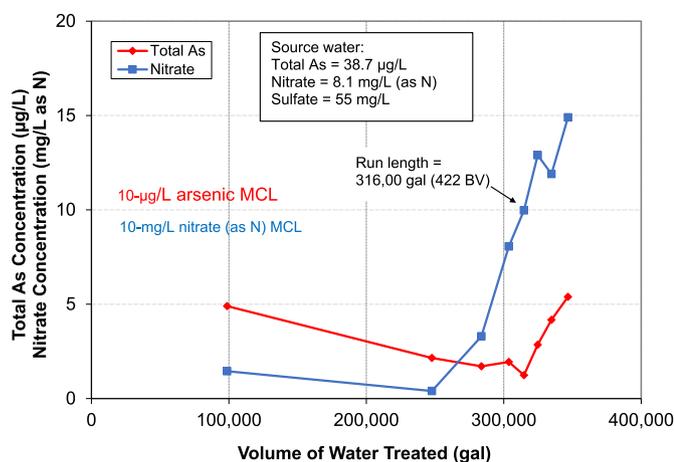


Fig. 1. Arsenic and nitrate breakthrough curves from a baseline run length study conducted at Site 1

Note: Volume of water treated can be converted to BV by dividing it by 748 gal.

preferred anion, was the first to reach exhaustion around 150 BV. At the baseline regeneration setpoint of 422 BV, uranium and molybdenum were removed to ≤ 0.1 $\mu\text{g/L}$ in all but a few samples, indicating that they were highly preferred by the resin. Vanadium appeared to be more preferred to arsenic and even sulfate, as evidenced by a set of incidental samples (due to a faulty sensor) collected at 534,000 gal (714 BV), well beyond the setpoint of 422 BV and, thus, a delayed regeneration. At 714 BV, as arsenic peaking had already occurred (as shown by 41.4 and 46.3 $\mu\text{g/L}$ in the effluent vs. 34.2 $\mu\text{g/L}$ in the influent) and as sulfate had already reached over 87% breakthrough, vanadium continued to be removed to 2.1 $\mu\text{g/L}$ (from 35.4 $\mu\text{g/L}$ in the influent) (data not plotted in Fig. 2c due to improper regeneration). Meanwhile, uranium and molybdenum were also removed continually to <0.1 $\mu\text{g/L}$ (from 16.6 $\mu\text{g/L}$) and 0.7 $\mu\text{g/L}$ (from 12.2 $\mu\text{g/L}$), respectively, indicating that they might be even more preferred to vanadium. Effluent sulfate concentrations were reduced to below 1 mg/L in all but five samples, which were attributed to some regeneration problems. These more preferred anions might have displaced nitrate from the resin, resulting in the chromatographic peaking as discussed above.

The useful run length observed at Site 1 was comparable to the 450 BV reported by Clifford et al. (2011), but shorter than the 4200 BV by Clifford and Lin (1986). The difference in run length might be caused, in part, by the different sulfate concentrations in the raw waters (i.e., 53 mg/L in this study vs. 90 mg/L in the 2011 study vs. 5 mg/L in the 1986 work).

3.2.3. System performance issues

As shown in Fig. 2, relatively high concentrations of As, NO_3^- and V were detected shortly after regeneration at Site 1, indicating early leakage. Of the seven samples collected before 28,000 gal (37 BV) of water treated, up to 40 $\mu\text{g/L}$ of arsenic was detected, which was then tapered down to just over 10 $\mu\text{g/L}$. Similarly, nitrate (although below its MCL) and vanadium concentrations also were elevated in these samples. The early leakage was caused, in part, by incomplete rinse of the IX resin during regeneration, as further discussed in Section 3.2.6. During the following year of the demonstration study, the regeneration process was modified in an attempt to mitigate the leakage issue but produced limited results (Wang et al., 2010). The early leakage observed at Site 1 was not as evident at Site 2.

Fig. 3 presents arsenic breakthrough pattern based on 28 sets of weekly water samples collected at Site 2 (Study Period I), where Arsenex II, a proprietary arsenic-selective resin (Table 2), was used.

