

Removal of Methylated Arsenic in Groundwater with Iron Filings

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Field and laboratory experiments were conducted to study the potential use of Fe filings to remove monomethyl arsenate (MMA) and dimethyl arsenate (DMA) from contaminated waters. Batch experiments show that the affinity of MMA for Fe filings is comparable to that of inorganic arsenate, but lower than that for arsenite. In contrast, very little DMA was retained by Fe filings or their corrosion products. The wide range of affinities of different As species for Fe filings was confirmed by a series of retention and selective-leaching experiments using small columns and As-spiked groundwater. The effectiveness of Fe filings was also demonstrated with a field deployment at a U.S. Superfund site where groundwater is highly contaminated with both organic and inorganic As species. Over the course of 4 months, a 3 L cartridge of Fe filings removed >85% of As contained in 16000 L of groundwater containing 1–1.5 mg/L total dissolved As, ~30% of which was organic As. The results indicate that Fe filings could be used to treat groundwater contaminated with MMA, which is the main organic form of As at most contaminated sites. Indications of partial demethylation in the column of Fe filings suggest conditions might be optimized further to enhance the removal of DMA.

Introduction

Methylated As species, monomethyl arsenate (MMA) and dimethyl arsenate (DMA), occur as important pollutants in groundwater at sites with a history of pesticide manufacturing and improper disposal. A query of the United States Superfund Site Database (<http://www.epa.gov/superfund/sites/npl/basic.htm>, accessed April 10, 2005) showed that about 42% of 1236 sites that are currently on the National Priority List contain As, with at least 107 sites reporting MMA contamination. Although DMA is not included in the database, this species is often produced along with MMA and therefore probably present at many of the sites as well. At the Vineland Superfund site in New Jersey, for example, high levels of both inorganic and organic forms of As are

present in the dissolved and the solid phases. Total As concentrations reach thousands of parts per million in contaminated soils and are as high as tens of milligrams per liter in groundwater extracted from wells tapping the main contaminant plume (1). An elaborate groundwater pump and treat system that processes 2 million gallons of contaminated groundwater per day relies on the oxidation of organic As with hydrogen peroxide, followed by coagulation with ferric chloride, polymer flotation, and subsequent sand filtration (1). The process is effective in the sense that concentrations of As in the effluent discharged to a nearby stream are typically <30 µg/L. Complete oxidation of organic As species is notoriously difficult and costly to achieve, however, even under UV radiation (1–3). The current operation to remediate the situation is expected to last several decades at a projected cost of ~\$100 000 000. The present study explores an alternative method to treat either groundwater or sediment washings contaminated with both inorganic and organic As species that could potentially reduce the cost of mitigation.

Effective removal of inorganic As(V) and As(III) from groundwater by zerovalent Fe has been demonstrated for practical use with flow-through cartridge systems as well as permeable reactive barrier systems (4–7). The mechanism of As removal by zerovalent Fe is not fully understood but is generally believed to involve adsorption onto iron(II) and/or iron(III) oxyhydroxides that are continuously generated by corrosion of the Fe filings (4, 8–13). Whereas oxidation of As(III) on corroded Fe surfaces has been observed, reduction of As(V) has not (9, 11). Electrochemical and spectroscopic studies have confirmed strong binding of both inorganic As(V) and As(III) to the corroded surfaces of Fe filings (10, 13). Since the molecular structure of MMA and DMA is similar to that of arsenate (Supporting Information, Table S.1), these organic species could therefore conceivably also be removed by Fe filings. Laboratory experiments have indeed shown that MMA and DMA adsorb onto freshly precipitated iron(III) oxyhydroxides as well as alumina at pH < 7 (14, 15).

In the present study, the removal of MMA and DMA by Fe filings is compared to the removal of inorganic As(V) and As(III) under similar conditions. The removal of As species by Fe filings and the dependence on groundwater pH and phosphate concentrations are first quantified in a set of parallel batch experiments. Small flow-through columns of Fe filings were then used to evaluate the removal efficiency of As species in different groundwater matrices. Columns loaded with different As species were also subjected to three-step sequential leaching while the As levels in the effluent were monitored to study the various retention mechanisms. Finally, the performance of a cartridge system containing Fe filings and sand was evaluated for a mixture of inorganic and organic As species contained in contaminated groundwater from the Vineland Chemical Superfund site.

