Mobilization of iron and arsenic from soil by construction and demolition debris landfill leachate

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ABSTRACT

Column experiments were performed to examine (a) the potential for leachate from construction and demolition (C&D) debris landfills to mobilize naturally-occurring iron and arsenic from soils underlying such facilities and (b) the ability of crushed limestone to remove these aqueous phase pollutants. In duplicate columns, water was added to a 30-cm layer of synthetic C&D debris, with the resulting leachate serially passed through a 30-cm soil layer containing iron and arsenic and a 30-cm crushed limestone layer. This experiment was conducted for two different soil types (one high in iron (10,400 mg/kg) and the second high in iron (5400 mg/kg) and arsenic (70 mg/kg)); also monitored were control columns for both soil types with water infiltration alone. Despite low iron concentrations in the simulated C&D debris leachate, elevated iron concentrations were observed when leachate passed through the soils; reductive dissolution was concluded to be the cause of iron mobilization. In the soil containing elevated arsenic, increased iron mobilization from the soil was accompanied by a similar but delayed arsenic mobilization. Since arsenic sorbs to oxidized iron soil minerals, reductive dissolution of these minerals results in arsenic mobilization. Crushed limestone significantly reduced iron (to values below the detection limit of 0.01 mg/L in most cases); however, arsenic was not removed to any significant extent.

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1. Introduction

A documented occurrence at waste disposal sites (landfills) is the mobilization of naturally-occurring iron (Fe) and arsenic (As) from native soils into the groundwater (Keimowitz et al., 2005; Delemos et al., 2006; Parisio et al., 2006; Di Palma and Mecozzi, 2010). In soils that naturally contain arsenic and iron, arsenic will typically bind to oxidized iron (Fe(III)) minerals, such as ferrihydrite, hematite, and goethite (Heron et al., 1994; Altundogan et al., 2002; Mandal and Suzuki, 2002; Catalano et al., 2008; Perez-Lopez et al., 2011). When landfill leachate infiltrates the underlying environment (soil, aquifer), the leachate provides a carbon source for biological activity and creates reducing conditions (as a result of the high organic matter content and reduced compounds present in leachate that enters the soil beneath the landfill). The formation of distinct groundwater redox zones downgradient of landfills, including iron-reducing zones, is well established (Lyngkilde and Christensen, 1992; Heron and Christensen, 1995; Christensen et al., 2001). The reductive dissolution of iron, where the insoluble state of ferric iron (Fe(III)) is converted to the soluble state of ferrous iron (Fe(II)), can result in the mobilization of arsenic (Cummings et al., 1999; Delemos et al., 2006; Ghosh et al., 2006; Minyard and Burgos, 2007; Pique et al., 2010). While the waste may not be the source of the arsenic, the geochemical conditions created by the discharge from uncontrolled waste disposal (e.g., no liner system, leachate discharge to the environment) result in iron and arsenic mobilization (Delemos et al., 2006).

Elevated concentrations of arsenic, regardless of their source (waste or native soil), raise concern because of arsenic's known toxicity and low risk-based water quality thresholds (e.g., the World Health Organization (WHO) and US EPA drinking water standards for arsenic = 0.01 mg/L; WHO, 2008; US EPA, 2010). Despite the less severe human toxicity, elevation of iron concentrations in groundwater can also pose a concern. In Florida, US, for example, several unlined landfills have been required to undergo corrective action to remediate groundwater, largely because of elevated iron concentrations. While the US EPA secondary drinking water standard for iron of 0.3 mg/L (US EPA, 2011) is frequently exceeded in landfill groundwater monitoring wells, such exceedances did not historically receive regulatory scrutiny as secondary standards exist to address aesthetic concerns (e.g., taste, color, staining). However, given that a newer health-based water quality threshold for iron of 4.2 mg/L (FDEP, 2005) was developed for Florida and is often exceeded in groundwater at landfill sites, an

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increase in monitoring requirements and implementation of remedial action has occurred. Iron concerns have been exacerbated when high-Fe(II) groundwater intercepts a surface water body, causing oxygen depletion and producing iron-rich flocs as a result of oxidation of reduced iron, where Fe(II) is oxidized to Fe(III) (Dalzell and Macfarlane, 1999; Randall et al., 1999; Parisio et al., 2006).

In this research, we investigated the potential for leachate from unlined construction and demolition (C&D) debris landfills to promote reductive dissolution of naturally occurring iron and arsenic in underlying soils. Many US states do not require liners for C&D debris landfills (Clark et al., 2006), thus leachate may directly enter the underlying soil system and groundwater. As a result of the types of waste found in C&D debris (building materials such as concrete, asphalt, wood, drywall), leachate from C&D debris landfills is expected to contain less readily biodegradable organic matter compared to landfills used for disposing household waste containing food and paper products (Townsend et al., 1999; Weber et al., 2002). The organic matter present in C&D debris leachate largely originates from woody materials such as lumber and vegetative matter and should be more recalcitrant to biodegradation.