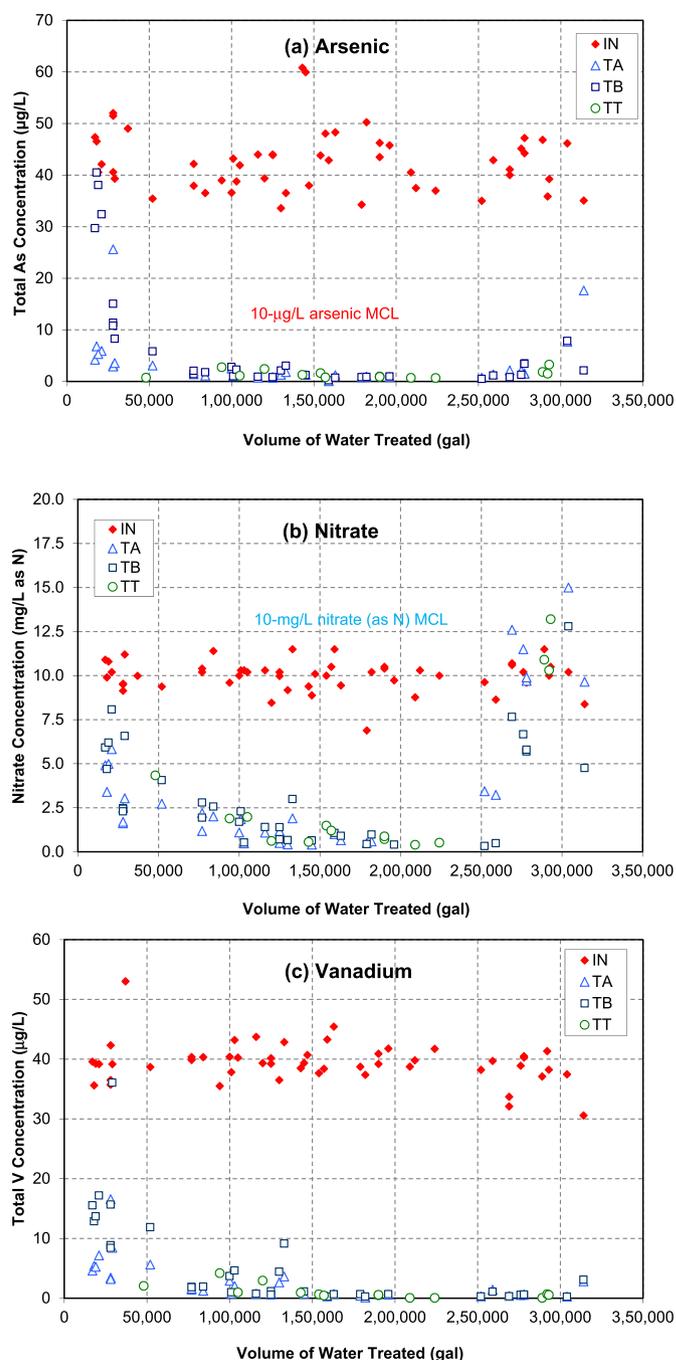


Fig. 2. Contaminant concentrations as a function of throughput measured weekly at Site 1. (a) arsenic; (b) nitrate; (c) vanadium.

Note: Plots for alkalinity, U and Mo shown in SI. U removed from 13.8 to 24.9 $\mu\text{g/L}$ in raw water to <2.5 $\mu\text{g/L}$ in IX-treated water. Mo removed similarly from 11.6 to 15.9 $\mu\text{g/L}$ to <0.8 $\mu\text{g/L}$. Volume of water treated can be converted to BV by dividing it by 748 gal.

Comparing to A300E, Arsenex II's performance had deteriorated much more rapidly, as reflected by the continually decreasing run lengths – from the baseline level of 404 BV to 323 BV in just four months and then to 271 BV in another three months. The overall reduction during the seven-month period was 33%. The shortened run length resulted in more frequent regeneration and, thus, more wastewater being discharged to the evaporation pond. Designed based on a regeneration setpoint of 600,000 gal (431 BV), the evaporation pond was filled faster than expected, presenting a challenge to the city.

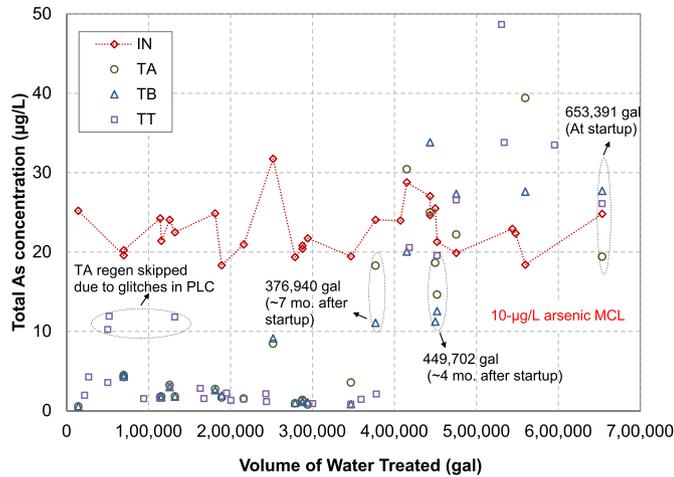


Fig. 3. Total arsenic concentrations as a function of throughput measured weekly at Site 2 (Study Period I)

Note: Volume of water treated can be converted to BV by dividing it by 1392 gal.

Due to deteriorating resin performance at Site 2, resin core samples were collected from IX vessels and examined by the manufacturer. Under a microscope, the resin beads were visibly fouled with particulates and organic buildup. The resin samples were then cleaned in the manufacturer's laboratory with a 10% brine solution or a mixture of 2% caustic and 10% brine followed by resin analyses. Results are shown in Table 7. The caustic and brine mixture appeared to be more effective than brine alone, restoring the resin's volumetric capacity to 94% (vs. 69% achieved by brine only). Nonetheless, 9.6 mg TOC/g of resin still remained after cleaning. Seven months later, resin cleaning was performed in the field using a mixture of 5% caustic and 10% brine, which achieved similar results as in the laboratory (Table 7). The resin run length had been restored to approximately 80% of the baseline level based on a subsequent run length study (Wang et al., 2010), consistent with the restored strong base capacity of the cleaned resin (average of 79%). Six months following the field cleaning, the resin was fouled again, as evidenced by the organic buildup (e.g., 61 mg of TOC/g of resin) and shortened run length (e.g., approximately 60% of the baseline level). A decision was then made to abandon the resin and explore the use of a TOC scavenger resin to address the fouling issue.

Table 7
IX resin analyses after laboratory or field cleaning.

