

Redox reactions of arsenic in As-spiked lake water and their effects on As adsorption

Federico G. A. Vagliasindi and Mark M. Benjamin

ABSTRACT

Removal of inorganic arsenic from As-spiked Lake Washington water by sorption onto activated alumina, iron-oxide-coated sand (IOCS), and an ion exchange resin was studied in laboratory systems. The sorption results could be rationalized only by invoking unanticipated changes in arsenic speciation between As(III) and As(V) in the feed reservoir. The changes in As speciation were subsequently confirmed in independent experiments, and the factors controlling the changes were investigated. Oxidation and reduction reactions sometimes occurred in the same system sequentially over a period of days to weeks, and in other systems both oxidation and reduction seemed to be proceeding simultaneously.

Because As(III) has a much lower affinity for the adsorbents than does As(V), arsenic breakthrough was much more rapid when the influent arsenic was in the reduced form. In some cases, the combination of speciation changes in the influent and differential sorption of As(III) and As(V) generated breakthrough curves for total arsenic in which the breakthrough increased and then declined for a period before increasing again.

Reduction of As(V) to As(III) was facilitated by filtration of the sample and by incubating the sample in the light, and it was impeded by the addition of PO_4 to solution. Neither filtration nor exposure to light had a discernible effect on the rate of As(III) oxidation. As(III) oxidation was facilitated by autoclaving the sample either before or after the As(III) was added.

Although arsenic speciation changes are reproducible and explainable when investigating the behaviour of a given water sample under well controlled laboratory conditions, they are not easily extrapolated to other laboratory systems or field conditions, because they result from chemical and microbially mediated reactions that are strongly interrelated and evolve with time.

Key words | adsorption, arsenic, ion exchange, iron oxide, oxidation, reduction

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INTRODUCTION

Severe arsenic poisoning in a few locations in the world due to the consumption of water with high natural arsenic concentrations and concerns about the toxicological effects of long-term, low-level arsenic ingestion have spawned numerous recent studies of arsenic removal from potable waters (e.g. McNeill and Edwards 1995, 1997; Waypa *et al.* 1997; Bajpai and Chaudhuri 1999; Amy *et al.* 2000; Meng *et al.* 2000). Several of these studies have focused on adsorption technologies, in part because arsenate (As(V)) species sorb strongly onto iron and

aluminium oxides, which are already widely used in water treatment. Arsenate adsorption onto freshly precipitated iron and aluminium oxides can remove a substantial fraction of the arsenic from solution in conventional or enhanced coagulation processes (Cheng *et al.* 1994; McNeill and Edwards 1995; Scott *et al.* 1995), and adsorption onto granular forms of such solids or ion exchange resins in packed columns might be even more effective (Rosenblum and Clifford 1983; Joshi and Chaudhuri 1996; Driehaus *et al.* 1998; Ghurye *et al.* 1999). Sulfate ions can

compete effectively with As(V) species for adsorption sites on ion exchange resins, so such resins are typically not attractive for arsenic removal in systems with more than approximately $150 \text{ mg l}^{-1} \text{ SO}_4$ (Clifford and Lin 1986). However, sulfate is typically less effective at competing with As(V) for adsorption sites on oxides (Amy *et al.* 2000). Phosphate ions do compete effectively with As(V) species for surface sites on oxides, but the phosphate concentration of natural waters is typically low enough that such effects do not negate the viability of adsorption as a treatment option.

Arsenite (As(III)) species sorb much less strongly to most solids (Al and Mn oxides, clays, soils) than As(V) species do (Sorg and Logsdon 1978; Edwards 1994; Hering *et al.* 1996; Lin and Puls 2000); the exception seems to be Fe oxides, onto which sorption of arsenic in the two oxidation states is comparable; the more strongly adsorbing form is sometimes reported to depend on solution pH (Pierce and Moore 1982; Manning and Goldberg 1997). In cases where As(III) is present in the raw water and is not expected to sorb strongly, it can be rapidly oxidized to As(V) upstream of an adsorption step (e.g. by chlorination or ozonation), making adsorption a potentially attractive treatment technology for arsenic removal from virtually any potable water source (Jekel 1994). Nevertheless, uncertainties remain regarding both the cost and the long-term technical feasibility and reliability of adsorption for arsenic treatment (Kempic 1997; Frey *et al.* 1998; Chen *et al.* 1999). One source of uncertainty is the incomplete understanding of the factors that control redox transformations of arsenic in natural waters and water treatment systems. Although these transformations have been studied extensively, evidence suggests that both oxidation of As(III) and reduction of As(V) can proceed by a variety of mechanisms, and the factors that lead a particular mechanism to dominate in a given system are unclear.

In aerobic systems that have reached equilibrium, As(III) is expected to be oxidized virtually completely to As(V) (Ferguson and Gavis 1972; Sadiq 1997), but both the coexistence of As(III) and As(V) species in many natural samples (Kuhn and Sigg 1993; Abdullah *et al.* 1995; Nagorski and Moore 1999) and direct experimental evidence (Eary and Schramke 1990; Kim and Nriagu 2000) indicate that the homogenous oxidation of As(III) by

dissolved oxygen is slow. One striking example of this fact was provided by Wilkie and Hering (1998), who reported on an aerobic stream with naturally elevated As(III) concentrations. In the stream, As(III) was oxidized almost completely to As(V) over the course of approximately an hour, but when water was removed from the stream, the reaction virtually ceased. Various lines of evidence led the researchers to conclude that bacteria on the surface of aquatic macrophytes were mediating the reaction in the stream. Several other workers have also reported evidence for microbially mediated As(III) oxidation (e.g. Hamsch *et al.* 1995), in some cases isolating specific bacteria (Weeger *et al.* 1999) or algae (Suhendrayatna *et al.* 1999) that can carry out the reaction.