The research presented here was motivated by uncertainty in the regulatory and waste disposal community in Florida regarding the cause of elevated iron and arsenic concentrations in monitoring wells at unlined C&D debris landfills. Although iron and arsenic are known to naturally occur in Florida soils, and evidence from elsewhere suggests that municipal solid waste (MSW) landfill leachate can result in mobilization, C&D debris components include both iron- and arsenic-containing materials (e.g., steel, arsenic-treated wood; Kartam et al., 2004; Jambeck et al., 2007; Hawley et al., 2009; Cochran and Townsend, 2010), and thus represents another possible contamination source. Thus, one objective of this work was to assess whether C&D debris leachate could promote reductive dissolution of soil iron minerals, and if present, the subsequent mobilization of arsenic. A second objective was to examine the approach of using calcium carbonate materials (e.g., limestone) to remove iron (and possibly arsenic) from groundwater plumes containing mobilized Fe(II). Calcium carbonate is an abundant material in Florida; such minerals have been noted to possess the potential for removing metals from groundwater (Aziz et al., 2001), and under certain environmental conditions Fe(II) can precipitate as a carbonate mineral (e.g., siderite).

2. Materials and methods

2.1. Column materials

Four different types of materials were employed in the columns: synthetic C&D debris, soil, drainage gravel, and crushed limestone. A simplified C&D debris composition was used to provide the major components of this waste stream (percentages by mass): concrete (40%), wood (45%), and drywall (15%). While other components also occur in C&D debris (e.g., metal, asphalt, cardboard), based on experience from similar studies, use of only the major components (i.e., concrete, wood, drywall) would meet the objectives of creating leachate with the typical organic matter composition (primarily from wood waste) and chemistry of C&D debris landfill leachate (Yang et al., 2006; Jambeck et al., 2008; Dubey et al., 2009). Wood (untreated southern yellow pine) and drywall were purchased from building material stores and the concrete was collected from a concrete processing facility. Each material was size-reduced (as needed) and screened to pass a No. 4 sieve (1.27 cm).

Two soils were used, each in separate columns. One soil (S1) was collected from a solid waste facility in Florida known to have elevated iron issues in the surrounding groundwater monitoring wells. This soil possessed an average iron concentration of 10,400 mg/kg, was low in arsenic (<0.5 mg/kg), had a pH of 4.7, and was yellow in color. Goethite was detected by XRD analysis. The other soil (S2) was collected from a site in New Hampshire known for elevated arsenic concentrations. This soil, S2, possessed an average iron concentration of 5820 mg/kg, an arsenic concentration of 72.4 mg/kg, had a pH of 6.2, and was brown in color. All soils used in the columns were sieved to less than 2 mm. A DI water extraction test was performed on both soil samples using a 1:1.4 soil/water ratio for 12 h. The Fe(II) and Fe(III) ion concentrations released into water were below detection limit (BDL). The content of amorphous iron contents was analyzed using the method of McKeague and Day (1966). S1 contained 988 mg/kg and S2 contained 427 mg/kg amorphous iron content.

Other than the detection of goethite in S1 through XRD analysis, specific information regarding the mineralogy of the iron and arsenic species in the soil was not determined. However, based on soil color, the primary Fe(III) minerals present in S1 were likely goethite, hematite, and akageneite, and those present in S2 were likely ferrihydrite, goethite, akageneite, hematite, and maghemite (Heron et al., 1994; Arimoto et al., 2002). Both arsenate and arsenite are known to sorb to iron oxides in soils and could therefore have both been present sorbed to the soil minerals (Cummings et al., 1999). The reductively soluble arsenic is often assumed to exist as the As(III) species (Cummings et al., 1999; Masscheleyn et al., 1991; Pique et al.; 2010).

The limestone was purchased from a mineral supply store and was screened to a particle size less than 0.8 mm. The composition of the limestone was determined to be 95% $CaCO_3$, 2.7% $MgCO_3$, and 2.3% other minerals by a Bruker AXS ARTAX 800 micro-XRF spectrometer. For the drainage layers, washed pea gravel from a building supply store was utilized.