Resin Sample	Moisture (%)	Volumetric Capacity (eq/L)	Percent Volumetric Capacity ^(a) (%)	Percent Strong Base Capacity ^(a) (%)	TOC (mg of C/g of resin)	Iron Content (mg/g)	Silica Content (mg/g)
Arsenex II –virgin	40–45	1.2	100	100	NA	NA	NA
10% Brine Cleaning in Laboratory							
Vessel A	35.5	0.83	69	92	12.0	26	129
2% Caustic/10% Brine Cleaning in Laboratory							
Vessel A	38.0	1.13	94	93	9.6	NA	NA
5% Caustic/10% Brine Cleaning at Site 2							
Vessel A–top	43.2	1.05	88	81	10.7	157	NA
Vessel A –middle	39.9	1.14	95	77	8.0	122	NA
Vessel A –bottom	38.7	1.15	96	79	8.6	14	NA
Six Months after Field Cleaning							
Vessel A	38.7	0.96	80	NA	61.0	120	NA

(a) % = actual capacity/virgin capacity.
IX = ion exchange; NA = not available.

3.2.4. Dual resin approach and McCook study

At the recommendation of the manufacturer, dual resins consisting of 82 ft³ of PFA300 top-dressed with 16 ft³ of A850END in each vessel (Table 2) was used to replace Arsenex II. The PFA300 resin is similar to A300E but has a more uniform particle size; A850END is a Type I acrylic IX resin capable of removing TOC. Prior to implementation, a two-day study was conducted at the treatment plant in McCook, NE, where the same dual resins were used to treat a source water containing elevated NOM, As, NO₃⁻, U and SO₄²⁻ (Table 5). Built in 2006, the 7-million gallons per day treatment plant consisted of six cationic IX vessels (for softening) and six anionic IX vessels (for removing NOM and anions) with staggered regeneration and blending of the effluent with raw water (Boodoo et al., 2008). A complete regeneration and service cycle of one dual anionic IX vessel was monitored to verify the resins' ability to simultaneously remove NOM and anionic contaminants. The breakthrough curves and elution profiles are shown in Figs. S6a and S6b in SI.

Results of the McCook study showed that, after more than two and a half years of service, the dual resin vessel remained effective in removing all anionic contaminants and NOM. NOM removal was evidenced by the below detection level of TOC in all effluent samples. The run length to the 10-µg/L arsenic MCL was around 100 to 150 BV, significantly shorter than that achieved at Site 1, likely caused, in part, by the higher sulfate (226 mg/L) and TDS (850 mg/L) levels in McCook's raw water. The results of the elution study showed that regeneration was effective in stripping off all anions and, especially, NOM, as reflected by >99% recovery of TOC and a distinctive tea color of the spent brine. The percent recovery was calculated by dividing the amount of TOC in the spent brine and rinse water by the amount removed from source water.

3.2.5. Performance of dual resins at Site 2

Following rebedding with dual resins, weekly sampling resumed and continued for 13 months (Study Period II). A run length study was also performed a month later to establish the baseline performance of the dual resins (Fig. 4a). The arsenic breakthrough curve in Fig. 4a was superimposed in Fig. 4b (in solid line), where total arsenic concentrations were plotted against volume throughput (in dots) when the weekly effluent samples were taken. The run length to the 10-µg/L arsenic breakthrough as reflected by the breakthrough pattern (in dots) was estimated to be 472,500 gal (385 BV, 1 BV = 1226 gal) that was very close to that shown by the baseline breakthrough curve. (Note that the number

of BV was calculated based on 82 ft³ of PFA300 resin in each vessel and that the regeneration throughput setpoint was set at 600,000 gal as desired by the city). Nearly overlapping of the breakthrough pattern with the baseline breakthrough curve clearly indicates that the dual resins were capable of maintaining the baseline-level performance throughout the entire Study Period II and that A850END resin had successfully protected the PFA300 resin from fouling. Not surprisingly, arsenic peaking occurred at and beyond 488,000 gal (398 BV).

As also shown in Fig. 4b, arsenic breakthrough reached 10 µg/L shortly after it had reached 5 µg/L, apparently due to a very sharp IX wavefront (Clifford et al., 2011). The run length for a 5-µg/L breakthrough was only about 12,000 gal (10 BV) less than that for 10 µg/L. As such, IX can be a viable treatment option should the treatment target be lowered to 5 µg/L.

Breakthrough patterns for other anions are provided in Figs. S7–S10 in SI. Nitrate breakthrough did not reach its 10-mg/L (as N) MCL due to its low influent concentrations. However, nitrate peaking occurred about the same time as the arsenic peaking (Fig. S7). Similar to Site 1, vanadium continued to be removed (i.e., from 51 to below 3 µg/L on average), confirming that it was more preferred to arsenic, nitrate and even sulfate (Figs. S7–S9). Alkalinity (i.e., bicarbonate) removal during the early part of the anion exchange cycle resulted in a pH reduction that could potentially create corrosion issues. This well-known phenomenon, often cited

as a disadvantage of IX treatment, could be minimized by staggering regeneration of a multiple tank system and/or by blending with raw water as being practiced at McCook, NE. As shown in Table S2c in SI and Fig. 4a, TOC was consistently removed to below 1 mg/L during the study, indicating that A850END resin was an effective TOC scavenger. As a precautionary measure, the dual resin beds were washed with a 5% caustic/10% brine mixture once every four months.