Substantial evidence also exists that, in many natural systems, As(III) oxidation is primarily abiotic. The oxidizing agents most often invoked in these cases are Mn oxides (Driehaus *et al.* 1995; Scott and Morgan 1995; Sun *et al.* 1999; Hering and Chiu 2000), but H_2O_2 might also be important (Pettine *et al.* 1999; Pettine and Millero 2000). In addition to the nature of the oxidant, several other water quality parameters (pH, ionic strength) can affect the oxidation rate. In particular, a number of studies have suggested that the reaction can be catalysed by the presence of certain clays or oxide minerals and by alkaline pH (Manning and Goldberg 1997; Foster *et al.* 1998; Lin and Puls 2000).

The capability of microorganisms to reduce As(V) is well established (Langner and Inskeep 2000; Knauer and Hemond 2000). Although some bacteria reduce As(V) to As(III) as part of a detoxification process (Cervantes *et al.* 1994), others have been identified that use As(V) as a terminal electron acceptor for anoxic respiration (Blum *et al.* 1998; Newman *et al.* 1998; Stolz and Oremland 1999).

The combination of multiple mechanisms for arsenic oxidation and reduction and the possibility for the As(V)/As(III) redox couple to be meta-stable in a highly non-equilibrated state have led to some surprising observations in both natural and experimental systems. For instance, Kuhn and Sigg (1993) report that As(III) is the dominant form of arsenic in the oxic epilimnion of Lake Greifen, Switzerland, in the summer (due to reduction by phytoplankton), while As(V) is simultaneously dominant in the

anoxic hypolimnion. Similarly surprising phenomena have been observed in water treatment systems such as consistent and substantial oxidation of As(III) in some parts of a small distribution system, but not others (Hering and Chiu 2000).

In a carefully controlled study of sample preservation procedures for arsenic speciation, Hall *et al.* (1999) found that trace amounts of As(V) (0.5 or $5 \mu\text{mg l}^{-1}$) added to deionized water could be quantitatively reduced to As(III) at 22°C over a 2-day period. The authors attributed the reduction to bacteria in the DI water that might have been growing on the deionizing resin beads. However, if that is the case, similar bacteria must have been present in natural samples, since a similar reaction occurred when the As(V) was spiked into $0.45\text{-}\mu\text{m}$ filtered Ottawa River water. In the latter case, but not the former, the As(III) was re-oxidized to As(V) within a few additional days. In all cases, the transformations were prevented by storing the samples at 5°C , rather than 22°C . The above results were reproduced in several replicate experiments. In addition, good closure of the mass balances was achieved after independent analyses of As(III) and As(V). Quantitative reduction of As(V) to As(III) has also been reported in rainwater during a 3-day storage period, even though the water was presumably aerobic throughout the time of storage (Edwards *et al.* 1998).

Volke and Merkel (1999) also reported evidence of both oxidation and reduction of arsenic in distilled and deionized As-spiked water. In deionized water containing $50 \mu\text{g l}^{-1}$ each of As(III) and As(V) and stored in the dark at room temperature, there was net reduction of As(V) to As(III) over the course of a few days and subsequent oxidation of all the arsenic in the sample over the course of a few weeks. The ultimate oxidation, but not the interim reduction, was also observed when distilled rather than deionized water was used. On the other hand, the net change in the speciation was reduction of As(V) over a several week period when the sample was stored at room temperature in the light.

There are, of course, also numerous studies of arsenic behaviour and treatability in which the results are readily interpreted and not anomalous in any way. In some of those studies, changes in speciation might have occurred but not been noticed, but in many the arsenic speciation

was, in all likelihood, stable. What is clear is that even in the purest samples, changes in arsenic speciation can and often do occur; the likelihood of such changes being significant undoubtedly increases as the total arsenic concentration declines.

Redox reactivity and adsorption of arsenic are potentially linked in several ways. First, as noted above, As(III) tends to adsorb less strongly than As(V), although As(III) can be preferentially adsorbed by Fe oxides under some conditions (Manning and Goldberg 1997). In addition, metal oxide adsorbents might play a direct role in arsenic speciation by oxidizing As(III), or an indirect role by making As(V) less available to microbes that could reduce it (Langner and Inskeep 2000). Not surprisingly, then, unexpected and/or inconsistent patterns of redox activity have been reported to confound adsorption studies in at least a few cases (Clifford 1990; Vagliasindi and Benjamin 1998), and such activity might well have occurred but not been detected in others.

The research reported here was undertaken to assess and compare the feasibility of removing arsenic from potable water by sorption onto various solids. In the course of the study, unexpected patterns of arsenic breakthrough were observed and attributed to changes in its redox state, so additional experiments were conducted to explore the factors controlling those changes.

MATERIALS AND METHODS

The methods and materials used in the research are summarized below. Additional details are provided elsewhere (Vagliasindi 1998; Amy *et al.* 2000).

Materials

All chemicals were reagent grade and were used without further purification. All solutions were prepared using ultra-pure water (Milli-Q, Millipore Co., Bedford, MA) or water that was purified by passing tap water sequentially through a $5\text{-}\mu\text{m}$ filter, a mixed-bed ion exchange resin, a

reverse osmosis membrane, an activated carbon filter, and a 0.2- μm filter. As(V) and As(III) stock solutions (100 mg l^{-1} as As) were prepared by dissolving $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and NaAsO_2 , respectively, in ultra-pure water. Phosphate and sulfate solutions were prepared from K_2HPO_4 and Na_2SO_4 , respectively.

Three types of adsorbent media were investigated: iron oxide coated sand (IOCS), which was prepared as described by Benjamin *et al.* (1996); activated alumina (AA) (ABA-2000, Selecto, Inc., Norcross, GA); and a strong base ion exchange (IE) resin (Ionac ASB-1, Sybron Chemicals, Inc., Birmingham, NJ). The only pretreatment for the IOCS was equilibration of the media to the desired pH. The IE resin was wet sieved to select particles in the size range $0.59 < d < 1.18$ mm (#16–#28 sieve sizes), converted to the chloride form, rinsed with DI water, and air-dried. When the AA was wet-sieved, the particles shrank steadily due to dissolution and abrasion. Therefore, the AA was dry-sieved to select particles in approximately the same size range (0.85–1.27 mm) as the IE resin.