Materials and Methods

Materials. Iron filings were used as received from Connelly-GPM, Inc. of Chicago, IL (stock no. CC-1004, ~12–18 mesh). Silica sand was no. 4 Q-Rok mined by U.S. Silica in Berkeley Springs, WV (16–20 mesh). Small 20 mL columns used for bench-scale studies and the larger 3 L cartridges deployed in the field were packed with a 1:1 (by volume) mixture of Fe filings and sand. The resulting porosity of the columns was ~35%. The small columns were made with the barrel of 20 mL polypropylene syringes (9.5 cm length, 1.8 cm i.d.),

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capped with a silicone stopper, and connected via color-coded two-stop silicon tubing (Cole-Parmer, EW07616-46) to a peristaltic pump. The components of the larger 3 L cartridges have been described elsewhere (6).

Sodium arsenite (Sigma-Aldrich, no. 57400), sodium arsenate (Sigma-Aldrich, no. 59663), cacodylic acid (dimethylarsinic acid or DMA, $C_2H_7AsO_2$; Sigma-Aldrich, no. C0125), and monosodium acid methane arsonate sesquihydrate (or MMA; Chem Service Inc., no. PS-429) solids were used to prepare 1000 ppm As stock solutions that were subsequently diluted for the various experiments. A 1000 ppm inorganic As(V) solution in 5% HNO_3 (High Purity Standards, no. 10003-1) was used in some of the early tests with small columns. Organic As concentrations are referred to throughout this paper as the weight per volume of As.

Batch Experiments. Relative Affinity of As Species for Fe Filings. The removal of different As species by Fe filings was compared by equilibrating 1 g of Fe filings with 1, 2, 5, 10, 20, 50, and 100 mg/L As(V), As(III), DMA, and MMA in 25 mL scintillation vials. Preliminary experiments indicated poor retention of DMA; therefore, solutions containing 0.05, 0.1, 0.2, and 0.5 mg/L DMA were also tested. All experiments were run in duplicate using a 0.01 M KCl solution as the background electrolyte. Scintillation vials were filled to the point where no headspace was left after capping and kept in the dark for 5 days. Previous work with Fe filings has shown that equilibrium is normally reached after ~ 1 day (12). At the end of each experiment, ~ 5 mL of supernatant was passed through a $0.45 \mu m$ syringe filter and acidified to 1% HCl.

Effect of Groundwater pH and Phosphate. In another series of batch experiments, 1 mg/L As(V), MMA, or DMA solutions were equilibrated with 1 g of Fe filings after adjustment of the pH. The solution pH was adjusted with 0.1 M HCl or NaOH to values between 4 and 8 in 0.5 unit increments. Freshly collected water from well RW-5 at the Vineland Superfund site provided the groundwater matrix for a final set of batch experiments. In this case, four aliquots were spiked with a 1 mg/L concentration of the various As species and another aliquot was left unspiked. Each of the five aliquots were then divided across four scintillation vials containing 1 g of Fe filings and spiked to 0, 0.5, 1.0, and 2.0 mg/L P (in the form of KH_2PO_4), respectively. The entirely filled vials were kept sealed and in the dark for 20 h before filtering and acidification of the supernatant.

Small-Column Experiments. The efficiency of removal by Fe filings was also investigated for individual As species by pumping As-spiked groundwater through 20 mL columns at a flow rate of 0.6 mL/min, equivalent to a residence time of ~ 10 min in the column. The first experiment used Lamont Doherty Earth Observatory tap water, which is groundwater containing $<0.1 \mu g/L$ As, low Fe (0.8 mg/L), and ~ 0.6 mg/L P (phosphate), and was spiked to 1 mg/L inorganic As(V), MMA, or DMA. The second experiment used groundwater again from well RW-5 at the Vineland Chemical Superfund site containing 470 $\mu g/L$ inorganic As but no detectable organic As ($<5 \mu g/L$) or phosphate ($<0.01 \mu M$) and with a high dissolved Fe concentration (12 mg/L). This particular experiment was conducted in a N_2 -filled glovebag. Groundwater from RW-5 was spiked by 1 mg/L concentration of the various As stock solutions. Effluent from the small-column experiments collected every ~ 50 mL was also filtered and acidified.

