Modeling Fate and Transport of Arsenic in a Chlorinated Distribution System

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Abstract

Experimental and modeling studies were conducted to understand the fate and transport properties of arsenic in drinking water distribution systems. Pilot scale experiments were performed in a distribution system simulator by injecting arsenic and measuring both adsorption onto iron pipe material and the oxidation of arsenite by hypochlorite in tap water to form arsenate. A mathematical model describing these processes was developed and simulated using EPANET-MSX, a hydraulic and multi-species water quality software for pipe networks. Model parameters were derived from the pilot-scale experiments. The model was applied to both the distribution system simulator and EPANET example network #3, a real-world model of a drinking water system serving approximately 78,000 customers. The model can be applied to systems-level studies of arsenic fate and transport in drinking water resulting from natural occurrences, accidental spills, or intentional introduction into water.

Keywords: fate and transport, arsenic, EPANET-MSX

1. Introduction

Arsenic (As) is a naturally occurring toxic material that is highly soluble and often found in water sources.¹ The U.S. Environmental Protection Agency reduced maximum contaminant level (MCL) for As from 50 ppb to 10 ppb ($\mu\text{g/L}$) in 2001.² This MCL reduction and the known toxicity of As have resulted in significant research into technologies to remove As from drinking water.^{3–44} Due to the high affinity of iron-based materials for As, many of these studies have investigated how much As adsorbs onto different iron-based materials in order to understand their viability for As removal in drinking water treatment.^{3–31,34,35,42,44}

Iron-based pipe materials can be found in the majority of drinking water distribution systems. Cast iron, ductile iron, and steel have been used in water distribution systems for many years. While some of this infrastructure is slowly being replaced with other materials, such as cement-lined cast iron, many older pipes within a distribution network may still have exposed iron-based surfaces. Over time, these iron-based pipes corrode and can also acquire mineral deposits or biofilms.^{45–49} The corroded surface of iron pipes has been found to contain a mixture of different species of iron, such as amorphous ferrihydroxide, goethite, ferrihydrite, siderite, lepidocrocite, and magnetite.⁴⁶ If arsenic is present in the water, it can adsorb to these iron-based pipe materials. Segments of pipes taken out of service have been found to contain elevated As levels even though only low As levels were present in the water.⁴⁶

The goal of this study was to develop a predictive model of arsenic fate and transport in drinking water systems. To this

end, experimental studies were conducted to measure arsenic adsorption to and desorption from pipe walls and arsenite oxidation in chlorinated water. Cast iron coupons that were allowed to corrode in tap water were used to mimic the inner surface of pipes in older distribution systems, or where defects may have formed in newer cement-lined iron pipes. A mathematical model was developed that incorporates adsorption, desorption, advection, and reaction with chlorine. Model parameters were estimated from data collected during pilot-scale experiments. The model was simulated using EPANET-MSX, a hydraulic and multi-species water quality modeling tool, and applied to models of both a pilot scale pipe loop and a real-world drinking water system. The model is simple enough to apply to full-scale distribution system models to investigate naturally occurring arsenic or accidental contamination with arsenic species.

2. Background

Despite having been extensively studied, there is little agreement within the literature regarding the selection of adsorption models and associated parameters for modeling arsenic adsorption. Differences in test materials, research goals, and experimental designs have led to a wide range of numerical parameters for each adsorption model. General trends in adsorption behavior are consistent between various studies, but the interpretation of the behavior varies. Further, the species of iron involved in the adsorption process will also alter the affinity for arsenic.

A significant body of research has highlighted arsenic's affinity for iron-based materials. Pierce and Moore^{3,4} reported adsorption characteristics for arsenite (As^{3+}) and arsenate (As^{5+}) on

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amorphous iron hydroxide particles as well as other iron compounds. They found that arsenite has a maximum adsorption at neutral pH values (pH 7), with slight decreases at higher or lower pH values. Maximum arsenate adsorption occurs at low pHs, and decreases with increasing pH. Additionally, the adsorption behavior (concentration vs. adsorption) for arsenate was shown to be linear at high concentrations (> 1 ppm As) and follow the Langmuir isotherm at lower concentrations (< 1 ppm As).⁴ Arsenic adsorption on other iron-based materials has been previously fit to the Langmuir isotherm,^{3,4,15,16} the Freundlich isotherm^{7,8,26,29} or both^{6,19,24,27,44} under different experimental conditions.

The capacity of iron-based materials to adsorb As varies based on the chemical composition of the pipe material. In addition, the accessible adsorption surface area varies for each type of iron specie. Increasing the available surface area generally increases the adsorption capacity of the material. Measured surface areas of particulate forms for various materials ranges from as low as 1.16 m^2 for hematite ($\alpha\text{-Fe}_2\text{O}_3$)¹⁴ to $600 \text{ m}^2/\text{g}$ for amorphous iron hydroxide.¹² A reduction in surface area was also observed as corrosion products aged.⁵⁰ This wide range of experimentally reported surface areas highlights the variability in the structures of iron oxides and hydroxides.