Most tests were conducted using Lake Washington (LW) water, which was collected on nine occasions from a dock near the University of Washington campus. The ranges of some key water quality parameters in the samples were: pH = 7.6; DOC = 2.8–3.2 mg l^{-1} ; $\text{SO}_4 = 4\text{--}8$ mg l^{-1} ; Cl = 4 mg l^{-1} . Immediately after collection, the water was passed through two cartridge filters in series (nominal pore sizes 5 μm and 0.45 μm) and then stored in polypropylene buckets kept in the dark at room temperature. Unfiltered LW water and ultra-pure water were used in some tests. Phase contrast microscopy showed that pennate diatoms were the dominant organisms in the unfiltered samples.

Depending on the number of set-ups running at a given time, a stock feed solution for the continuous flow adsorption experiments was prepared every 2–5 days by spiking 18 l of Lake Washington water with the desired arsenic species. This stock solution was then mixed into the feed reservoirs for the various columns as needed. The feed solution reservoirs were polypropylene barrels that were kept loosely covered in the dark. The dissolved oxygen concentration in the influent reservoirs and in effluent samples was measured intermittently and was generally ~ 6 mg O_2 l^{-1} .

Methods

Set-ups for continuous flow experiments consisted of two glass columns (1-cm inner diameter) connected in series, each packed with 5 ml of adsorbent media. Deionized water that was continuously adjusted to pH 7 was circulated through the system for 12 hours prior to the experiments.

Influent was delivered to the columns by a peristaltic pump at a flow rate of 2 ml min^{-1} , yielding an empty bed contact time (EBCT) of 2.5 min in each column (5 min in each two-column set-up). All data shown below are for the effluent from the second column. In some experiments, 7.04×10^{-5} mole l^{-1} HOCl (equivalent to 5 mg Cl_2 l^{-1}) was injected into the feed solution at a point that allowed approximately 10 minutes of detention time before the solution contacted the adsorbent media. Water samples were collected from various points in the flow path. Immediately after collection, samples were adjusted to pH 2 with nitric acid and were capped and refrigerated until analysis, which occurred weekly. The ion exchange resin was regenerated intermittently by passing 500 ml of 0.2 N NaCl through the columns at a flow rate of 2 ml min^{-1} . The columns were then rinsed with 500 ml of ultra-pure water adjusted to pH 7.

Changes in arsenic speciation over time were evaluated in batch systems by storing solutions in 2.5-l clear glass jugs which were cleaned, acid washed, rinsed with ultra-pure water and autoclaved prior to use. Before each test, each jug was partially filled and rinsed with the solution to be used in the test. It was then emptied and filled with 2.5 l of solution. The jugs were stored at 20°C either in the dark or illuminated by a 40-watt fluorescent lamp at a distance of approximately 30 cm (Colortone 50, Philips Lighting Co., Somerset, NJ). Samples were collected by pouring approximately 50 ml of the solution into autoclaved centrifuge tubes. Immediately after each sample was collected, As(III) was separated from As(V) as described below. The samples were then refrigerated until analysis.

In one batch test, the solution was inoculated with microorganisms that had been cultured from the feed line tubing that was immersed in the reservoir containing the arsenate-spiked feed solution used in the continuous flow tests. The microbes were grown on plates of Bacto nutrient

agar containing 3 g l^{-1} of Bacto-beef extract, 5 g l^{-1} of Bacto-peptone, and 15 g l^{-1} of Difco-agar. After 8 days of incubation at 25°C , the colonies that developed were observed on a phase contrast microscope. All the bacteria were rod-type. The organisms were inoculated into the batch water samples by scraping a colony from the surface of the plate using a sterile rod, and dipping the rod in the water sample.

Analytical methods

An ICP (Jobin-Yvon Model 138 Ultrace) was used to analyse arsenic. The arsenic was converted to its hydride immediately before injection into the instrument by acidifying the solution on-line with 6 M HCl and then mixing it with a solution of 10 g l^{-1} sodium borohydride in 0.1 M sodium hydroxide.

Arsenic speciation was determined by separating As(III) from As(V) using the same anion exchange resin as was used in the column tests. However, the time frame, solution:resin ratio, and pretreatment of the water were very different in the two cases. Specifically, in the speciation tests, approximately 10 ml of resin was packed as a slurry into a 20-ml polypropylene column. The resin was equilibrated with deionized water adjusted to pH 3, the interstitial water was flushed with air, and approximately 50 ml of sample adjusted to pH 3 was passed through the column. In both cases, the solutions were acidified with nitric acid. The last 7 ml of sample exiting the column was collected. Samples that had passed through the resin and others that had not were stored and were chlorinated approximately 1 hour prior to analysis on the ICP.

At pH 3, soluble As(V) is present primarily as an anion (H_2AsO_4^-) whereas As(III) is non-ionic (H_3AsO_3). As a result, passage through the resin removes the As(V) quantitatively but does not remove As(III), so analysis of total arsenic in the resin-treated water indicates the As(III) concentration. The concentration of As(V) in the original sample is then determined by the difference between total arsenic in the untreated and treated samples. The reliability of this method was checked on several occasions by analysing for As(III) or As(V) in freshly prepared standard solutions that contained only

one of the two forms of arsenic. In addition, on a few occasions, experimental solutions that had been passed through the resin were chlorinated and passed through the resin a second time; in all cases, the As that was present in the effluent from the first pass was quantitatively removed in the second pass. Similar methods have been used by Ficklin (1983), Clifford *et al.* (1983), McNeill and Edwards (1995), and Edwards *et al.* (1998).

Phosphate was analysed spectrophotometrically by the method of Murphy and Riley (1962).