2.2. Column construction and operation

Eight laboratory leaching columns were constructed of 10.2-cm (4-inch) diameter PVC pipe (four experimental scenarios were simulated in duplicate columns). Column construction details and configurations are presented in Fig. 1. Columns 1 and 3 (and their duplicates) included a waste layer for producing C&D debris leachate, a soil layer (S1 was used for column 1 and S2 was used for column 3), and a remedial layer (limestone). Drainage layers (used for sample collection) were placed below each layer. From the top to the bottom of the column, the strata consisted of the C&D waste layer (30 cm), a drainage layer (15 cm gravel), a soil layer (30 cm), a drainage layer (15 cm), a limestone layer (30 cm), and a final drainage layer (15 cm). Additional columns were prepared to serve as control columns, containing only a soil layer (30 cm) with a drainage layer (15 cm gravel) above and beneath (column 2 for S1 and column 4 for S2). A piece of nonwoven geotextile was used to separate the different layers in the columns. Ports for sample collection (labeled A, B, and C in Fig. 1) were installed in the drainage layers of the test columns. For the control columns, samples were collected only from the bottom of the drainage layer, Fig. 1.

During operation, a total of 2 L of DI water was added to the top of each column weekly. A peristaltic pump (Cole-Parmer Instrument Co.) was used to feed the water at a flow rate of 10 mL/min until the 2-L reservoir was exhausted. The water passed through the column by gravity, taking approximately 30 min to pass through the waste layer, 40 min to pass through the soil layer, and 120 min to pass through the limestone layer. A 100-mL leachate sample was collected from all three ports of the experimental columns weekly. Remaining liquids from the bottom of the column were discarded; no liquids were recirculated and only DI water was added to the top of the column. For the control columns,
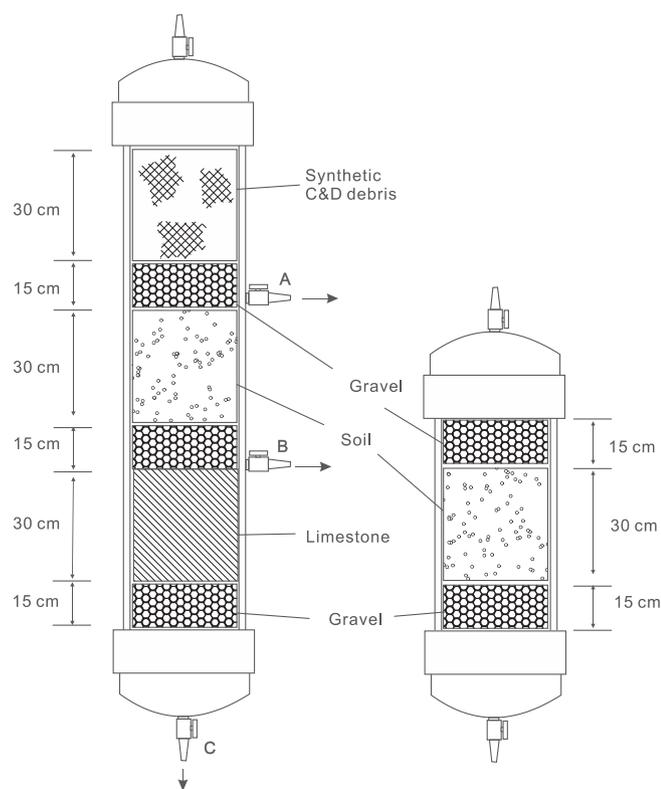
Fig. 1. Schematic of testing (left) and control (right) columns used in the study (for the testing columns ports A, B, and C) shows the sampling ports for leachate after it passes through the different layers of synthetic construction and demolition (C&D) debris, soil, and limestone.

one sample was collected from the bottom of the column. The total operation time for columns 1 and 2 was 34 weeks and the total operation time for columns 3 and 4 was 27 weeks. The experiments were concluded at the same time.

2.3. Chemical analysis

The pH, oxidation–reduction potential (ORP) (Accumet Co., Model 20), dissolved oxygen (DO) (Thermo Inc., Model 23), and Fe(II) (Standard Method 3500) (APHA, 1995) were measured in all leachate samples. The detection limit of Fe(II) was 0.01 mg/L. The concentrations of iron, arsenic, and other cations (e.g., calcium and sodium) in the soil and leachate were analyzed by digesting the samples following US EPA SW846 3050B method and US EPA SW846 3010A method, respectively, followed by analysis using inductively coupled plasma atomic emission spectroscopy per US EPA SW846 6010C method (ICP-AES, Thermo Jarrell Ash Corp. Model 95970). Detection limits of iron, arsenic, calcium, and sodium were 0.01 mg/L, 0.004 mg/L, 0.1 mg/L, and 0.3 mg/L, respectively. Soil pH values were analyzed per US EPA method SW846 9145D. Additional leachate was sampled on days 7, 49, 119, and 189 and analyzed for non-purgeable organic carbon (NPOC) (Shimadzu total organic carbon analyzer, TOC-V_{CPH}), total dissolved solids (TDS) (Standard Method 2540), and alkalinity (Standard Method 2320) (APHA, 1995). During analysis, laboratory blanks, matrix spikes, and calibration checks were performed as appropriate for quality control. Analyses of blank samples were consistently below detection limits; matrix spike samples and calibration check samples showed recoveries between 90 and 110%. Statistical analyses were performed using one-way analysis of variance (ANOVA) followed by a post hoc Dunnett's test utilizing the control columns as a reference. A p value of less than 0.05 was considered to be statistically significant.