Kinetic adsorption studies have revealed that arsenic adsorbs onto iron-based materials rapidly, within 4 hours.^{4,5,7-9,23,24,27} Pierce and Moore commented that the adsorption rate for arsenate was faster for higher starting concentrations.⁴ Pierce and Moore also speculate that there may be multiple types of surface sites on amorphous iron hydroxide that may have differing affinities to As.⁴ Later studies confirmed the presence of multiple adsorption complexes containing As and iron.^{10,31,34,35}

For this study, adsorption and reaction modeling of As in water distribution systems was performed with EPANET-MSX. EPANET-MSX^{51,52} is the multi-species extension of the hydraulic simulator, EPANET⁵³, which allows for user-defined reaction mechanisms between multiple chemical species simultaneously. EPANET and EPANET-MSX have been used to study the fate and transport of numerous substances in bulk water and on pipe walls within water distribution systems.^{51,53-60}

Previous research by some of the authors of this paper reported on arsenate experiments conducted at the pilot-scale⁵⁵ and initial mathematical model development^{54,55}. The EPANET-MSX user's manual^{51,52} provides an example of the arsenite oxidation and arsenate adsorption model in a chloraminated environment. This paper presents new data from pilot-scale experiments with oxidation of arsenite to arsenate in chlorinated drinking water. The model presented herein was validated with the pilot-scale data and was applied to a larger scale distribution network in order to provide a more realistic context for application of these models. The model was developed to capture the dominant As adsorption behavior in iron-based pipe material, since it is unlikely that a utility would know the exact chemical make-up of the inside surface of the pipes and the model would become computationally intractable if individual iron species were modeled separately.

Figure 1: Image of the DSS.

3. Material and Methods

This study included both experimental and modeling work and methods for each are discussed here.

3.1. Experimental Methods

3.1.1. Distribution System Simulator

The Distribution System Simulator (DSS), see Figure 1, was constructed at EPA's Testing and Evaluation (T&E) facility in Cincinnati, OH in 2005 to support water security research projects, focusing on the persistence and decontamination of contaminants in water distribution systems.^{61,62} The DSS is a pilot scale test loop constructed primarily of polyvinyl chloride (PVC) pipe. The total system volume is approximately 833 L, and the total internal surface area is approximately 16 m^2 . There is approximately 23 m of linear pipe—consisting mainly of 15 cm diameter pipes, but with some 5 and 10 cm diameter pipes. There are three system pumps to allow for multiple flow rates. A 397 L stainless steel recirculation tank is in-line with the main pipe and another large tank supplies fresh tap water to the pipe loop.

One segment of pipe within the DSS contains holes that accept threaded fittings, and coupons can be inserted flush with the interior surface of the surrounding pipe to study adsorption, desorption, and presence and impact of a biofilm. Coupons can be removed periodically throughout experiments by turning off the pump, isolating the pipe section, removing the coupon and replacing it with a PVC blank. The system's flow was stopped for approximately 30 seconds during these coupon exchange. Sensors are installed in the DSS to monitor standard water quality parameters, such as, pH, turbidity, free chlorine, total chlorine,

specific conductivity, temperature and oxidation-reduction potential. Additionally, pressure and flow rate can be monitored continuously.

The flow rate in the DSS was maintained at 315 ± 1 L/min during normal operation, which equates to an approximate 1.5 minute hydraulic cycle through the system. The flow was stopped only to remove coupons. The system pH and temperature were approximately 8.5 and 20°C , respectively, throughout the experiments. All sensors were calibrated prior to the experiments and were maintained according to the manufacturers' recommendations as necessary throughout. The schematic showing the injection and sample ports, recirculation tank, and coupon pipe in the DSS is shown in Figure 2. The arsenic solutions were injected in a port that was after the pump in the system. Bulk liquid samples were taken from a sample port in the pipe before the water entered the recirculation tank.

Sixty (60) small (1", 2.54 cm, diameter) circular coupons were fabricated from cast iron pipes that had been removed from service from the Greater Cincinnati Water Works (GCWW) distribution system. Thirty (30) were installed in the DSS for each of the two experiments. The coupons provided an initial surface area of 152 cm^2 onto which As could adsorb. Prior to performing each experiment the coupons were conditioned in the DSS for approximately eight weeks, which allowed the coupons to corrode and a biofilm to form in water supplied by GCWW.

3.1.2. Coupon and Bulk Water Analysis

Arsenic concentrations on the coupons were determined using Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES) using Standard Method 3120B. The minimum detection limit for ICP-OES for As is 0.006 mg/L (6 ppb). Solid samples were digested in nitric acid according to Standard Methods 3030D and 3030E⁶³. Coupon samples were prepared by scraping the surface with a clean, sterile scalpel onto a clean pre-weighed porcelain 30 mL crucible. Coupons were rinsed over the crucible with deionized water to remove any residual material. Samples were dried in a 60°C oven for at least 24 hours, or until the samples were dry. Crucibles were cooled and reweighed to determine the mass of solids scraped from the coupons. Dry solids were digested in nitric acid and analyzed using ICP-OES. Aqueous phase arsenic concentrations were directly analyzed with ICP-OES.