RESULTS AND DISCUSSION

Arsenic breakthrough and speciation in packed columns

When LW water that had been spiked with As(V) and chlorinated just upstream of the media was fed to columns packed with the different adsorbents, arsenic effluent concentrations increased steadily in all cases (Figure 1). In the system packed with the IE resin, arsenic breakthrough was accompanied by chromatographic peaking that coincided with breakthrough of sulfate (Figure 1a), indicating that sulfate was outcompeting As(V) for binding sites on the resin. Similar chromatographic peaking of As(V) in the presence of sulfate is commonly observed when solutions containing both As(V) and sulfate are treated in ion exchange columns (Clifford 1990; Ghurye *et al.* 1999).

Figure 2 presents profiles of arsenic speciation in the influent and effluent of set-ups that received As(V)-spiked LW water that had not been chlorinated. The profile of total arsenic (As_{tot}) exiting the resin set-up was unremarkable, with the concentration increasing rapidly to essentially complete breakthrough (Figure 2a). By contrast, As_{tot} exiting the IOCS system increased quite rapidly to ~50% of the influent concentration and then stabilized for almost one thousand hours before gradually increasing towards complete breakthrough (Figure 2b). The breakthrough profile of As_{tot} in the AA system (Figure 2c) was even more unusual, with arsenic breaking through the column almost completely and then being

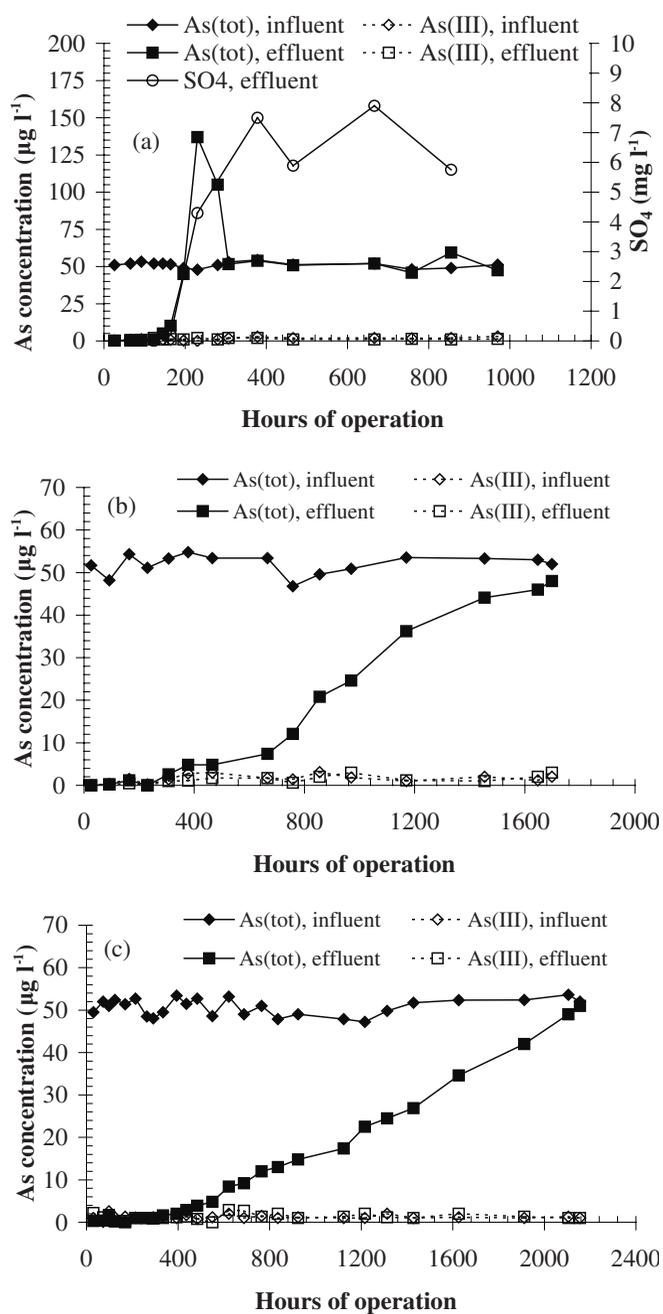


Figure 1 | Arsenic vs. time profiles for columns packed with (a) ion exchange resin, (b) IOCS, or (c) AA, fed chlorinated As(V)-spiked LW water. Breakthrough of SO_4 is also shown for the ion exchange resin. The empty bed contact time in the adsorbent columns was 2.5 min in each column, 5 min overall.