Sequential Extraction of As from Fe Filings. Arsenic in the form of inorganic As(III), As(V), MMA, and DMA was first loaded onto freshly prepared 20 mL columns of Fe filings by pumping 0.5 L of solutions containing 10 mg/L As at a rate of 0.1 mL/min (residence time ~ 1 h). By analogy to the batch extraction procedure developed by Keon et al. (16), the following solutions were then used to leach each column,

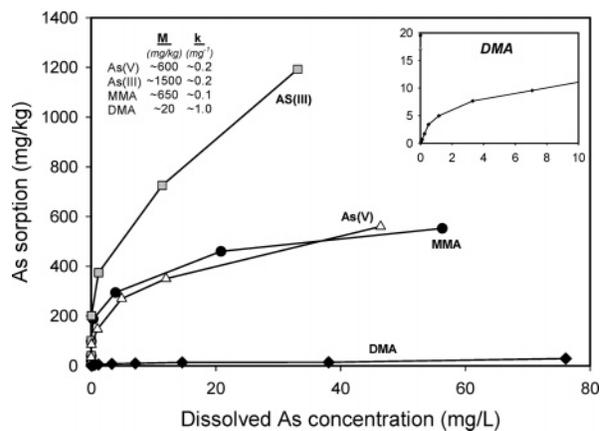


FIGURE 1. Arsenic sorption as a function of equilibrium As concentration in the solution. A 1 g portion of Fe filings was equilibrated for 5 days with 1, 2, 5, 10, 20, 50, and 100 mg/L As(V), As(III), DMA, and MMA, and with 0.05, 0.1, 0.2, and 0.5 mg/L DMA in 25 mL scintillation vials. All experiments were run in duplicate using a 0.01 M KCl solution as the background electrolyte. The *m* and *k* values were inferred assuming a Langmuir model.

also at a flow rate of 0.1 mL/min: (1) a 1 M $MgCl_2$ solution, adjusted to pH 8.0, (2) a 1 M NaH_2PO_4 solution at pH 5.0, and (3) a 0.2 M ammonium oxalate solution at pH 3.0. The volume of each leaching solution pumped through the columns ranged from 500 to 650 mL, depending on the rate at which effluent As concentrations decreased to $<10 \mu g/L$. In the case of the two columns loaded with MMA or DMA, the first 50 mL of effluent from each leaching step was also analyzed for As speciation (see below).

Cartridge Deployment in the Field. Two 3 L cartridges of Fe filings connected in series were tested over a period of nearly 3 months at one of the most contaminated wells (RW-4) of the Vineland Chemical Superfund site in 2004. Upward flow through the column (6) was maintained by pressure at an outlet from the contaminated stream at a pumping well. The flow rate was periodically monitored and adjusted to ~ 100 mL/min, which corresponds to a residence time in the column of ~ 10 min. Influent and effluent samples for each cartridge were collected periodically, and acidified on site to 1% HCl. On one occasion, to test for further removal of As, the effluent leaving the cartridges were vigorously bubbled with air for 2 min. Samples of this effluent were also acidified after removal of the brown Fe flocs produced by oxidation with a $0.45 \mu m$ syringe filter.

Analytical Methods for As Concentration and Speciation. Total As concentrations were determined either by high-resolution inductively coupled plasma mass spectrometry (HR ICP-MS; single-collector VG Axiom) (17) at LDEO or by graphite-furnace atomic absorption spectrometry (GFAAS; Perkin-Elmer Analyst 600) in a field laboratory at the Vineland Chemical Superfund site. The detection limits for As were ~ 0.1 and $\sim 1 \mu g/L$ by HR ICP-MS and GFAAS, respectively. Some analyses of As speciation were done by HPLC and HR ICP-MS (Supporting Information).