3.2.6. Elution studies and waste characterization

Elution studies were performed multiple times at both IX sites to help improve regeneration efficiency and reduce waste production. Only one elution study performed at Site 1 is described herein. Fig. 5 presents elution curves for As, NO₃⁻, SO₄²⁻, TDS and pH from regeneration of one IX vessel at Site 1. The elution profiles shown were typical of an IX system and similar to those observed previously (Wang et al., 2002). After an 8% brine was drawn into the vessel, as reflected by a sharp increase in TDS, As, NO₃⁻ and SO₄²⁻ on the exhausted resin were displaced by the highly concentrated chloride ions and eluted into the spent brine. Peak arsenic (18.9 mg/L) and sulfate (49 g/L) concentrations were detected first, followed immediately by peak nitrate (2.2 g/L as N). Towards the end of the fast rinse step, 35 µg/L of arsenic was still measured in the rinse water, thus contributing to the early leakage observed after the IX system had returned to service (Section 3.2.3). Extending the fast rinse time from 6 to 15 min, however, did not completely address the issue. (In contrast, at Site 2, the arsenic concentration at the end of the fast rinse was <0.1 µg/L) As shown in Fig. 5, pH values also rose sharply from 7.5 to around 9.0, presumably due to the release of bicarbonate from the resin, but fell eventually to around 6.0 at the end of fast rinse due to removal of bicarbonate by the freshly regenerated resin.

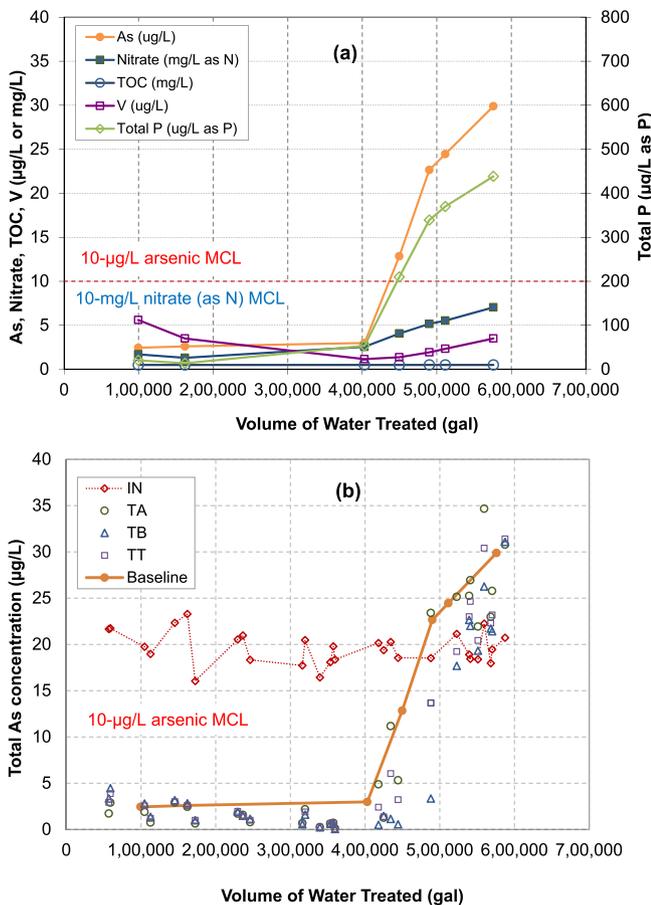


Fig. 4. (a) Breakthrough curves from a dual resin baseline run length study; (b) arsenic concentrations as a function of throughput measured weekly at Site 2 (Study Period II with the use of dual resins) overlaid with the baseline arsenic breakthrough curve.

Note: Volume of water treated can be converted to BV by dividing it by 1226 gal.

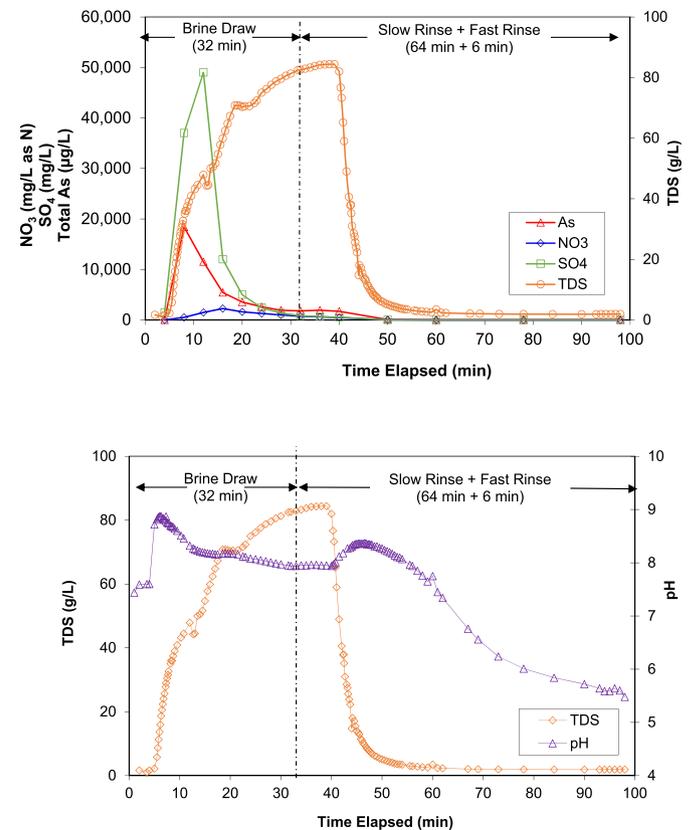


Fig. 5. TDS, pH As, NO₃⁻ and SO₄²⁻ elution profiles during resin regeneration at Site 1.