In the second DSS experiment, the concentration of arsenite in aqueous samples was determined using an anion exchange column. The anion exchange column used for speciation had been treated to have an acetate surface. Arsenate in a sample is bound to the column and arsenite is able to pass through. The effluent is analyzed with ICP-OES to determine arsenite concentration. Arsenate concentrations were calculated as the difference between the total arsenic and arsenite concentrations.

A control coupon was removed immediately prior to the injection of arsenic in each experiment to establish baseline arsenic content and biofilm growth. Biofilm growth was measured using Standard Method 9215C⁶³ to determine a heterotrophic

plate count (HPC). In this method the corrosion material was scraped into 10 mL of sterile monopotassium phosphate buffer (pH 7.2). Corrosion solids were then broken up with a glass stirring rod, followed by serial dilution and plating. Arsenic concentrations found on the corrosion solids were measured as described above.

3.1.3. Arsenate Experiment

An arsenate stock solution was prepared by dissolving 5.26 g of 99% sodium arsenate dibasic heptahydrate (Sigma-Aldrich, St. Louis, MO) into 1.5 L of deionized water. This produced a solution with a concentration of 842 (mg As)/L . One-liter (1 L) of the stock solution was injected into the DSS using a pressurized syringe fabricated at the T&E facility. The injection took 31 seconds to complete. Referencing the arsenate injection as time 0, duplicate coupons were removed at 1, 5, 15, 30, 60, 120, 180, 300, 420, 1440 and 4320 minutes and the remaining 3 coupons were removed at 7 days (8640 minutes). Bulk liquid-phase samples were taken at the sample port (see Figure 2)—where 10 mL of water was drained into new 50 mL polypropylene sampling tubes. Liquid samples were taken at 4, 8, 10, 15, 16, 17, 18, 19, 20, 22, 45, 76, 138, 199, 255, 333, 387, 439, 1447, 3013, 4340 and 8636 minutes after the injection.

3.1.4. Arsenite Experiment

A second DSS experiment was performed using 99% anhydrous sodium arsenite (Sigma-Aldrich, St. Louis, MO) as the injected contaminant. A stock arsenite solution was produced with a final concentration of $1,200\text{ (mg As)/L}$. The water supplied to the DSS is chlorinated, which oxidized arsenite to form arsenate following the general reaction form:

The sodium arsenite injection was performed in the same way as the sodium arsenate injection. Bulk aqueous samples were taken at times 0 (immediately prior to injection), 4, 7, 8, 9, 10, 11, 13, 15, 17, 19, 30, 60, 120, 180, 240, 300, 360, 420, 1440, 2880, 4320, 5760, 10080, 14400, 20160 and 30240 minutes. Coupons were removed at 1.33, 10.25, 22.5, 39.75, 72.5, 133.167, 194.75, 317, 435, 1440, 2880, 4320, 5760, 10080, 14400, 20160 and 30240 minutes. In order to extend the length of the adsorption testing, single coupons were removed at many sample times rather than duplicates. More samples were taken in the first 30 minutes of the experiment to better capture fast oxidation of arsenite. The duration of the experiment was extended to 21 days in order to better capture the desorption of arsenic from the pipe.

3.2. Modeling and Simulation Methods

EPANET-MSX was used to model the fate and transport of As species within the DSS. A one-second timestep was used for hydraulic, water quality and pattern timesteps. The absolute

and relative concentration tolerance values were set to 10^{-9} for the model of the DSS, and 10^{-6} for the model of the larger system [Net3] (systems discussed further below). The fifth-order Runge-Kutta integrator was used for all simulations.

3.2.1. Adsorption Model and Parameter Estimation

The adsorption model used within this study was the Langmuir isotherm. The Langmuir isotherm is capable of modeling both adsorption and desorption of a chemical specie. The Langmuir isotherm assumes mono-layer adsorption on a smooth surface. The adsorption rate equation for the Langmuir isotherm⁵⁵ is:

$$\frac{d[As^{5+}]_w}{dt} = \frac{[As^{5+}]_{aq}(S_{max} - [As^{5+}]_w) - K_{eq}[As^{5+}]_w}{\frac{1}{k_1} + \frac{1}{k_f}(S_{max} - [As^{5+}]_w)} \quad (1)$$

where $d[As^{5+}]_w/dt$ is the rate of arsenic adsorption onto the coupon material ($mg/(m^2 \cdot min)$), $[As^{5+}]_{aq}$ is the bulk water arsenate concentration (mg/L), S_{max} is the maximum adsorbance density (mg/m^2), $[As^{5+}]_w$ is the adsorbed arsenate density (mg/m^2), k_1 is the adsorbance rate constant ($L/(mg \cdot min)$), K_{eq} is the equilibrium constant (mg/L), and k_f is the mass transfer coefficient ($L/(m^2 \cdot min)$).