Results

Batch Experiments. Adsorption Capacity of Fe Filings. The first set of batch experiments shows that the affinities of DMA and MMA for Fe filings differ. At a solid:solution ratio of 1:25 and initial solution concentrations of up to 10 mg/L, $>95\%$ of the inorganic As(III) and As(V) was removed from solution (Figure 1). The proportion of DMA removed from an initial 10 mg/L solution was much lower ($\sim 10\%$). At higher loadings, the proportion of MMA and inorganic As(V) retained by Fe filings gradually declined to $\sim 30\%$, while about 60%

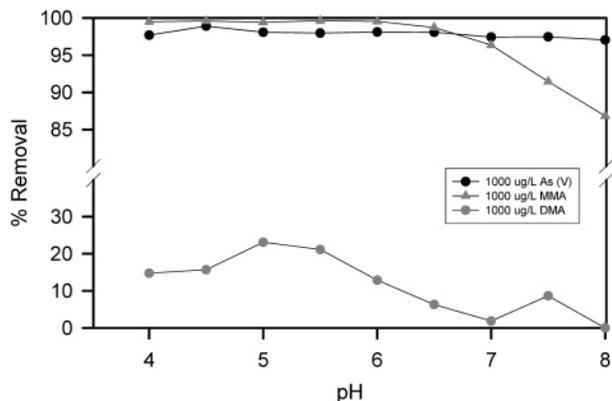


FIGURE 2. Effects of the initial water pH on the removal of individual As species by iron filings in a batch experiment. A 1 g portion of Fe filings was equilibrated for 20 h with pH-adjusted solutions containing 1 mg/L As(V), MMA, or DMA.

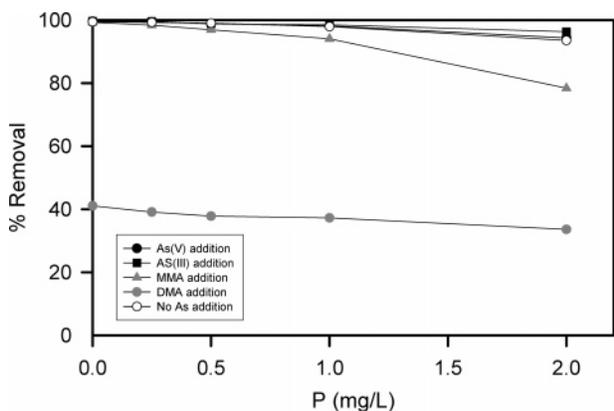


FIGURE 3. Effects of phosphate concentrations on the removal of individual As species by iron filings in a batch experiment. Four aliquots of freshly collected water from well RW-5 were spiked with a 1 mg/L concentration of the various As species; another aliquot was left unspiked. Each of the five aliquots were then divided across four scintillation vials and spiked to 0, 0.5, 1.0, and 2.0 mg/L P (in the form of KH_2PO_4), respectively, and equilibrated with 1 g of Fe filings for 20 h.

of the As(III) was retained at the highest loading. In contrast, only a third of the DMA was removed by Fe filings even at concentrations <1 mg/L, and $<10\%$ was removed at initial concentrations >10 mg/L. The data for inorganic As(III), As(V), and MMA can be modeled with a Langmuir isotherm: $X = \frac{KMC}{1 + KC}$, where X and C are the amounts of As sorbed and in solution at equilibrium, respectively, and M is the maximum sorption capacity. The inferred maximum sorption capacity is ~ 600 mg/kg for MMA and As(V) and ~ 1500 mg/kg for As(III), with a considerably larger uncertainty for the estimate of this parameter for the latter species.

Dependence on pH and Phosphate. The sensitivity of the removal efficiency to pH varied from one As species to another (Figure 2). For scintillation vials containing 1 g of Fe filing and 25 mL of 1 mg/L As, the removal of inorganic As(V) remained $>95\%$ between pH 4 and pH 8. Although the removal of MMA was greater than for DMA, there was a $\sim 15\%$ decline in removal efficiency for both organic species at pH > 7 .

The removal efficiency of all four As species was reduced by the addition of phosphate, but not to the same extent (Figure 3). At an As:P ratio of 0.5 (2 mg/L in P), the largest reduction of $\sim 20\%$ in removal efficiency was observed for MMA. Although inorganic As(III), As(V), and DMA were also affected, the decline was considerably smaller ($<5\%$).