Composite wastewater samples collected from the same elution study showed an average of 6270, 216 and 24 $\mu\text{g/L}$ of As; 933, 124 and 5.9 mg/L (as N) of NO_3^- and 10, 800, 314 and 18 mg/L of SO_4^{2-} in spent brine, slow rinse water and fast rinse water, respectively. Considering the volume of wastewater produced from each regeneration step, it was estimated that 47.2 g of As, 7.9 kg of NO_3^- (as N) and 79.1 kg of SO_4^{2-} was discharged to the city sewer.

3.3. POE RO system

Prior to the startup of the POE RO system, the existing distribution system in the school buildings was converted into a duplex system with a separate potable and a non-potable lines. The potable line supplied RO-treated water only to kitchen sinks and dishwasher (both cold and hot water), water fountains and cold water faucets in restrooms. Faucets associated with the non-potable line were tagged with "Do Not Drink" signs so that the water was not accidentally consumed for potable purpose.

During the 8-month study, a total of 21 sampling events took place and the results are summarized in Table 8. After passing through the RO unit, alkalinity values were reduced from 206 mg/L (as CaCO_3) in raw water to 5.6 mg/L in permeate water, while pH values decreased from 7.9 to 6.9 (a lower pH value of 5.7 was observed during the pre-demonstration pilot study). The permeate water was mineralized to bring the pH back up to 7.4 and chlorinated prior to entering the potable line. Arsenic and antimony concentrations were reduced from 18.1 and 10.8 $\mu\text{g/L}$, respectively, in source water to below 0.1 $\mu\text{g/L}$ in permeate water, corresponding to a rejection rate of >99%. Their concentrations in reject water averaged 31.9 and 17.7 $\mu\text{g/L}$, respectively (data not shown). In addition to removing arsenic and antimony, the RO unit also removed a variety of ions such as SO_4^{2-} , SiO_2 , alkalinity, TDS and hardness, all with over 96% rejection. The ability of the RO unit to remove As (III) was not evaluated due to the absence of As(III) (averaging 0.2 $\mu\text{g/L}$) in source water.

The dual plumbing with the smaller 1200-gpd RO system was found to be more cost effective than the originally proposed 9600-gpd RO unit treating the entire water supply. The major cost saving was from the use of an existing building to house the system and the reduced quantity of reject water being discharged to the existing septic system.

3.4. POU RO units

Water usage at one of the nine homes was monitored using a totalizer. This and four other residences reached the 500-gal automatic shut-off point and, thus, replaced the pre- and post-filter cartridges for continuing water production.

Table 9 presents average concentrations/values of key analytes sampled at wellhead and nine residents during the one-year study. Following the RO treatment, average pH values were reduced from 7.3 (source water) to 6.6 due, again, to removal of bicarbonate ions. As expected, the softeners effectively removed Ca and Mg hardness (>99%). Total As concentrations in permeate water were <0.1 $\mu\text{g/L}$ except for four samples (8.7, 5.1, 1.2 and 1.2 $\mu\text{g/L}$ [data not shown]). Based on the average As concentration of 57.8 $\mu\text{g/L}$ in source water, the rejection rate was >99%. Up to 3.0 $\mu\text{g/L}$ of As(III) was measured in four source water speciation samples. The rejection rate for As(III) was 73%. These and other results shown in Table 9 clearly demonstrate that the RO treatment was capable of effectively and consistently removing As, NO_3^- , and U to well below their respective MCLs and V to below 2 $\mu\text{g/L}$.

The reject water contained, on average, 74.1 $\mu\text{g/L}$ of total As, 13.9 mg/L of NO_3^- (as N), 32.1 $\mu\text{g/L}$ of U and 40.2 $\mu\text{g/L}$ of V. When using POU RO units, frequently cited limitations including the relatively low fraction of treated water produced, high concentrations of contaminants in the reject water, waste disposal limitations and energy costs did not appear to pose a problem to homes at Site 4.

4. Conclusions

Assessment of the long-term performance data from the ADP demonstrates that both IX and RO can be used by small water systems to simultaneously remove arsenic, nitrate and other COCs from drinking water supplies. To achieve desired treatment objectives, however, care must be taken to identify any operational and performance issues (especially for IX systems) so that they may be resolved timely. The following conclusions are drawn from the study:

- The two ADP IX systems can remove arsenic, nitrate and uranium to below the respective MCLs and vanadium and molybdenum to below 2 $\mu\text{g/L}$, provided that the systems are regenerated properly and in a timely manner. Otherwise,

Table 8
Key RO treatment results at Site 3^(a).

Analyte	Sampling Location	Average Concentration	Percent Removal
pH (S.U.)	IN	7.9	
	RO	6.9	
	AP	7.4	
As, total ($\mu\text{g/L}$) ^(b)	IN	18.1	>99
	RO	0.1	
Sb, total ($\mu\text{g/L}$) ^(c)	IN	10.8	>99
	RO	<0.1	
SO_4^{2-} (mg/L)	IN	9.8	>99
	RO	<0.1	
SiO_2 (mg/L)	IN	11.2	96
	RO	0.5	
Alkalinity (as CaCO_3) (mg/L)	IN	206	97
	RO	5.6	
TDS (mg/L)	IN	255	97
	RO	8.6	
Hardness (as CaCO_3) (mg/L)	IN	217	>99
	RO	1.2	

(a) Data from 13 weekly and 8 monthly speciation sampling events.

(b) As existed almost entirely as As(V).

(c) Existing predominately in soluble form.