3.2.2. Arsenic Fate and Transport Model

The change in the bulk water concentration of arsenic during the DSS experiment was modeled as:

$$\begin{aligned} \frac{d[As^{5+}]_{aq}}{dt} = & -\frac{1}{r_h} \frac{[As^{5+}]_{aq}(S_{max} - [As^{5+}]_w) - K_{eq}[As^{5+}]_w}{\frac{1}{k_1} + \frac{1}{k_f}(S_{max} - [As^{5+}]_w)} \\ & - v \frac{d[As^{5+}]_{aq}}{dx} + k_{ox}[HOCL][As^{3+}]_{aq} \end{aligned} \quad (2)$$

where $d[As^{5+}]_{aq}/dt$ is the rate of change of arsenate concentration in the bulk water ($mg/(L \cdot min)$), t is time (min), r_h is the hydraulic radius (L/m^2), v is velocity, and x is the longitudinal distance.⁶⁴ Here, k_{ox} is the oxidation rate constant and $[HOCL]$ is the concentration of hypochlorite. The oxidation rate for arsenite to arsenate in a chlorinated system was taken from Dodd *et al.*,³³ $k_{ox} = 1.56 \times 10^7$ ($L/(mol \cdot min)$).

The mass transfer coefficient was calculated by EPANET-MSX for each pipe in the model, using an empirical relationship for turbulent flow through a circular pipe⁶⁵, as follows,

$$k_f = 0.026 \frac{D}{d} \left(\frac{dv^0}{v} \right)^{0.8} \left(\frac{v}{D} \right)^{1/3} \quad (3)$$

where k_f is the mass transfer coefficient, d is the pipe diameter, D is the diffusion coefficient, v^0 is the average velocity and v is the kinematic viscosity.

The rate of change in the chlorine concentration was modeled as follows:

$$\frac{d[HOCL]}{dt} = -k_{ox}[As^{5+}]_{aq}[HOCL] \quad (4)$$

Figure 2: Diagram of the DSS network as visualized in EPANET.

The value of S_{max} was selected to be 500 mg/m^2 based on analysis of adsorption capacities found in the literature³⁻⁴⁴, corrosion product masses from the DSS experiments and expected iron species found on similar pipes⁴⁶. The value of k_1 was fit to data from both arsenate and arsenite DSS experiments by simulating with EPANET-MSX. The value of k_1 was varied for each simulation and the results were compared to experimental results for each DSS experiment. The value of K_{eq} was set to 0.0539 mg/L for As on iron oxide materials that was reported by Pierce and Moore.⁴ A simulation focused on desorption alone was conducted used the maximum wall concentration measured in the arsenite experiment and comparing this model to the last three days of the arsenite experiment to ensure that desorption was being modeled well.

3.2.3. Simulation using EPANET-MSX

An EPANET⁵³ model of the DSS was simulated using EPANET-MSX^{51,52} using equations 1–4 to model changes in arsenic species within the system. Figure 2 shows the graphical representation of the EPANET infrastructure model of the DSS. Flow through the pipes was in the clockwise direction (as shown).

The modeled version of the DSS loop excludes bypass pipes and no-flow zones and thus has a slighter smaller system volume of approximately 805 L and internal surface area of approximately 14.5 m^2 . In the modeled system, adsorption of arsenic was restricted to only a small pipe that corresponds to the location of the coupons in the real system (see Figure 2). The simulated coupon pipe in the EPANET-MSX model was specified to have a pipe length of 0.0286 m. This length results in a surface area of that pipe equal to the surface area of 27 coupons (those present at the beginning of the injection experiments). The infrastructure model is fixed in EPANET-MSX and therefore was not able to account for the decreasing area available for adsorption that was the result of coupon removal in the DSS experiment. The initial wall concentration of arsenic was set to 20 mg/m^2 for both experiments to match the coupon samples taken after 1 minute in both DSS experiments (discussed further in the Results and Discussion section).

Figure 3: Network 3 Diagram. Injection location is shown with a red diamond. Pipe #249 highlighted in green. The diagram contains a river source, lake source, 3 tanks, 2 pumps, 92 junctions and 119 pipes.

3.2.4. Network 3 Example

To demonstrate the impact of As adsorption and desorption in a large scale network, the parameters listed in Table 1 were used to simulate an arsenite injection in the EPANET example network #3 (Net3, see Figure 3). Net3 models a 15 MGD system serving approximately 78,000 people and contains 92 nodes, 119 pipes, 2 sources and 3 tanks. The average residence time in the network is 13.5 hours and the maximum residence time is 130 hours. A 6-hour arsenite injection was simulated to occur at a rate of 1×10^6 mg/min at node 121 in Net3 on day 1 at noon, with a total simulation time of 505 hours (21 days). The network had an initial chlorine concentration of 2 mg/L, and each of Net3's two sources were set to supply 2 mg/L throughout the simulation. Simulations were performed with and without arsenate adsorption onto the pipe walls to investigate how much longer arsenic species remain in the network at aqueous concentrations exceeding the MCL of 10 ppb ($\mu\text{g/L}$) when arsenic adsorbs and desorbs from pipe walls. The initial adsorbed density of arsenic on the wall of the Net3 example was 0 mg/m². All pipes within Net3 were assumed to be iron based and were considered able to adsorb As. The demand schedule and other controls in the Net3 example were extended on a 24 hour cycle to create a 505 hour input file.