Column Tests. Differences in affinity among the various As species were confirmed by the column experiments. For uncontaminated groundwater containing 0.6 mg/L P (phosphate) and spiked with 1 mg/L As, the removal of As(V) and MMA was close to 100% and 94%, respectively, for 150 pore volumes passed through the columns (Table 1). In contrast, only $\sim 5\%$ of the DMA was removed under the same conditions. Similar behavior was observed when groundwater from RW-5, initially containing 0.47 mg/L inorganic As and was amended with an additional 1 mg/L As in the various forms, was passed. In these experiments, the removal efficiency of MMA increased to 99%. The overall removal efficiency for groundwater spiked with DMA was 31%.

Sequential Column Leaching. The three-step leaching experiments with preloaded columns provide further evidence of different affinities of the various As species for Fe filings. By far the largest proportion of the loaded DMA ($\sim 75\%$) was mobilized by merely pumping a 1 M MgCl_2 solution through the columns (Figure 4). MMA was mobilized to a lesser extent by the same treatment (20%), whereas inorganic As(V) and As(III) were not released at all. Pumping 1 M NaH_2PO_4 through the columns led to a release of an additional $\sim 50\%$ of the MMA and inorganic As(V) loaded onto the columns, but a release of only 20% in the case of As(III). The final treatment with ammonium oxalate released only modest additional quantities ($<10\%$) of inorganic As(III), As(V), MMA, and DMA.

Speciation data indicate that organic As species are largely preserved by loading onto the columns followed by elution. In the case of the column loaded with MMA, no more than 2% of the total eluted As was in the inorganic form (Table 2). The proportion of As no longer in the form of DMA when eluted from the other column loaded with organic As was somewhat higher at $\sim 15\%$, much of it in the form of inorganic As. A minor amount of partial demethylation of DMA to MMA was also observed.

Extended Field Test. RW-4 was selected for a long-term field test at the Vineland Chemical Superfund site because of the elevated As content of 900–1500 $\mu\text{g/L}$ drawn from this well, including ~ 300 $\mu\text{g/L}$ As in organic form (25% of which as DMA). Over the course of the deployment, the residual As content of the effluent from the first column declined steadily from 300 to 100 $\mu\text{g/L}$ (Figure 5). The removal efficiency during the last month of the deployment was therefore $>90\%$. There was a parallel decline in the residual As content of the eluent from the second column at $\sim 30\%$ lower concentrations. The second column removed most of the residual As content of the eluent from the first column on only two sampling occasions.

A significant export of Fe was measured in the eluent of the first column. The dissolved Fe concentration, mostly Fe(II) under these reducing conditions and at this pH, ranged from 10 to 20 mg/L. Precipitation of this potential adsorbent phase as iron(III) oxyhydroxides upon oxygenation of the water did not dramatically raise the removal efficiency of the system. After vigorous bubbling with air for 2 min and filtering of the abundant orange precipitate, residual As concentrations were reduced from 253 to 82 $\mu\text{g/L}$ in the eluent from the first column and from 180 to 39 $\mu\text{g/L}$ in the eluent from the second column. Speciation analysis indicated that most As in the bubbled and filtered eluent from the second column was in the form of DMA, with less than 10% present as MMA (3 $\mu\text{g/L}$) and inorganic As (<1 $\mu\text{g/L}$).

Discussion

Relative Affinity of As Species for Fe Filings. The batch and column experiments consistently indicate a decrease in affinity of As species for Fe filings in the following order: inorganic As(III) $>$ inorganic As(V) $>$ MMA $>$ DMA (Figures 1 and 4). The pH above which a noticeable decline in removal

TABLE 1. Efficiency of Removal of DMA and MMA by Fe Filings for Different Matrices^a