3. Results and discussion

3.1. C&D debris leachate quality

General water quality characteristics of leachate collected from the bottom of the waste layers (port A of columns 1 and 3) fell within the typical range of C&D debris leachate from previous lab experiments and field measurements (Table 1). The average pH and ORP values of the samples from the experimental columns are presented in Fig. 2. The pH ranged from 6.1 to 6.9. Leachate pH from the waste layers of columns 1 and 3 varied until day 100 of the experiment, but stabilized at approximately 6.4 for the rest of the experimental period, on the lower end of the range typical of C&D debris landfill leachate (6.5–7.6) as shown in Table 1. The ORP of the C&D debris leachate in both columns shifted from positive to negative values within two weeks. These results, coupled with the increase in alkalinity, indicate a shift in the C&D debris layer from oxidizing to reducing conditions. When drywall or similar gypsum wastes are present, reducing conditions in C&D debris landfills develop as a result of the activity of sulfate-reducing bacteria that consume organic matter and utilize sulfate (present in large amounts because of gypsum) as an electron acceptor (Yang et al., 2006; Jambeck et al., 2008). The concentrations of NPOC, TDS, sodium, and calcium fell in the range of those found in typical C&D debris leachate.

Arsenic concentrations in the C&D debris leachate were below detection limit (4 μg/L) during the experimental period. The majority of the Fe(II) leachate measurements throughout the experimental period were below detection limit (0.01 mg/L). Iron and arsenic have routinely been detected in other C&D debris leachate evaluations (Table 1), but the absence of these two chemicals in the present study was not surprising. Previous studies reported total iron and not Fe(II), so it is difficult to assess the true extent of dissolved iron concentrations. Particulate-bound iron is common in leachate and small amounts were observed periodically in this study (<1 mg/L). In the form of steel, iron will exist in the zero-valent form and thus is not expected to undergo reductive dissolution. However, some oxidized iron (surfaces of steel wastes, landfill cover material) will be present in such landfills and thus some leachate iron is expected; no steel materials were included in the waste stream in this study since a major objective was to assess the potential for the soil to act as the source of dissolved iron. The concentrations of arsenic measured in previous studies have most often been a result of arsenic-treated wood (Jambeck et al., 2007; Dubey et al., 2009), and in this research, no such material was added.

3.2. Iron mobilization

Fig. 3 shows the Fe(II) concentrations with time in samples collected from ports A and B for the columns containing the S1 soil. Dissolved Fe(II) concentrations measured after water passed through the layer simulating C&D debris (port A) were in nearly all cases lower than the detection limit (0.01 mg/L), whereas the Fe(II) concentrations in the leachate after it passed through the soil were in the range of 3–6 mg/L. These concentrations were more than an order of magnitude greater than the concentrations measured from the control columns (<0.01–0.03 mg/L) and considered statistically significant at the 95% confidence interval for 32 of 37 sampling events for S1 and 29 of 37 events for S2, including the initial event at 0 days for S1 and S2. Similar results were encountered in the columns containing the S2 soil (S2); see Fig. 4. Fe(II) concentrations increased above 1 mg/L after 30 days and remained in a range of 1–2 mg/L through the remainder of the experiment (a maximum concentration of 1.8 mg/L was measured). The Fe(II)

Table 1
Comparison of measured construction and demolition (C&D) debris leachate parameters with published literature values.

Parameters	This study[a]	Melendez, 1996[b]	Jang and Townsend, 2003[c]	Weber et al., 2002[d]	Jambeck, 2004[e]	Dubey, 2005[e]
pH	6.40	6.45–7.60 (6.95)	6.5–7.0	6.90	6.5–7.0	6.5–7.0
Alkalinity (mg/L as CaCO₃)	75–725	38.2–6520 (970)	–	530	550–2000	1500–2500
NPOC (mg/L)	20–36	19.0–1900 (310)	–	21.1	–	–
TDS (mg/L)	873–2010	990–3530 (2260)	1640–3000	2120	1720–4160	2200–7000
Sodium (mg/L)	21–37	11.0–1290	–	42.8	130–500	–
Calcium (mg/L)	274	90–600 (270)	300–690	470	210–790	–
Iron (mg/L)	<0.01[f]	0.05–275 (36)	–	1.65	–	–
Arsenic (µg/L)	<4.0	1.4–24.6 (12.3)	10–380	41.4	12.5–38.1	50–300