4. Results and Discussion

The predictive model (equations 1–4) utilized three values that were determined experimentally under similar conditions (pH 8, room temperature) were selected from the literature. Pierce and Moore reported a value for the equilibrium constant for arsenate, K_{eq} , of 0.0539 mg As/L for iron oxide in water at pH 8 (reported as 0.719 $\mu\text{M/L}$).⁴ Tanaka *et al.* reported the

arsenate diffusion coefficient as 7.27×10^{-6} cm²/s.⁶⁶ Dodd *et al.* reported the rate of oxidation for arsenite in systems with hypochlorite as 1.56×10^7 (L/(mol·min)) (reported as 2.6×10^5 (L/(mol·s))).³³ Further, a value of S_{max} was set to 500 mg/m². See Supplemental Information for more information on how the value of S_{max} was selected. Selecting a value for S_{max} ensured that the high affinity of As for iron-based materials was reflected in the model.

4.1. DSS Experiments

Immediately prior to As injection during the arsenate experiment the control coupon was found to have a surface concentration of 2.9 (mg As)/m², despite source water with As levels below the detection limit. This finding is consistent with those from other researchers that found high levels of surface accumulation of As, despite relatively low concentrations of source water.⁴⁶ Biofilm density on the coupon, as measured by HPC, was measured to be 720 ± 110 CFU/cm². The mass transfer coefficient, k_f , was calculated by EPANET-MSX using equation 3 to be 0.43 (L/(m²·min)) within the pipe containing the coupons.

Table 1 contains the parameters used within EPANET-MSX to model As dynamics for both arsenate and arsenite injections. The values of the diffusion coefficient, D , oxidation rate, k_{ox} , and equilibrium coefficient, K_{eq} , were selected from the literature. The value of S_{max} was selected to be consistent with previous experimental adsorption values^{3–44}, described above, and k_1 was adjusted until model results matched those measured during the DSS experiments.

Table 1: EPANET-MSX Model Parameters

Parameter	Value	Unit	Citation
k_1	0.0004	L/(mg · min)	4
K_{eq}	0.0539	mg/L	
S_{max}	500	mg/m ²	33
k_{ox}	1.56×10^7	L/(mol·min)	
D	7.27×10^{-6}	cm ² /s	66

4.1.1. Arsenate Results

Figure 4 shows the results of the DSS arsenate experiment in terms of bulk arsenate concentration (4a) and the adsorbed arsenate concentration (4b). Arsenate concentrations throughout the arsenate injection experiment are shown in Figure 4a. Liquid samples taken from the sample port are marked with a symbol ('×') and modeled concentrations for the node that represents the sample port are shown as a solid line. Both modeled and experimental results show the system had reached a mixed state after approximately 20 minutes. Essentially no detectable As was present in the system after 1 day. This is a result primarily due to dilution because water was removed from the system at 3 L/min, and it was replaced with fresh water with no detectable As. Approximately 0.11% of the injected arsenate was calculated to have adsorbed onto the coupons, suggesting that for this system adsorption has little impact on the observed bulk

Figure 4: (a) Arsenate concentration in bulk, (mg As)/L, measured at the sample port of the DSS (see Fig. 2). (b) Adsorbed arsenate for DSS experiment after sodium arsenate injection. Experimental As concentration and adsorbed As data is marked with a 'x'. Modeled adsorption using parameters from Table 1 are shown as a solid line. Error bars represent the standard deviation of measurement device.

concentration change. This was because only a small percentage of the DSS surface area (i.e., the 27 coupons) was expected to be active in the As adsorption process during experiments.

Figure 4b shows the adsorbed density throughout the arsenate injection experiment. Experimental results are marked with a symbol ('x') and the modeled behavior is marked as a solid line. An initial wall adsorbed density was selected to be 20 mg/m² to match the coupon samples taken at 1 minute in both experiments.

Modeled adsorbed As densities within the first two days matches the experimental samples well. The modeled arsenate solution concentration drops to approximately zero (<1 ppb) one day after the injection, while the experimental samples show concentrations on the order of 10 ppb. This absence of arsenate in the modeled system reduces the driving force for adsorption, suggesting that there should not have been increasing adsorption after 24 hours—at least not to the degree that was observed. It is unclear why the last five coupons had adsorbed densities exceeding 100 mg/m². Arsenic may have re-

mained longer in the DSS due to mixing in dead-zones (or no-flow zones) or have adsorbed onto then desorbed from the PVC piping or have been retained in the biofilm which were not modeled by EPANET-MSX. The model results predicted an order of magnitude lower aqueous As, which would have resulted in much lower predicted adsorption during that period. Additionally, the actual active surface area for adsorption decreases due to removal of cast iron coupons, which was not modeled in the EPANET-MSX model, which could affect adsorption behavior. However, since similar behavior was not observed during arsenite experiments (see Section 4.1.2) the last five coupons were not used in the fitting process. The continued adsorption observed during the arsenate experiment does suggest that even low concentrations of As (~10 ppb or below) can continue to adsorb due to the high affinity for iron.

4.1.2. Arsenite Oxidation

The arsenite injection experiment was assumed to follow a two-stage process; oxidation of arsenite to arsenate caused by a reaction with hypochlorite, followed by adsorption of arsenate onto the cast iron surface. A three week experiment was conducted in the DSS to investigate both the adsorption and the desorption process. The parameters listed in Table 1 were used to model this reaction and adsorption process.