As spike	total As	DMA	MMA	effluent As	% removal
As-Free Groundwater (pH 6.0, [P] = 0.6 mg/L, [Fe] = 0.8 mg/L, [As] < 0.1 µg/L)					
1 ppm As(V)	1000	0	0	2	99.8
1 ppm DMA	1000	1000	0	947	5.3
1 ppm MMA	1000	0	1000	63	93.7
RW-5 Groundwater (pH 5.4, [P] = 0.1 mg/L, [Fe] = 12 mg/L, [As] = 470 µg/L, Inorganic)					
1.0 ppm As(V)	1470	0	0	2	99.9
1.0 ppm As(III)	1470	0	0	3	99.8
1.0 ppm MMA	1470	0	1000	9	99.4
1.0 ppm DMA	1470	1000	0	1024	31.4

^a This was tested with 20 mL columns at a flow rate of 0.6 mL/min. Effluent As levels are the average for ~150 pore volumes (~1 L). All units are micrograms per liter unless otherwise specified.

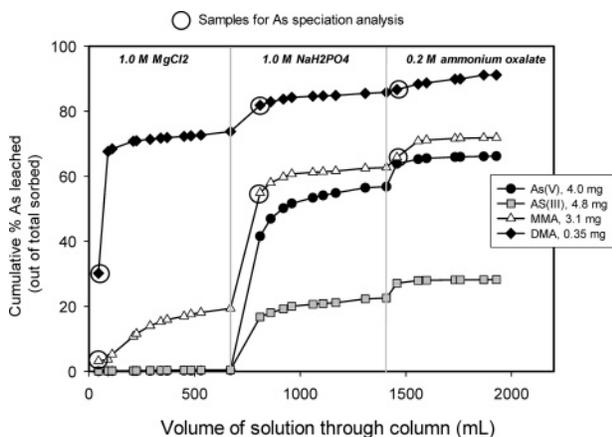


FIGURE 4. Stepwise leaching of 20 mL columns of iron filings loaded with single As species with 1 M MgCl₂ (pH 8.0), 1 M NaH₂PO₄ (pH 5.0), and 0.2 M ammonium oxalate (pH 3.0). The flow rate was fixed at 0.1 mL/min.

TABLE 2. Speciation of As in Leachate Solutions from Columns Loaded with MMA and DMA^a

leachate	effluent speciations (%)				% organic As demethylated (estimated)
	% eluted	As(V) + As(III)	MMA	DMA	
MMA (Total 3.1 mg Retained in the Column)					
MgCl ₂	19.4	0.8	99.2		
PO ₄	43.3	3.7	96.3		
oxalic acid	9.2	5.7	94.3		
cumulative	71.9				2.3
DMA (Total 0.35 mg Retained in the Column)					
MgCl ₂	73.7			100	
PO ₄	12.1	89.1	6.2	4.7	
oxalic acid	5.4	34.9	37.8	27.3	
cumulative	91.2				2.8 to MMA, 12.7 to inorganic As

^a Speciation was determined for the first 50 mL sample from each leaching step. Cumulative percentages of demethylation were estimated for the portion of As eluted in the experiment.

efficiency was observed for batch experiments decreases in the same order for the three species that were tested (Figure 2). A greater affinity of MMA for iron(III) oxyhydroxides compared to DMA has previously been reported for the pH range (~7–9) typical of systems containing Fe filings, but the difference was not as pronounced (14, 15). This discrepancy may be because iron(III) oxyhydroxides are not representative of the main adsorbent produced by corrosion of Fe filings (9, 18, 19). The experiments also confirm that, under the same conditions, As(III) is removed by Fe filings

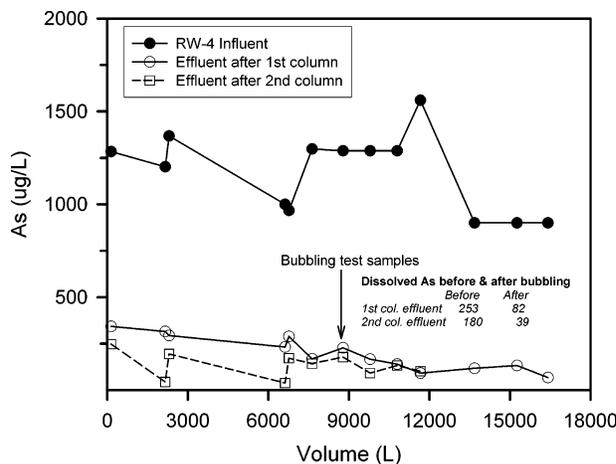


FIGURE 5. Pilot testing of a 3 L cartridge iron filing system for mixed As species removal at recovery well no. 4 at the Vineland Superfund site. Flow was maintained at ~100 mL/min throughout. Well water contained 900–1500 µg/L total As, dominated by As(III), and ~300 µg/L methylated As (25% DMA). Other constituents included Na (4.4 mg/L), Mg (2.7 mg/L), Si (5.1 mg/L), K (3.5 mg/L), Ca (8.6 mg/L), P (0.02 mg/L), S (4.4 mg/L), and Fe (2.9 mg/L).