AP = after calcite filter; IN = at combined header; RO = after RO unit; TDS = total dissolved solids.

Table 9
RO treatment results at Site 4^(a).

Analyte	Sampling Location	Sample Count	Average Concentration	Percent Removal
pH (S.U.)	IN	9	7.3	
	WS	9	7.6	
	RO	7	6.6	
As, total ($\mu\text{g/L}$)	IN	12	57.8	
	WS	100	57.2	
	RO	100	0.4	>99
As(III) ($\mu\text{g/L}$)	IN	4	1.5	
	WS	4	1.5	
	RO	4	0.4	73
NO_3^- (mg/L as N) ^(b)	IN	12	10.2	
	WS	100	10.3	
	RO	100	1.0	90
U, total ($\mu\text{g/L}$) ^(b)	IN	12	27.4	
	WS	22	27.2	
	RO	22	<0.1	>99
V, total ($\mu\text{g/L}$) ^(b)	IN	12	32.4	
	WS	22	33.1	
	RO	22	0.2	>99
SO_4^{2-} (mg/L)	IN	12	167	
	WS	100	168	
	RO	100	0.6	>99
SiO_2 (mg/L)	IN	12	66.5	
	WS	100	66.6	
	RO	100	2.8	96
Alkalinity (as CaCO_3) (mg/L)	IN	12	295	
	WS	100	294	
	RO	100	12.4	96
TDS (mg/L)	IN	12	685	
	WS	100	704	
	RO	100	26.2	96
Hardness (as CaCO_3) (mg/L)	IN	12	238	
	WS	100	1.7	
	RO	100	0.5	>99

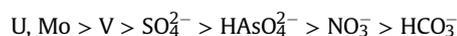
(a) Data from 12 monthly sampling events at nine homes and four quarterly speciation events at one home.

(b) Existing predominately in soluble form.

IN = at wellhead; RO = after RO unit; TDS = total dissolved solids; WS = after water softener.

chromatographic peaking of nitrate and/or arsenic may occur due to the presence of more preferred anions such as sulfate. Nitrate peaking, in particular, should be avoided because of its potential acute health effects. It would be prudent for water systems to conduct run length studies at the system startup to establish baseline performance and track signs of run length deterioration during long-term operation.

- Based on the breakthrough behavior of various anions observed in this study, their removal by SBA resins appears to follow a selectivity sequence shown below:



Additional research may be warranted to confirm the relative order of preference for vanadium and molybdenum.

- The presence of NOM in source water, even as low as 2 mg/L, can cause severe resin fouling and deteriorating run length. In this study, 15% reduction in run length was observed in 13 months at Site 1 whereas 33% reduction in 7 months at Site 2. The use of a dual resin approach – an acrylic SBA resin underlain by a polystyrene SBA resin – can effectively remove NOM and prevent the resin from fouling.
- The POU/POE RO systems are highly effective in removing arsenic, COCs (such as nitrate, antimony, vanadium and uranium) and other common ions in the water. In particular, RO is one of the few technologies capable of removing antimony. Coupled with dual plumbing, POE RO can be a lower-cost alternative where only a portion of the water supply is treated for potable use.

- Either IX or RO can be a viable treatment option for water systems required to meet a more stringent arsenic standard of 5 $\mu\text{g/L}$ (such as in New Jersey and New Hampshire). In this study, the run length to 5- $\mu\text{g/L}$ arsenic breakthrough was only about 10 BV shorter than that to 10- $\mu\text{g/L}$ arsenic breakthrough.

While the treatment technologies evaluated in this paper are effective in reducing multiple inorganic contaminants, secondary considerations must be made when selecting the most appropriate treatment technology. Residuals disposal options and composition are key consideration. For example, IX and RO produce a liquid brine waste and concentrated reject wastewater, respectively, that require on-site disposal options. Equally important are capital and operating costs of the systems that must also be considered in the treatment selection process (Sorg et al., 2015).

Disclaimer

The U.S. Environmental Protection Agency, through its Office of Research and Development, funded and managed, or partially funded and collaborated in, the research described herein. It has been subjected to the Agency's peer and 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.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The staff of the Public Works at the Cities of Fruitland, ID, and Vale, OR, the staff of Carmel Elementary School in Carmel, ME, and homeowners of the Sunset Ranch Development in Homedale, ID, collected operational data and water samples and performed onsite speciation and analyses. Battelle staff members, including Wendy Condit, Gary Lewis and Anbo Wang, assisted with demonstration coordination and data compilation and Battelle ICP Laboratory staff for metal analyses.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2019.115455>.