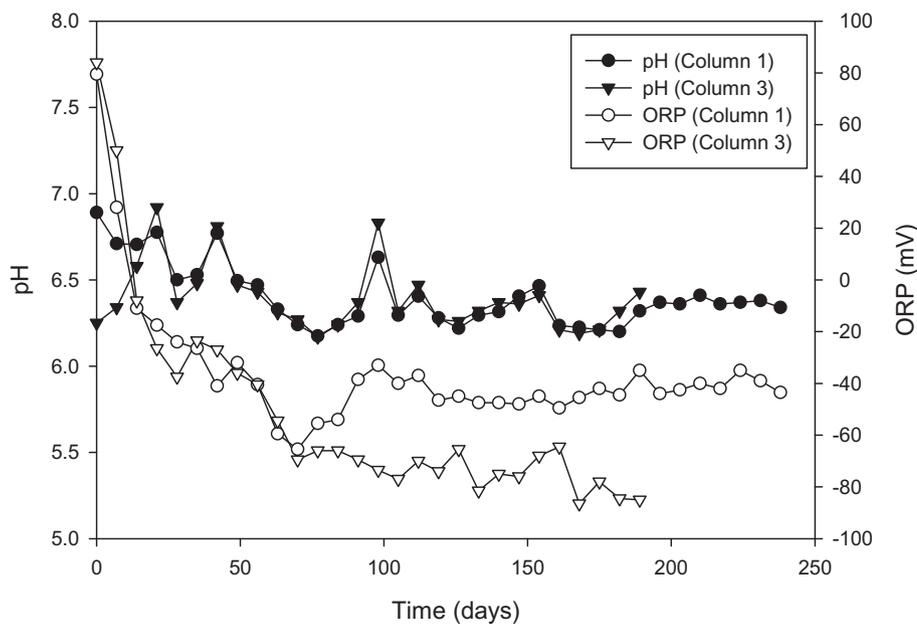[a] Average/ranges experimental columns 1 & 2.
[b] Full-scale study. Concentration ranges from literature review of C&D leachate, values in parentheses indicate average value for each parameter.
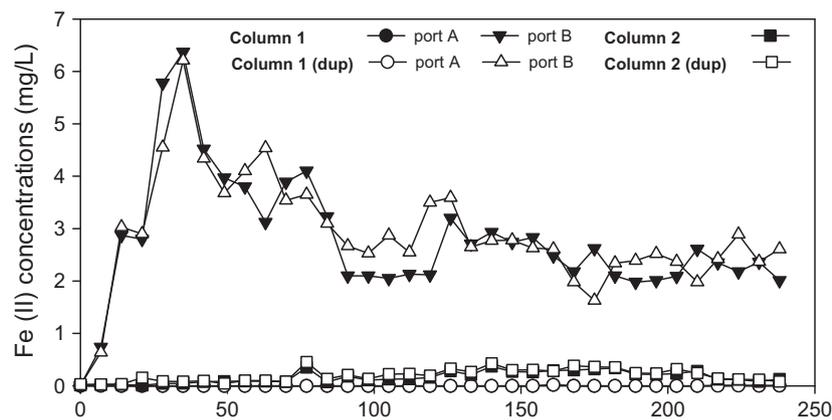[c] Lab-scale C&D lysimeter study (0.5% CCA treated wood added).
[d] Field-cell average.
[e] Pilot-scale C&D lysimeter study (control column: no CCA treated wood added).
[f] Measured as Fe(II).

Fig. 2. Changes in pH and oxidation–reduction potential (ORP) of C&D debris leachate (port A) over time. Values represent the average of duplicate columns.

Fig. 3. Change of ferrous iron concentration in leachate before (port A) and after (port B) passing through iron-rich soil (S1) as a function of time.

concentrations of the control columns were relatively stable and consistently lower than 0.4 mg/L.

Within the S1 columns a one-way ANOVA test showed that the Fe(II) concentrations from ports A, B, and C varied significantly at