Figure 5 shows the results of the arsenite experiment. Figure 5a contains the concentration profiles for arsenate (green), arsenite (red), chlorine (black) and total arsenic (blue) for both experimental (symbols) and modeled results (solid lines).

Similar to the arsenate experiment results, the initial slug corresponding to the injection can be observed. Examination of the data reveals four distinct regimes of behavior. Immediately following the arsenite injection, both arsenite and chlorine (in the form of hypochlorite) were rapidly consumed in the oxidation reaction; this process occurred within the first ten to twenty minutes after injection, which corresponds to the time it takes for the arsenite to completely mix within the DSS and consume the available chlorine. The apparent oxidation rate during the period following chlorine consumption was limited by how much new chlorine was added from the make-up water. Fresh tap water containing 0.68 mg/L chlorine at a rate of 3 L/min was added to the system—this fresh chlorine was rapidly consumed. Complete consumption of arsenite had taken place after approximately two hours. Throughout this period, the concentration of arsenate was constant—arsenate concentration loss from the overflow in the tank was approximately equal to arsenate generation from the oxidation reaction. Following the consumption of arsenite, arsenate was the only As specie present and was lost from the system to the overflow process; no arsenic exists in solution after one day. Similar to the arsenate experiment, the model reaches very low arsenate concentrations earlier than those measured from the sample port in the DSS.

Arsenic was being adsorbed throughout these first three time periods. The final period consisted of arsenic desorption. After the first day, essentially no arsenic was present in the aqueous

(a) Solution Concentration

(b) Adsorbed Concentration

Figure 5: (a) Concentrations of species in bulk, mg/L, measured at the sample port of the DSS (see Fig. 2). Blue 'o' indicate total arsenic, green 'x' indicate arsenate, red '+' indicate arsenite and the dashed black line indicates chlorine concentrations. Solid lines corresponding to these colors indicate the modeled concentrations of that specie. Error bars represent the standard deviation of experimental measurements. (b) Arsenate adsorption during the sodium arsenite DSS experiment. Experimental measurements are marked with an 'x' and modeled results are shown as a solid line. Error bars represent the standard deviation of measurement device.

phase, which results in desorption of As from pipe surfaces. Unlike during the arsenate experiment, no continued As adsorption was observed after the first day, when As levels in solution had essentially approached non-detectable levels.

Figure 5b shows arsenic adsorption density throughout the arsenite injection experiment. Similar to the arsenate experiment, less than 0.1% of the injected arsenic adsorbed to the coupons' surfaces. It was assumed that arsenate was the dominant specie adsorbed for two reasons: the majority of the arsenite was oxidized quickly within the system and arsenite has a higher mobility within aqueous systems.⁶⁷

Figure 6 shows the desorption period of the arsenite experiment beginning on day 3. A simulation was performed with a starting wall concentration of 65 mg/m² to replicate the maximum wall concentration observed during the arsenite experiment. In order to be consistent with Figure 5b, the *x*-axis starts at 3 days.

Figure 6: Adsorption density profile of arsenic desorption. Experimental measurements marked with a 'x' and modeled adsorption is indicated by a solid line. Error bars represent the standard deviation of measurement device.

Model times were adjusted by 3 days (4,320 minutes) to align the desorption model with the final 18 days of experimental results. Modeled desorption agreed well with the coupon measurements. Desorption times of As from goethite was previously reported to take between 45 minutes to 7 months to occur.¹³ Extending the time frame of a simulation suggests that it would take approximately a year to completely desorb As if the entire surface of the DSS had a contamination level of 65 mg/m². Desorption of As from only the coupon surface area would take approximately 6 months. These time frames are consistent with the high bonding affinity of As for iron-based materials and kinetics reported previously^{3-44,46,49,68,69}.

In reporting the adsorption behavior, it was stated above that neither injection experiment adsorbed more than 1% of the injected material onto the coupons. It is important to remember that this is an artifact of the available adsorption surface in the DSS, which only contains a small active surface area of thirty 1-inch diameter coupons. If all of the surface was treated as being iron-based, the maximum adsorbed density would have reached approximately 40 mg/m² of As, which translates to approximately 430 mg of As adsorbed on the walls of the DSS (not shown). This maximum modeled wall concentration was lower than measured in the experiments, however more total mass would have been adsorbed to the much larger pipe surface area. The increased available surface area would lower the bulk As concentration faster, and subsequently reduces the driving force for adsorption faster. In this example, approximately one third of the injected As would have adsorbed to the pipe walls.

Comparing the model to experimental results shows good agreement with both experiments. However, continued adsorption of As onto the coupons beyond 1 day was observed in both DSS experiments (Figures 4b and 5b). After 1 day, the modeled concentrations within the DSS were on the order of 10⁻³ mg/L, whereas the experimentally measured concentrations were on the order of 10⁻² mg/L. This suggests that mass was retained in the DSS longer than was being predicted by the model. This material retention may be caused by: slower mixing or mass transport within pipes and tanks; adsorption

and desorption from non-coupon DSS surfaces; or, diffusion or mixing of water into no-flow or dead-zone segments of the DSS. Adsorption densities in the arsenate experiment (see Figure 4b) are 2–3 times higher in the final 5 coupons relative to the coupons removed after 1 day. The same behavior was not observed to the same extent in the arsenite experiment (see Figure 5b). For this reason, no attempt was made to fit the model to the final 5 coupons taken from the arsenate experiment. Parameters that were able to produce modeled adsorptions that fit those coupons overestimated adsorptions for earlier times.