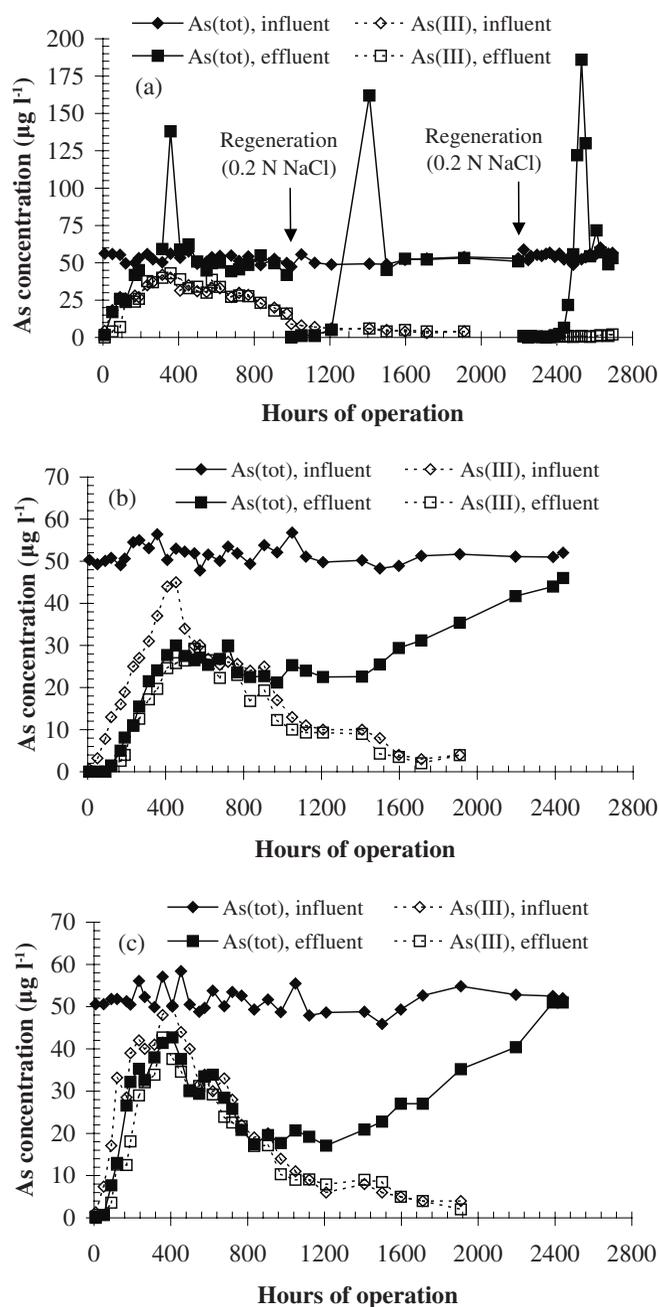


Figure 2 | Arsenic breakthrough profiles for columns packed with (a) ion exchange resin, (b) IOCS, or (c) AA and fed unchlorinated As(V)-spiked LW water. The empty bed contact time in the adsorbent columns was 2.5 min in each column, 5 min overall.

removed more efficiently later in the run. The breakthrough profiles for total arsenic in systems fed As(III)-spiked influent (Figure 3) were similar to those

that received As(V)-spiked influent (only set-ups packed with AA and IE were used with the As(III)-spiked feed water).

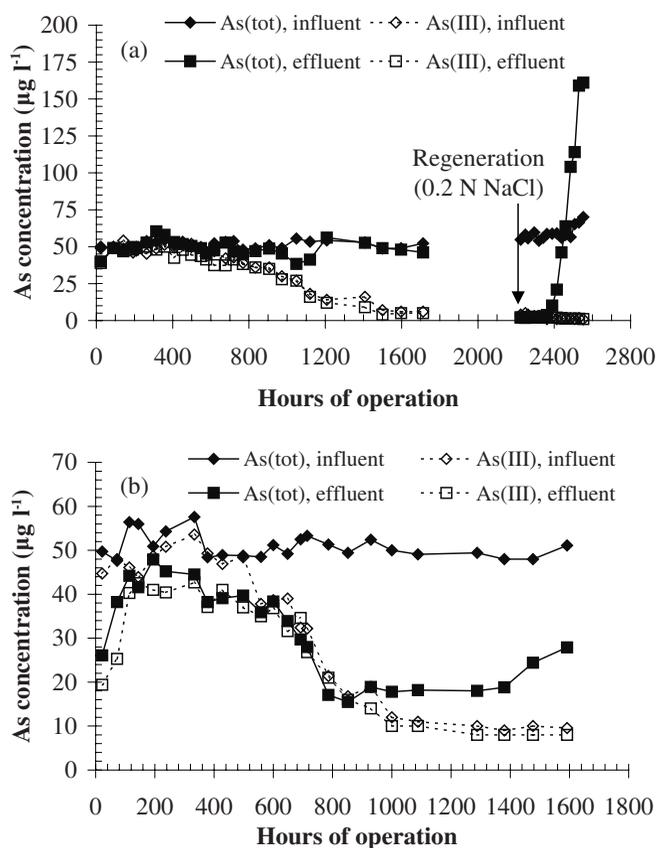


Figure 3 | Arsenic breakthrough profiles for columns packed with (a) ion exchange resin, or (b) AA and fed unchlorinated As(III)-spiked LW water. The empty bed contact time in the adsorbent columns was 2.5 min in each column, 5 min overall.

The breakthrough curves shown in Figures 2 and 3 can be rationalized by considering the arsenic speciation in the column influents, which was often unexpectedly different from the speciation of the chemicals used to prepare the feed solution. Consider, for instance, the speciation shown in Figure 2b for the IOCS system spiked with As(V). The As(III) concentration in the influent to this system increased steadily to $>40 \mu\text{g l}^{-1}$ over the first 450 hours of this test and then declined to $<5 \mu\text{g l}^{-1}$ over the subsequent 1,200 hours. Because the different forms of As do not sorb equally well to IOCS, the As speciation in the effluent differed from that in the influent. For the first 600 hours, the As(III) concentration in the effluent was less than that in the influent and equal to effluent As_{tot} , indicating that some of the As(III) and all the As(V) in the

influent were being removed in the column. Later in the test, the influent and effluent concentrations of As(III) were equal (i.e. breakthrough of As(III) was complete), and some As(V) appeared in the effluent as well. Thus, the breakthrough curve for each arsenic species followed a conventional pattern, and the unusual breakthrough curve for As_{tot} resulted from the combination of these patterns with the changes in the arsenic speciation in the influent. Essentially the same discussion applies to the AA column fed from the reservoir prepared with As(V).

The breakthrough curve for As_{tot} in the IE system treating As(V)-spiked influent had a conventional shape, but this result turns out to have been deceptively simple. In that set-up, the complex redox reactions occurring in the influent were masked by the relatively rapid breakthrough of As(V) and the virtually instantaneous and total breakthrough of As(III). The failure of the IE resin to remove As(III) is consistent with earlier studies (Clifford 1990) and is attributable to the fact that As(III) is present almost entirely as uncharged H_3AsO_3 at the pH of the test. As shown in Figure 2c, the As_{tot} breakthrough pattern in the IE resin was repeated after each of the two periods in the run that the resin was regenerated, although during those periods the influent speciation was more stable, with almost all the arsenic present as As(V).