the 95% confidence interval ($p < 0.05$) for 34 of 37 sampling events. Further post hoc analysis (one-sided Dunnett's test) demonstrated that the variation between these ports showed that Fe(II) concentrations in port B varied significantly from Fe(II) concentrations in
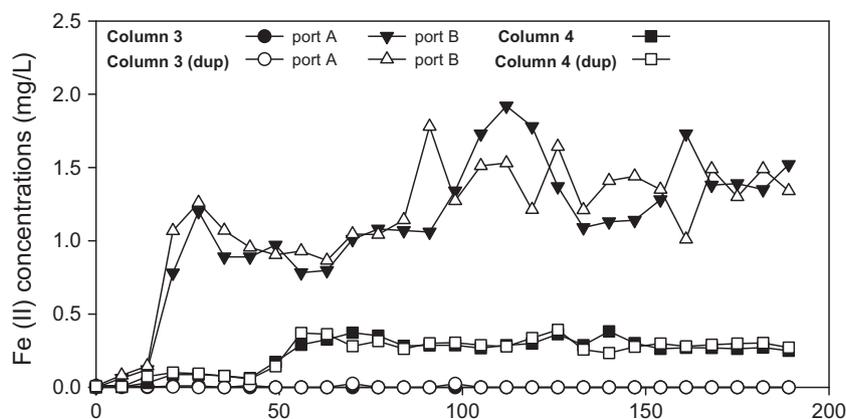
Fig. 4. Change of ferrous iron concentration in leachate before (port A) and after (port B) passing through iron- and arsenic-rich soil (S2) as a function of time.

ports A and C only during the first measurement in the study (at 0 days), when concentrations from ports A and C were below detection and resulted in a *t* statistic lower than $t_{critical}$. Also the relatively low degrees of freedom in the experiments influenced a relatively high value of $t_{critical}$. No significant difference in Fe(II) concentrations was observed between ports A and C for both the S1 and S2 soil columns.

A primary objective of our research was to assess whether the infiltration of C&D debris could promote the reductive dissolution of iron from soil, and the results demonstrate that this can occur. Previous research on MSW landfills, for example Di Palma and Mecozzi (2010), shows that leachate can result in the mobilization of naturally occurring elements in soil. Even though C&D debris landfill leachate does not contain the same readily degradable organic matter as expected with MSW landfill leachate, the present research demonstrates such leachate can similarly promote reducing conditions. Several factors could contribute to promoting reducing conditions (e.g., providing organic matter for consumption by iron-reducing bacteria, the chemically reducing nature of the C&D debris leachate), and this study was not designed to determine the relative role of these factors (future work should target this). Some degree of reductive dissolution and iron mobilization might occur at a landfill site regardless of leachate infiltration because of the other geochemical changes that develop (e.g., interruption of natural water cycles and soil vapor exchange); this merits further attention.

The results support that reductive dissolution was the primary cause of iron release, though no specific experiments were conducted to determine the role of biotic versus abiotic reduction; the authors suspect that biotic reductive dissolution was dominant. Changes in pH, which result from both the pH of the leachate as well as the subsequent reduction reactions, can also impact iron release. Figs. S1 and S2 in the Supplementary material depict the log Fe(II) concentrations over the range of pH values observed in the study. Among the different sample types (leachate from waste, leachate passing through soil, water passing through soil), pH values were relatively similar throughout the experiment and thus no dramatic difference in Fe(II) concentration as a function of pH was noted. In a study by Di Palma and Mecozzi (2010), column tests were conducted using soil taken from under a municipal landfill and groundwater from the same site; their results showed no significant difference in dissolved iron leached from soil at pH values of 6.5 and 8.5.

The concentration of iron observed in the leachates after passing through both soils was greater than the secondary drinking water standard (0.3 mg/L) and in the case of S1, at times greater than Florida's risk-based threshold (4.2 mg/L). However, care must be taken in comparing column results to regulatory thresholds, as many other factors would influence the concentrations likely to be reached in the environment at a landfill site (e.g., waste deposit area, aquifer thickness, groundwater velocity). Measurements observed by the authors at Florida landfills are often 10 mg/L or greater. Delemos (2006) found iron levels in groundwater surrounding a closed, capped MSW landfill to range from 10 to 70 mg/L. Minyard and Burgos (2007) performed a column experiment using an iron-rich coastal sand (20,400 mg/kg extractable iron, predominantly hematite), synthetic groundwater, and a source of organic material and bacteria, and reported mobilized Fe(II) concentrations in the range of 33–40 mg/L.

While the solutions collected from the control columns (the soils exposed to water, not leachate) were lower in Fe(II) concentration compared to those exposed to leachate, some Fe(II) was mobilized from the soils; Fe(II) was not initially present in the pore water collected from the base of the columns, but increased over time to a steady magnitude. This was more pronounced for the S2 soil even though its total iron concentration was half that of the S1 soil (5800 mg/kg vs 10,400 mg/kg). The results suggest that the geochemical environment created in the soil layer with water addition supported reductive dissolution (though to a lesser extent than under similar conditions with leachate addition), and characteristics of S2 were more amenable to reductive dissolution occurring. Based on the current literature, it is speculated that iron release occurred primarily from the amorphous (poorly crystalline) iron oxides found in the soil, as they have been shown to reduce more readily under biological and chemical means (Lovley and Phillips, 1986; Wahid and Kamalam, 1993; Roden, 2003).