The discrepancies in model results may be related to variability in the composition of the corrosion materials on the surface of the pipes, loss of corrosion material from the coupon surface throughout the experiment, variability in biofilms on coupon surfaces, or the nature of the adsorption process that is occurring in each system. The biofilm may enhance adsorption of As on the PVC, or provide a barrier to adsorption onto the coupons. No attempt was made to model adsorption of As on PVC in this study; however, adsorption, and subsequent desorption, of As on PVC may explain the further adsorption behavior that was witnessed in experimental results. This behavior was not observed in the arsenite experiment, so it is possible that these high As densities resulted from differences in surface characteristics found on those coupons. Previous DSS experiments revealed some arsenic adsorbance on PVC blanks at various flow rates, however, this adsorption behavior was not consistently observed.⁶¹

Previous pipe sampling work⁴⁶ highlights that As has been found to be adsorbed to distribution pipes in systems with low concentrations of As in the bulk water. Those findings support iron's high affinity for As, and highlights that a more permanent chemisorption process may also be involved in As adsorption. It is possible that if As were to adsorb to the PVC (or other system components), the subsequent desorption process may not be detectable with the current analytical method but could continue to adsorb to the cast iron.

The model presented herein assumed that arsenite did not adsorb to the coupon surface. Dixit and Hering¹² showed that arsenite did not have a lower affinity (or higher mobility) within their tests, suggesting that it could compete with arsenate in the adsorption process. Both species of As have high affinities for iron, but arsenate is present in the system much longer than arsenite, and residual chlorine may remain on the coupon surface, oxidizing any arsenite during the period when arsenite is still present in the bulk phase. The modeled behavior in Figure 5b reveals that the arsenate-only adsorption matches experimental values, suggesting arsenite adsorption may not have played a role in these experiments. Additionally, no speciation of adsorbed As was performed during these experiments, which prevented modeling arsenate and arsenite adsorption separately. Further experiments are needed to accurately determine if arsenite would play a role in adsorption if it were present in excess in the system after chlorine is depleted, or in unchlorinated systems.

Selection of an initial wall density of 20 mg/m² was done so

that the model would better match long term behavior. Coupons taken early in both experiments were exposed to mostly clean water followed by the brief high concentration of the initial slug related to the injection. Due to the higher concentration of the slug, the initial kinetics of adsorption was expected to be fast, but also brief. The initial transient period related to the initial slug of material was not captured perfectly in the model. Although the experimental stop and restart periods were included in the model, not including an initial wall density resulted in faster adsorption and desorption kinetics overall, which did not match experimental data from later coupons. This initial value was selected to account for experiment specific conditions and should not be necessary for larger systems. The values presented in Table 1 capture longer term behavior associated with As adsorption.

This work set out to use experimental data to generate a simple model for arsenite oxidation and arsenate adsorption in iron-based water distribution networks using hypochlorite. Literature values for some parameters were used where possible, and remaining parameters were fit to the experimental data. Previous works from Klosterman *et al.*^{54,55} discuss models generated based on the arsenate experiments used herein, and the EPANET-MSX user's manual⁵¹ provides a model for arsenite oxidation in a chloraminated system and arsenate adsorption. The arsenite injection discussed above provided data about longer term desorption behavior that was not available for previous models. The model and parameters discussed herein yielded model values that were consistent with experimental data collected in both the arsenate and arsenite experiments and can be used to model long term adsorption and desorption processes within chlorinated water distribution networks.

4.2. Network 3 Example

In order to better understand how this model might be applied to evaluate the behavior of As in a larger system, a 6-hour injection with a rate of injected arsenite of 1×10^6 mg/min was simulated to have occurred at node 121 in Net3⁵³ (see Figure 3). The simulation ran for 505 hours (21 days). The features of this simulation were selected to replicate an intentional introduction of As at a node in Net3, rather than naturally occurring As. This example set out to highlight the impact of modeling adsorption on the behavior and persistence of As within a full-scale water distribution system.

The simulation results showed that the contamination spread rapidly through the majority of the network, and most customer nodes (82 of the 92 total) exceeded the As MCL of 10 ppb at some point during the 21 day simulation. Arsenite rapidly oxidized to arsenate, and arsenate adsorbed to most of the 119 pipes in the network. After 21 days, 104 of the pipes still had wall concentrations exceeding 1 mg/m² and a total mass of 3.37×10^6 mg As remained on the pipe walls. As desorption returned arsenic to the bulk water, many customer nodes exceeded the MCL long after the initial slug of contamination had passed through the network. These results show that arsenic

Figure 7: Concentration of arsenic present in pipe #249 in Net3 through time. The red line represents the concentration of As in pipe #249 when adsorption was modeled, and the black line when adsorption was not modeled.

can persist in real water distribution systems for long periods of time, and can result in exposure to harmful levels of As.