The preceding discussion indicates that As(V) was first reduced and later oxidized in the influent reservoir, after which it remained in the oxidized state for the duration of the tests. Consistent with the results from the latter part of that test, the arsenic in the reservoir spiked with As(III) was gradually oxidized to As(V) (after a lag period of several hundred hours), after which it remained in the higher oxidation state (Figure 3). Once again, the change in influent speciation provides the basis for understanding the observed breakthrough profiles.

For instance, Figure 3a indicates that breakthrough of As(III) in the resin system was complete essentially from the beginning of the test. Although the resin can sorb As(V), by the time that As(III) began to be oxidized to As(V) in the influent reservoir ($t \sim 600$ h), enough sulfate had adsorbed to the resin to prevent As(V) from sorbing. When the column was later regenerated ($t = 220$ h), As(V) did sorb. The same qualitative trends characterize the AA column (Figure 3b), except that some As(III) was removed

by the AA during the first 100–200 hours of the test. At $t > 200$ h, all the As(III) entering the column passed through into the effluent. However, the steadily increasing conversion of As(III) to As(V) in the influent and the removal of the As(V) by the adsorbent led to a steady increase in removal of As_{tot} until $t \sim 900$ h, at which time As(V) also began to penetrate into the effluent.

Thus, the sometimes complex breakthrough curves for As_{tot} in all the systems studied can be explained by a combination of changes in the arsenic speciation in the feed to the columns, preferential sorption of As(V) over As(III) by all the adsorbents, and competition between sulfate and As(V) for binding sites on the resin.

Redox reactions in arsenic-spiked solutions

The speciation changes described above demonstrate that arsenic can be either oxidized or reduced in samples of filtered natural waters held under normal laboratory conditions. The sequential reduction and oxidation in the reservoir spiked with As(V) are remarkably similar to the changes reported by Hall *et al.* (1999) in As-spiked filtered Ottawa River water. Overall, they suggest that the observable speciation changes represent a balance between competing processes, with the oxidation reaction generally but not always being dominant. In the next portion of the research, batch tests were conducted to explore some of the factors that might control the balance between the competing redox processes. Factors considered included the presence or absence of natural colloidal matter $> 0.45 \mu\text{m}$, the presence or absence of light, and the phosphate concentration. The various combinations of these factors that were tested are summarized in Table 1.

Results of experiments investigating the effects of light and sample filtration in systems initially dosed with As(V) are shown in Figure 4. For all possible pairwise comparisons (L + F vs. D + F; L + U vs. D + U; L + F vs. L + U; and D + F vs. D + U), the results indicate that both the presence of light and filtration of the sample facilitate reduction of As(V) to As(III), but they do not prevent the subsequent re-oxidation of As(III) to As(V). As noted above, Volke and Merkel (1999) also found that light facilitated As(V) reduction, though in their experiments the As(III) did not subsequently reoxidize.

The minimal effect of light and particulate matter on As(III) oxidation in such systems was confirmed in experiments in which samples were initially dosed with As(III) (Figure 5). In all these experiments, As(III) was substantially oxidized over the course of 150–200 hours, regardless of whether the sample was exposed to light during storage and whether it had been pre-filtered. In the unfiltered sample that was stored in the light, As(V) was reduced back to As(III) after approximately 150 hours. No such reaction was apparent in the other samples in this test, nor in any of the samples shown in Figure 4 after the arsenic in those samples had oxidized. However, the oxidation of As(III) to As(V) shown in Figure 4 was slower and less extensive in the unfiltered sample stored in the light than in any of the other samples. Thus, in both sets of batch experiments, the most favourable conditions for appearance or maintenance of As(III) in solution included pre-filtration of the sample and storage in the light.

The next set of experiments investigated the effect of phosphate on arsenic redox reactivity. Because phosphate is chemically analogous to As(V), the two chemicals might be expected to compete for adsorption sites, enzymes or other reagents in solution that are critical for As(V) reduction. Consistent with this expectation, addition of phosphate to either filtered or unfiltered samples dramatically inhibited the reduction of As(V) to As(III). As shown in Figure 6, addition of $20.6 \mu\text{g P l}^{-1}$ (P:As molar ratio of 1:1) delayed the appearance of detectable As(V) reduction by 300–400 hours, and addition of $206 \mu\text{g P l}^{-1}$ (P:As = 10:1) prevented As(V) reduction throughout the 700-hour duration of the experiment. Pre-filtration of the sample facilitated As(V) reduction in these systems, as it had in the previous experiments with no phosphate addition. In these experiments, the soluble phosphate concentrations decreased substantially in the unfiltered systems, but not in the samples that had been filtered (Figure 7).

The results presented above are summarized in the top three rows of Table 2. Briefly, filtration, exposure to light, and phosphate addition all affected the timing or rate of As(V) reduction. In contrast, filtration and exposure to light had no consistent, discernible effect on As(III) oxidation; the oxidation proceeded more or less equivalently

Table 1 | Summary of experimental conditions for batch speciation tests

Experiment	Figure	As(III) or As(V)	U or F ^(a)	L or D ^(a)	PO ₄ added ^(b)	Other
1	4	V	U	L	0	
2	4	V	U	D	0	
3	4	V	F	L	0	
4	4	V	F	D	0	
5	5	III	U	L	0	
6	5	III	U	D	0	
7	5	III	F	L	0	
8	5	III	F	D	0	30°C ^(c)
9	6	V	U	L	20.6	
10	6	V	U	L	206	
11	6	V	F	L	20.6	
12	6	V	F	L	206	
13	8	III	F	L	0	Autoclaved
14	9	III	F	L	0	Autoclaved, inoculated

^(a)U or F, unfiltered or filtered; L or D, light or dark.

^(b)Expressed as $\mu\text{g P l}^{-1}$.

^(c)This sample incubated at 30°C; all others at 20°C.

regardless of the sample treatment in these cases. Phosphate is chemically dissimilar from As(III) and therefore presumably would not have affected its oxidation.