References

- Amy, G.L., Edwards, M., Benjamin, M., Carlson, K., Chwirka, J., Brandhuber, P., McNeil, Vagliasindi, F., 2000. Treatability Options and Evaluation of Residuals Management Issues. AWWARF, Denver, CO.
- Akin, I., Arslan, G., Tor, A., Cengeloglu, Y., Ersoz, M., 2011. Removal of arsenate [as(V)] and arsenite [as(III)] from water by SWHR and BW-30 reverse osmosis. *Desalination* 281 (17), 88–92.
- Arnold, M., Kangas, P., Makinen, A., Lakay, E., Isomaki, N., Laven, G., Gericke, K., Pajuniemi, P., Kaartinen, T., Wendling, L., 2019. Mine water as a resource: selective removal and recovery of trace antimony from mine-impacted water. *Mine Water Environ.* 38, 431–446.
- Battelle, 2003. Revised Quality Assurance Project Plan for Evaluation of Arsenic Removal Technology. Prepared under Contract No. 68-C-00-185, Task Order No. 0019 for U.S. EPA (Cincinnati, OH).
- Boodoo, F., Schreiber, G., Satchell, T., Benton, L., Szczesny, B., Woo, E., Mielke, D., 2008. Simultaneous Ion Exchange Removal of Arsenic, Nitrate, Uranium, and TOC at City of McCook, NE. AWWA Inorganic Contaminants Workshop, Albuquerque, NM.
- Brandhuber, P., Amy, G., 1998. Alternative methods for membrane filtration of arsenic from drinking water. *Desalination* 117 (1–3), 1–10.
- Clifford, D.A., Lin, C.C., 1986. Arsenic Removal from Groundwater in Hanford, California – A Preliminary Report. Department of Civil/Environmental Engineering, University of Houston.
- Clifford, D.A., Sorg, T.J., Ghurye, G.L., 2011. Ion exchange and adsorption of inorganic contaminants. In: Edzwald, J.K. (Ed.), *Water Quality & Treatment: A Handbook on Drinking Water*, sixth ed. American Water Works Association, McGraw-Hill, New York.
- Cumbal, L., Sengupta, A.K., 2005. Arsenic removal using polymer-supported hydrated iron(III) oxide nanoparticles: role of donnan membrane effect. *Environ. Sci. Technol.* 39 (17), 6508–6515.
- Duranceau, S.J., Taylor, J.S., 2011. Membranes. In: Edzwald, J.K. (Ed.), *Water Quality & Treatment: A Handbook on Drinking Water*, sixth ed. American Water Works Association, McGraw-Hill, New York.
- Elicik, H., Celik, S.O., Cakmakci, M., Ozkaya, B., 2015. Performance of nanofiltration and reverse osmosis membranes for arsenic removal from drinking water. *J. Desalin. Water Treat.* 57 (43), 20422–20429.
- EPA, 2001. National primary drinking water regulations: arsenic and clarifications to compliance and new source contaminants monitoring. *Fed. Regist.* 40, 141–142. CFR Parts 9.
- EPA, 2003. Arsenic Treatment Technology Evaluation Handbook for Small Systems. Office of Water, Washington D.C. EPA 816-R-03-014.
- EPA, 2006. Point-of-Use or Point-of-Entry Treatment Options for Small Drinking Water Systems. Office of Water, Washington D.C. EPA 815-R-06-010.
- EPA, 2007. Removing Multiple Contaminants from Drinking Water: Issues to Consider. Office of Water, Washington D.C. EPA 816-H-07-004.
- EPA, 2009. Drinking water contaminant candidate list 3 – final. *Fed. Regist.* 74. FR 51850.
- EPA, 2016. Drinking water contaminant candidate list 4 – final. *Fed. Regist.* 81. FR 81099.
- EPA, 2018. 2018 Edition of the Drinking Water Standards and Health Advisories Tables. Office of Water, Washington, DC. EPA 822-F-18-001.
- EPA, 2019. Updated Problem Formulation and Systematic Review Protocol for the Inorganic Arsenic IRIS Assessment. U.S. Environmental Protection Agency, Washington, DC. EPA/635/R-19/049.
- George, C.M., Smith, A.H., Kalman, D.A., Steinmaus, C.M., 2006. Reverse osmosis filter use and high arsenic levels in private well water. *Arch. Environ. Occup. Health* 61 (4), 171–175.
- Guter, G., Jensen, P., 2003. Large-scale Arsenic treatment of drinking water sources – small-scale pilot testing is No substitute for large-scale demonstration when an arsenic removal strategy is implemented. *J. Am. Water Work. Assoc.* 95 (6), 64.
- Hering, J.G., Katsoyiannis, I.A., Theoduloz, G.A., Berg, M., Hug, S.J., 2017. Arsenic removal from drinking water: experiences with technologies and constraints in practice. *J. Environ. Eng.* 143 (5), 03117002.
- Hazardous Substances Data Bank (HSDB), 2006. Elemental Vanadium (Environmental Standards & Regulations – State Drinking Water Guidelines). US National Library of Medicine, Bethesda, MD.
- Hou, Y., 2017. An Improved Method of Arsenic (III) Removal by Reverse Osmosis Membrane. M.S. Thesis. Marquette University, Milwaukee, Wisconsin.
- Iesan, C., Bapat, S.S., Fries, B., Coman, D., Florea, D., 2004. Arsenic removal from drinking water by ion exchange resins. *Environ. Engrg. & Manag. J.* 3 (3), 283–291.
- Kang, M., Kawasaki, M., Tamada, S., Kamei, T., Magara, Y., 2000. Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes. *Desalination* 131 (1–3), 293–298.
- Kim, J., Benjamin, M.M., Kwan, P., Chang, Y., 2003. A novel ion exchange process for as removal. *J. Am. Water Work. Assoc.* 95 (3), 77–85.