An example of the persistence of As observed in the Net3 simulations is shown in Figure 7. Figure 7 shows the bulk concentration of total As within pipe #249 through time (highlighted in green in Figure 7). This pipe is located in the lower portion of the network, which experiences lower flow rates and does not experience the dilution effect which occurs in pipes closer to the system's sources. The red line indicates the concentration profile through time when adsorption onto pipes in the system was modeled and the black line when adsorption was not modeled. The initial slug of As travels through pipe #249 starting on day one and ending on day 2 of the simulation. The periodic peaks in both lines are caused by water being supplied from the contaminated tanks in the system. This result highlights that if a tank becomes contaminated it too will increase the duration that a contaminant will remain in the system. Only the initial slug results in a concentration that exceeds the MCL when adsorption is not modeled. In contrast, when adsorption is modeled the concentration in the pipe still contained peak concentrations above the MCL up to 11 days after the injection. The adsorbed wall concentration of pipe #249 exceeds 80 mg/m^2 at the end of the 505 hour simulation, having reached a maximum concentration of approximately 91 mg/m^2 during the passage of the initial slug. This shows the importance of modeling adsorption in order to better predict fate and transport of contaminants in water distribution systems. Such modeling could be used to assess exposure to contaminants, or evaluate decontamination strategies (e.g. altering pH to increase desorption or flushing to remove contaminants).

5. Conclusion

Experiments were conducted within a DSS to quantify adsorption and desorption of As onto iron pipe coupons and oxidation of arsenite in a chlorinated system. Results from these experiments were used to develop a general model for EPANET-MSX

that could be applied to larger water distribution systems of any size. The adsorption and desorption model described herein was able to predict the adsorption and subsequent desorption of arsenic onto iron-based pipe materials. Previously reported arsenite oxidation rates were also found to be consistent with experimentally recorded behaviors. The general model described herein is simple enough to be applied to larger scale systems without becoming computationally intractable, while providing a good prediction of fate and transport of arsenic species for iron-based distribution networks.

Applying this model to a larger system demonstrated that the adsorption of arsenic species onto pipe walls prolonged the presence of arsenic at higher levels within a water distribution network. Approximately one-third of the nodes in Net3 received water that had bulk arsenic concentrations which peaked above the maximum contamination level for approximately one week longer when adsorption and desorption were considered than if no adsorption occurred. These results highlight the importance of considering adsorption when modeling the fate and transport of As within water distribution networks.

Future work will include using EPANET-MSX to model the fate and transport of other contaminants of concern in water distribution systems.

Acknowledgments and Disclaimer

The U.S. Environmental Protection Agency through its Office of Research and Development funded and collaborated in the research described here under an Interagency Agreement with the Department of Energy's ORISE fellowship program and Contract EP-C-09-041 with Shaw Environmental. It has been reviewed by the Agency and approved for publication but does not necessarily reflect the Agency's views. No official endorsement should be inferred. EPA does not endorse the purchase or sale of any commercial products or services. The authors would like to acknowledge Greg Meiners, Tim Kling, Tim Gray, and Shekar Govindaswamy for their assistance with the experiments.

Supplemental Information

Adsorbance densities in this paper have the units $(\text{mg As})/(\text{m}^2 \text{ pipe surface area})$, which was simplified to mg/m^2 . Previously reported maximum adsorbance densities were commonly reported as $(\text{mg As})/(\text{g Fe})$ (or molar equivalents), $(\text{mg As})/(\text{g adsorbent})$, or $(\text{mg As})/(\text{m}^2 \text{ adsorbent surface area})$. The adsorbent's surface area was typically reported from BET isotherm experiments, with units of $\text{m}^2/(\text{g adsorbent})$. In order to more easily model adsorption within larger systems, adsorbance densities related to pipe surface area, rather than sorbent surface area, were needed. In order to convert between literature values and the S_{max} presented in this work, a factor was calculated based on experimental results. This factor was calculated by

dividing the mass of non-arsenic material in the corrosion material collected from each coupon (average = 0.3268 ± 0.0537 g) by the area of a coupon (1" diameter = 5.067×10^{-4} m²) to get 645.0 ± 106.0 (g adsorbent)/(m² of pipe surface area). This value was used to convert previously reported experimental adsorption densities to units relevant to larger scale models—specifically, to help guide the selection of a reasonable value for S_{max} . The reported mass corresponds to the average of the masses of the corrosion materials that were formed throughout conditioning and testing phases of this experiment. This factor is applicable to pipes with a uniform, thin layer of corrosion; pipes with large tubercles or mineral deposits may have a different active surface area per pipe surface area. For this work, a value of 500 mg/m² was selected for S_{max} . This value of was S_{max} was reasonable because it exceeded any adsorbed surface densities that were experimentally measured, however, due to iron's high affinity for As, S_{max} could be greater than 8,000 mg/m² (reported as 13,650 μ g As/g sample).⁴⁶ S_{max} values for adsorption onto pipe walls will likely be less than granular adsorption due to the reduction in accessible surface area to adsorption on pipes.

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