The physical and chemical factors discussed above could potentially affect the redox reactions of arsenic either directly and abiotically, or indirectly via their effects on microorganisms that might have been mediating the redox reactions or controlling the redox environment in the solutions. Two sets of experiments were therefore carried out to assess the role of microorganisms in these systems.

In one test, $50 \mu\text{g As(III) l}^{-1}$ was added to a filtered sample of LW water either before or immediately after the

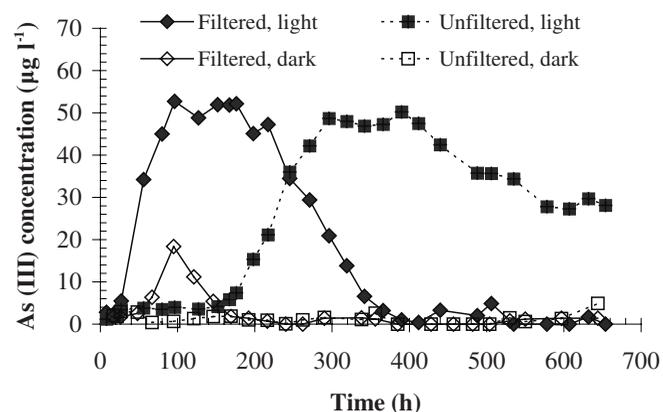


Figure 4 | Arsenic(III) in 0.45 μm -filtered and unfiltered LW water spiked with $50 \mu\text{g As(V) l}^{-1}$, with samples stored in light or dark conditions.

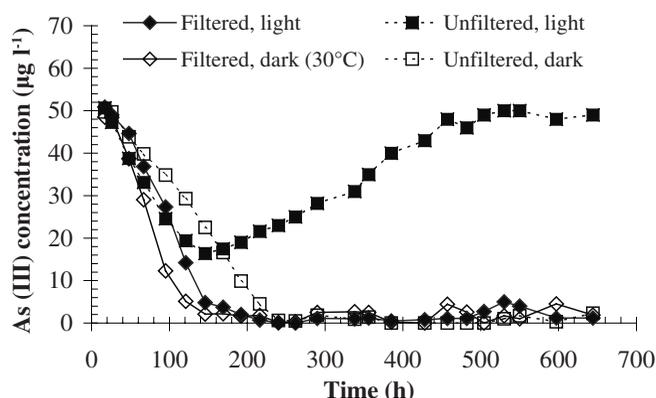


Figure 5 | Arsenic(III) in 0.45 µm-filtered and unfiltered LW water spiked with 50 µg As(III) l⁻¹.

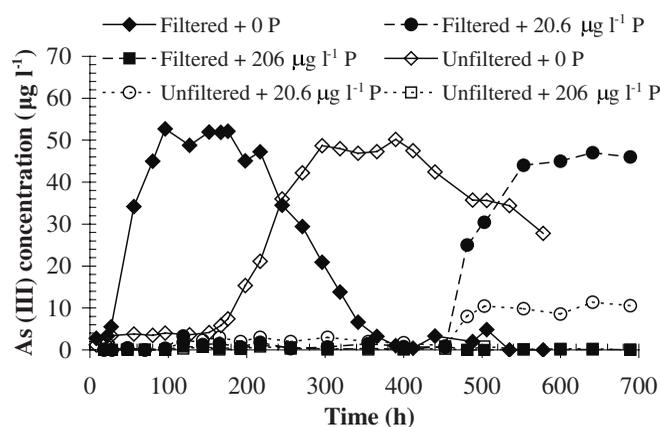


Figure 6 | Arsenic(III) in LW water spiked with 50 µg As(V) l⁻¹, with and without phosphate additions. All samples incubated in the light.

sample was autoclaved. In each case, a substantial fraction of the added As(III) was oxidized to As(V) in the first sample taken (Figure 8). The fraction oxidized was greater in the sample that had received the arsenic dose prior to autoclaving, and the extent of oxidation shortly after autoclaving was much greater than in the comparable solutions that were stored at 20°C (Figure 5). In both autoclaved solutions, the oxidation reaction continued when the reactor was kept in the light at room temperature at a rate comparable to that observed previously in the corresponding sample that had not been autoclaved. These results demonstrate unambiguously that the oxidation reaction could proceed abiotically at an

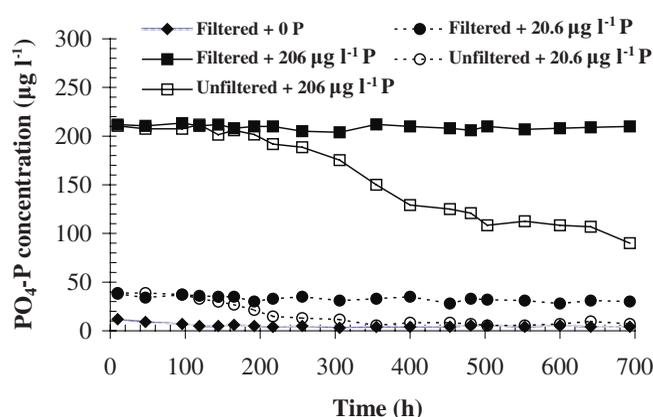


Figure 7 | Soluble phosphate concentrations in LW water samples spiked with As(V) and PO₄.

appreciable rate in our samples, and they suggest that the autoclaving step either released some oxidizing agent or catalyst to solution or killed microorganisms that were impeding the oxidation in the non-autoclaved samples. The results do not, of course, rule out a direct biological contribution to the oxidation process in systems where microorganisms are present.