3.3. Arsenic mobilization

Since the S1 soil did not contain a detectable arsenic concentration, arsenic mobilization in relation to iron reductive dissolution was only assessed using the S2 soil (Fig. 5). As expected, arsenic was not detected in the C&D debris leachate, but it was observed after the leachate passed through the soil (port B). Detectable concentrations of arsenic were first observed at day 50, after which they remained in the range of 10–25 μg/L. For perspective, this is greater than the EPA and WHO drinking water standard of 10 μg/L (WHO, 2008; US EPA, 2011). Using a one-way ANOVA comparing experimental column As concentrations from ports A, B, and C, concentrations were found to vary significantly ($p < 0.05$) for 10 of the 28 sampling events, which prompted a post hoc Dunnett's test. After 56 days, As concentrations in samples from Port B were significantly larger than Port A for 20 of 28 sampling events.

Arsenic mobilization did not immediately correspond to that observed with iron; arsenic release occurred at day 50, whereas iron release was observed at day 7 (Figs. 4 and 5). Several factors
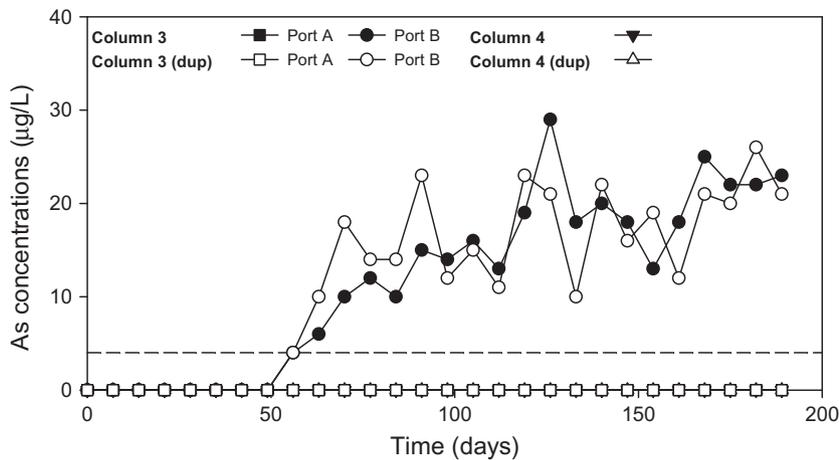
Fig. 5. Change of arsenic iron concentration in leachate before (port A) and after (port B) passing through iron- and arsenic-rich soil (S2) as a function of time.

may have contributed to this observation. As reductive dissolution occurs and arsenic is released into solution, some of the arsenic should sorb with remaining Fe(III) minerals, thus retarding travel through the soil layer. Carbonate ions have been reported to displace sorbed arsenic from Fe(III) minerals (Appelo et al., 2002), and in the present study, a large increase in leachate alkalinity between days 7 and 50 corresponded to the increase in arsenic concentrations measured in the leachate after passing through the soil layer (Fig. 5).

The discussion of arsenic thus far has been simplified, referring to arsenic as a single chemical species. However, much like the Fe(III)/Fe(II) redox couple, arsenic's fate and mobility are influenced by the As(V)/As(III) redox couple (Kumpiene et al., 2009). For example, Islam et al. (2004) discuss the mobilization of arsenic from aquifer sediments and describe the potential complex role of both Fe(III) and As(V) reduction after their subsequent fate. In batch studies, they observed an arsenic release that followed in time after an iron release (similar to observations from the present study) and attributed this in part to the redox potential of the Fe(III)/Fe(II) couple compared to the As(V)/As(III) couple. Similarly, Masscheleyn et al. (1991), in an experiment designed to test arsenic speciation and solubility at different Eh and pH values, observed the simultaneous reduction of As(V) to As(III) and increases in soluble As.

3.4. Efficacy of limestone

Limestone proved to be effective at removing Fe(II) from the leachate solutions that passed through the soil layers (columns 1 and 3), reducing Fe(II) concentrations from the range of 1–6 mg/L to less than the detection limit of 0.01 mg/L (see Fig. 6). Throughout the experiment, all of the iron concentrations measured in leachate passing through a limestone layer (columns 1 and 3, port C) were below the secondary drinking water limit (0.3 mg/L). Mettler et al. (2009) reported that Fe(II) sorbed on calcite particle surfaces rapidly, followed by co-precipitation to form Fe(II) minerals. Aziz and Smith (1992) reported that limestone has the ability to remove other bivalent metal cations; for example, manganese (II) was removed by greater than 95% from an initial concentration of 1 mg/L, and copper (II) was removed by greater than 90% from an initial concentration of 50 mg/L (Aziz et al., 2001). Future work will focus on identifying the responsible removal mechanisms, but candidate processing includes the formation of the mineral siderite ($FeCO_3$), the sorption of Fe(II) onto the limestone surface, and sorption followed by co-precipitation.