more efficiently than As(V). This is opposite to the generally recognized relative affinity of the two inorganic As species for iron(III) oxyhydroxides (20–22), and suggests a different adsorption mechanism for Fe filings.

Mechanism of Organic As Binding. The significant fractions of DMA and MMA loaded onto the columns that are mobilized by MgCl₂, 70% and 20%, respectively, suggest a binding mechanism that is markedly different from that of inorganic As species, none of which were desorbed under the same conditions (Figure 4). The evaluation of this first step of a sequential leaching procedure by Keon et al. (16) combined with the speciation data for this eluent phase suggests that, at least in their initial form, most of the DMA and some of the MMA are weakly bound to the phase(s) resulting from the corrosion of Fe filings.

The next leaching step, which desorbs more strongly bound As, underlines the difference between the affinities of DMA and MMA for the corroded surface of Fe filings. In the case of DMA, the increment of As released by this step is modest and the As is evidently no longer predominantly in the organic form that was loaded onto the column (Table 2). In contrast, the largest fraction of As, still largely in its original organic form, is desorbed by the phosphate treatment in the case of MMA. This suggests that a form of strong binding of the MMA molecule to iron oxyhydroxides is not available to the DMA molecule.

In the absence of spectroscopic data for adsorbed organic As species, one can only speculate about the nature of MMA and DMA binding to Fe filings by analogy to such information

which is available for inorganic As(III) and As(V). The inorganic As species were recently both shown to form strong, primarily bidentate inner-sphere complexes with the corrosion products of Fe filings (10–12). In that context, it is worth pointing out that the single methyl group of the MMA molecule preserves the possibility of forming bidentate complexes whereas the two methyl groups of the DMA molecule do not (Supporting Information, Table S.1). The very similar behavior of inorganic As(V) and MMA in response to the second leach suggests that a concentrated phosphate solution can competitively dislodge such bidentate complexes from the surface of Fe filings.

The minor impact of the third reductive-dissolution step on As mobilization suggests that only a minor fraction of inorganic and organic As species are coprecipitated with amorphous iron(III) oxyhydroxides (16). This may be because the mixed Fe(II/III) phases such as magnetite and other Fe(II) phases that have been identified as the corrosion products of Fe filings are relatively insensitive to reductive dissolution (20–22). Mass balance indicates that, unlike the case of DMA, about one-third of the As(V) and MMA that were loaded onto the columns remained strongly bound at the end of the leaching experiments. This was the case of two-thirds of the As(III) that was loaded. Conversion of MMA to more strongly bound As(V) or As(III) species cannot be excluded.

Practical Implications. The significant advantages of using Fe filings as the source of fresh and effective sorbent phases for inorganic As(III) and As(V) has been pointed out in a number of previous studies (4, 8, 9, 13). The present work demonstrates that, in addition, Fe filings also effectively remove MMA from contaminated groundwater. The conversion of a significant fraction of DMA loaded onto a test column to MMA and inorganic As suggests a potential avenue for overcoming the current limitation of the use of Fe filings to a site such as Vineland Chemical that is also contaminated with DMA. The ability to remove methylated As from groundwater with Fe(0) filings may be particularly useful for reducing the cost of treatment of contaminated sites. The origin of the increase in the removal efficiency of the Fe filing cartridge over time observed during the field deployment warrants further study.

Acknowledgments

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Supporting Information Available

Simplified molecular structure and acidity constants of arsenate, arsenite, MMA, and DMA (Table S.1) and the method description for arsenic speciation analyses using HPLC/HR ICP-MS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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