Next, a test was conducted in which 500 µg l⁻¹ As(III) was added to duplicate, autoclaved samples, which were stored in the light for 294 hours. During this time, approximately 40% of the As(III) in both samples was oxidized, lowering the As(III) concentration to 298 ± 8 µg l⁻¹. One of the solutions was then inoculated with organisms that had been cultured from the feed reservoir used in one of the column experiments, as described in the Methods section. As(V) reduction was proceeding in this reservoir at the time the organisms were cultured. Over the next 700 hours, the As(III) concentration decreased by 39% (from 290 to 177 µg l⁻¹) in the control (not inoculated) sample, but only by 16% (from 307 to 258 µg l⁻¹) in the inoculated one (Figure 9). Since the only difference in the two samples was the addition of the microorganisms, this test suggests that organisms played a significant role in facilitating reduction (or reducing the rate of oxidation) in the test systems. Again, the results do not prove that reduction occurs solely by biological activity, but they do support its significance in at least some systems. The

Table 2 | Summary of redox changes in batch speciation tests

Parameter	Experiment numbers for comparison	Effect of parameter on As(V) reduction	Experiment numbers for comparison	Effect of parameter on As(III) oxidation
Exposure to light during experiment	1 vs 2; 3 vs 4; 2 vs 5 ⁺ > 150 h	Facilitates As(V) reduction	5 vs 6; 7 vs 8	No clear effect on As(III) oxidation to As(V); the oxidation occurs in the light or dark
Filtration of sample prior to dosing As	1 vs 3; 2 vs 4	Facilitates As(V) reduction to As(III)	5 vs 7; 6 vs 8	No clear effect on As(III) oxidation to As(V); the oxidation occurs in filtered and unfiltered samples
Addition of PO ₄	1 vs 9 vs 10; 3 vs 11 vs 12	Delays or prevents As(V) reduction to As(III)	Not investigated	
Autoclaving		Not investigated	13	Oxidizes some As(III) immediately
Inoculating with organisms from a solution where As(V) reduction is occurring		Not investigated	14	Inhibits or reduces extent of As(III) oxidation

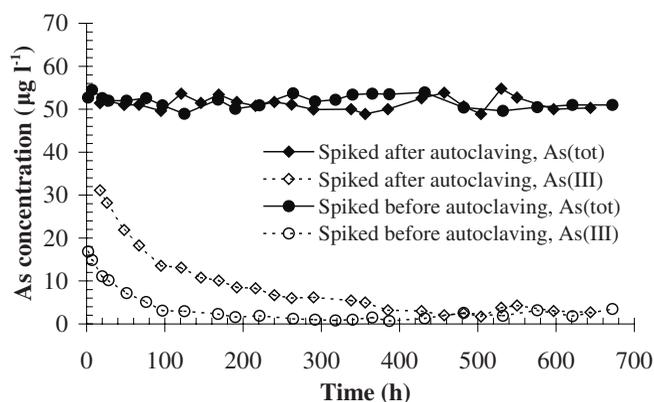


Figure 8 | Arsenic speciation in filtered and autoclaved LW water spiked with $50 \mu\text{g As(III) l}^{-1}$.

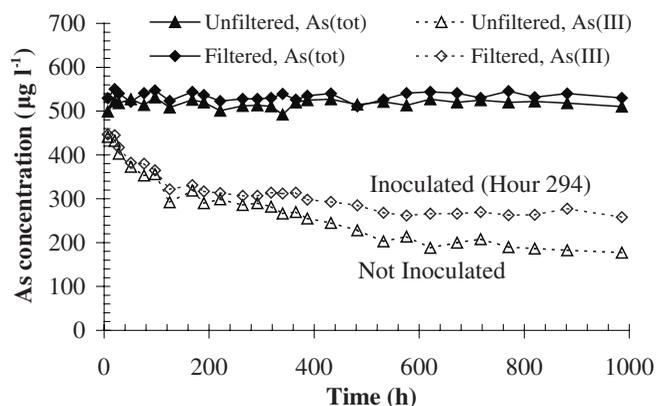


Figure 9 | Arsenic speciation in autoclaved LW water spiked with $500 \mu\text{g As(III) l}^{-1}$.

results of the batch tests investigating the microbial contribution to arsenic redox reactions in these systems are included in Table 2.

CONCLUSIONS

It is well established that arsenic adsorption onto oxide minerals and ion exchange resins is sensitive to the oxidation state of the arsenic, with As(V) species generally binding more strongly than As(III). In this study, the As oxidation state in filtered lake water being fed to adsorption columns underwent significant changes under

ambient laboratory conditions. Both oxidation and reduction of arsenic occurred during the test period, leading (in some cases) to highly unusual profiles for breakthrough of total arsenic into the column effluents. These profiles could be rationalized when the changing arsenic speciation in the influent was considered along with the preferential adsorption of As(V) over As(III) and the competition between As(V) and SO_4 for adsorptive sites.

Redox reactivity of arsenic was also studied in batch systems. These tests indicated that As(V) reduction was facilitated by exposure to light and pre-filtration of the water and was severely inhibited by the addition of phosphate to solution. Neither exposure to light nor pre-filtration had a consistent, discernible effect on As(III) oxidation. It appeared that both oxidation and reduction were proceeding simultaneously in the same system at times, and it is clear that the dominant reaction changed over time in a given solution, sometimes cyclically. Experiments involving autoclaved solutions suggested that As(III) oxidation in these systems was primarily an abiotic process, and that autoclaving facilitated the process. Reduction of As(V) might have also proceeded abiotically, but at least some reduction was apparently microbially mediated in the systems studied.

Although this study sheds some light on the qualitative effects of individual water quality parameters and sample incubation conditions on changes in arsenic speciation, the details of the chemical and biological processes responsible for those changes remain obscure. These details are difficult to unravel, in part because the speciation changes apparently reflect the net result of at least two, and possibly many more, competing processes. Because the reactions that are dominant in the initial solution depend on the chemical and microbiological history of the sample, and because any given parameter that is altered experimentally might affect several of the reactions, speciation of arsenic should be evaluated directly and frequently in experimental systems, even in the absence of overt evidence of speciation changes. In light of the mandate to remove arsenic from drinking water to ever lower levels, researchers and water utility personnel will need to be more cognizant of small changes in arsenic speciation and their effects on arsenic removal.

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