- Korngold, E., Belayev, N., Aronov, L., 2001. Removal of arsenic from drinking water by anion exchangers. *Desalination* 141, 81, 2001.
- Kuo, C.-C., Moon, K.A., Wang, S.-L., Silbergeld, E., Navas-Acien, A., 2017. The association of arsenic metabolism with cancer, cardiovascular disease, and diabetes: a systematic review of the epidemiological evidence. *Environmental Health Perspectives* 125 (8), 87001–1–87001–15.
- Lin, T.F., Hsiao, H.C., Wu, J.K., Hsiao, H.C., Yeh, J.H., 2002. Removal of arsenic from groundwater using point-of-use reverse osmosis and distilling devices. *Environ. Technol.* 23 (7), 781–790.
- Moon, K.A., Oberoi, S., Barchowsky, A., Chen, Y., Guallar, E., Nachman, K.E., Rahman, M., Soheli, N., D'Ipolliti, D., Wade, T.J., James, K.A., Farzan, S.F., Karagas, M.R., Ahsan, H., Navas-Acien, A., 2018. A dose-response meta-analysis of chronic arsenic exposure and incident cardiovascular disease. *International Journal of Epidemiology* 46 (6), 1924–1939.
- National Institute of Health, 2014. Arsenic Fact Sheet. <https://www.niehs.nih.gov/health/topics/agents/arsenic/index.cfm>.
- New Hampshire Public Radio, 2019. <https://www.nhpr.org/post/nh-becomes-second-state-sharply-lower-arsenic-limit-drinking-water#stream/0>.
- Ning, R.Y., 2002. Arsenic removal by reverse osmosis. *Desalination* 143 (3), 237–241.
- Pawlak, Z., Zak, S., Zablocki, L., 2006. Removal of hazardous metals from groundwater by reverse osmosis. *Pol. J. Environ. Stud.* 15 (4), 579–583.
- Persinger, D.A., Woolard, C.R., 2005. Evaluation of Point-of-Use and Centralized Treatment Systems for Arsenic Removal in Small Drinking Water Systems in Alaska. World Water and Environ, Resources Congress.
- Purolite, 2016. Application Guide: Purolite Resins for Potable and Groundwater Treatment.
- Sarkar, S., Blaney, L.M., Gupta, A., Ghosh, D., SenGupta, A.K., 2007. Use of ArsenXnp, a hybrid anion exchanger, for arsenic removal in remote villages in the Indian subcontinent. *React. Funct. Polym.* 67 (12), 1599–1611.
- Schmidt, S.A., Gukelberger, E., Hermann, M., Fiedler, F., Brobmann, B., Hoinkis, J., Ghosh, A., Chatterjee, D., Bundschuh, J., 2016. Pilot study on arsenic removal from groundwater using a small-scale reverse osmosis system towards sustainable drinking water production. *J. Hazard Mater.* 318 (15), 671–678.
- Sorg, T.J., Chen, A.S.C., Wang, L., 2014. Arsenic species in drinking water wells in the USA with high arsenic concentrations. *Water Res.* 48 (1), 156–169.
- Sorg, T.J., Wang, L., Chen, A.S.C., 2015. The costs of small drinking water systems removing arsenic from groundwater. *J. Water Supply Res. Technol. - Aqua* 64 (3), 219–234.
- Sorlinia, S., Gialdina, F., Collivignarellib, M.C., 2014. Survey on full-scale drinking water treatment plants for arsenic removal in Italy. *Water Pract. Technol.* 9 (1), 43–51.
- Sylvester, P., Westerhoff, P., Möller, T., Badruzzaman, M., Boyd, O., 2007. A hybrid sorbent utilizing nanoparticles of hydrous iron oxide for arsenic removal from drinking water. *Environ. Eng. Sci.* 24 (1), 104.
- Uddin, T., Mozumder, M.I., Figoli, A., Islam, A., Drioli, E., 2007. Arsenic removal by conventional and membrane technology: an overview. *Indian J. Chem. Technol.* 14, 441–450.
- Vagliasindi, F.G.A., Benjamin, M.M., 1998. Arsenic removal in fresh and non-preloaded ion exchange packed bed adsorption reactors. *Water Sci. Technol.* 38 (6), 337–343.
- Walker, K., Seiler, R.L., Meinert, M., 2008. Effectiveness of household reverse-osmosis systems in a western U.S. Region with high arsenic in groundwater. *Sci. Total Environ.* 389 (2–3), 245–252.
- Wang, L., Chen, A.S.C., Sorg, T.J., Fields, K.A., 2002. Field evaluation of as removal by IX and AA. *J. Am. Water Work. Assoc.* 94 (4), 161–173.
- Wang, L., Chen, A.S.C., Wang, A., 2010. Arsenic Removal from Drinking Water by Ion Exchange. U.S. EPA Demonstration Project at Fruitland, ID. Final Performance Evaluation Report. Office of Research and Development, Cincinnati, OH. EPA/600/R-10/152.
- Wang, L., Chen, A.S.C., Wang, A., Condit, W.E., 2011a. Arsenic and Nitrate Removal from Drinking Water by Ion Exchange. U.S. EPA Demonstration Project at Vale, OR. Final Performance Evaluation Report. Office of Research and Development, Cincinnati, OH. EPA/600/R-11/040.

Wang, L., Lewis, A.M., Chen, A.S.C., 2011b. Arsenic and Antimony Removal from Drinking Water by Point-of-Entry Reverse Osmosis Coupled with Dual Plumbing Distribution. U.S. EPA Demonstration Project at Carmel Elementary School in Carmel, ME. Final Performance Evaluation Report. Office of Research and Development, Cincinnati, OH. EPA/600/R-11/026.

Waypa, J.J., Elimelech, M., Hering, J.G., 1997. Arsenic removal by RO and NF membranes. *J. Am. Water Work. Assoc.* 89 (10), 102–114.

World Health Organization, 2011. Arsenic in Drinking-Water. Background Document for Development of WHO Guidelines for Drinking-Water Quality.