The limestone layer was largely ineffective at decreasing the arsenic concentration (data not shown). Using a one-sided post hoc t-test at 95% confidence, no As concentrations from port B compared to port C were found to vary significantly. Other studies have
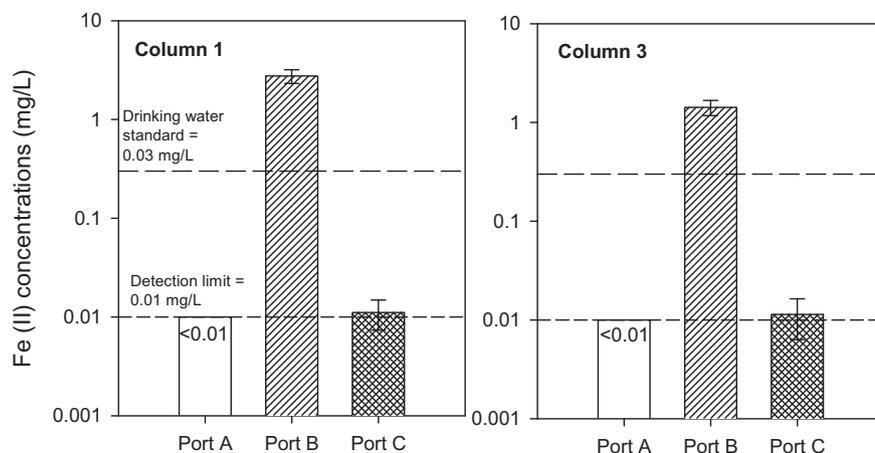

Fig. 6. Comparisons of Fe(II) concentrations in leachate collected from ports A, B, and C of columns 1 and 3 for days 100 through 150. In computing statistics, concentrations below the detection limit were set equal to the detection limit.

suggested that limestone has a weak affinity on arsenic (Hossain and Islam, 2008; Nillson et al., 1994). Gibert et al. (2010) studied arsenic removal by mixing zero-valent iron, limestone, and compost, and summarized that arsenic was removed through co-precipitation with iron and aluminum (oxy) hydroxides and even more so by sorption onto zero-valent iron, and not by sorption onto or reaction with limestone.

4. Summary and conclusions

Column experiments were performed to examine whether C&D debris leachate (without iron and arsenic) can mobilize naturally-occurring iron and arsenic from soils that might exist at unlined landfill sites. In addition, the potential for limestone to react with and remove mobilized iron and arsenic was examined. This research was restricted to the analysis of two soils, one high in iron (10,400 mg/kg) and one high in iron and arsenic (5400 mg/kg iron and 70 mg/kg arsenic). The soils were exposed to the infiltration of C&D debris leachate created by DI water passing through synthetic C&D debris. Control columns were included for both soil types, allowing the water to only pass through the soils.

Low iron and arsenic concentrations (below US federal drinking water limits) were consistently encountered in water that had passed through the C&D debris layer to create leachate. The infiltration of this leachate through both soil types resulted in the mobilization of Fe(II). While leachate from C&D debris landfills is thought by some to be relatively inert in comparison to MSW landfill leachate, the results demonstrate that for landfills containing soils amenable to reductive dissolution of Fe(III) minerals, discharge of leachate from an unlined disposal area can result in Fe(II) mobilization. Although iron in a C&D debris landfill's leachate may represent a discharge source to the underlying aquifer, iron presence in the leachate is not required for Fe(II) mobilization. The environmental impact of elevated iron concentrations in groundwater at a C&D debris landfill may be debated, but the occurrence should not represent a surprise.

Arsenic mobilization from the high-arsenic soil examined also occurred, again indicating that at unlined C&D debris landfill sites with certain soils (containing arsenic, subject to reductive dissolution), elevations of arsenic concentrations in groundwater well samples should be anticipated, regardless of whether arsenic-containing materials are present in the waste. Measurements of arsenic release did not immediately correspond to iron mobilization; additional work will be needed to assess the specific nature of arsenic release and mobilization, and its interrelation with iron reductive dissolution.

Crushed limestone was successfully utilized to remove iron from the soil-impacted leachate (from a maximum concentration of 6 mg/L to below 0.01 mg/L). However, arsenic was not removed appreciably. The ability of limestone to remove Fe(II) from groundwater opens the door for alternative remedial strategies to more commonly practiced pump-and-treat systems. One example currently under investigation is the use of calcium carbonate or similar materials as a passive reactive barrier, especially at key points where aquifers discharge into surface waters and create ecological impairment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.wasman.2011.11.016.

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