Published in final edited form as:

Environ Pollut. 2006 May ; 141(1): 22–29. doi:10.1016/j.envpol.2005.08.028.

Extraction of arsenate and arsenite species from soils and sediments

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Abstract

The primary objective of this study was to develop a simple method that can be used to extract the more readily mobilizable and bioavailable arsenic species from soil and sediment while at the same time minimizing the transformation between (As^{III}) and (As^V), the two most commonly found arsenic species in the environment. Several extraction strategies were evaluated using phosphate as extractant in combination with either ethylenediaminetetraacetic acid (EDTA), hydroxylamine hydrochloride (NH₂OH·HCl), or sodium diethyldithiocarbamate trihydrate (NaDDC). The addition of EDTA in the phosphate solution did not prevent As^{III} from oxidation. While promising results were shown when 1% NH₂OH·HCl was added, conversion of As^{III} began to occur with extended extraction time (>12 h). Good results were achieved using 10 mM phosphate and 0.5% NaDDC where As^{III} oxidation was clearly minimized. The combined phosphate and NaDDC solution was applied to several soil and sediment samples. As^{III} spiked was quantitatively recovered in all soil types tested.

Keywords

Arsenic speciation in soil; Arsenite; Arsenate; HPLC-HG-AFS

1. Introduction

Research on arsenic biogeochemical cycling and its health effects has spanned the spectrum from occurrence and exposure to intervention and medical treatment. Arsenic study is complicated by the fact that both organic and inorganic arsenic forms can exist in environmental and biological systems (Cullen and Reimer, 1989; Frankenberger Jr., 2002). Arsenic is also a redox sensitive element which can exist in multiple oxidation states (5, 3, 0, and -3). Conversion between different oxidation states occurs readily in environmental and biological systems (Frankenberger Jr., 2002; Meng et al., 2003; Watt and Le, 2003). The environmental fate, bioavailability and toxicity of arsenic vary dramatically with its chemical forms. Therefore, assessment of arsenic fate and transport, environmental impact and human health risk based only on measurement of total arsenic concentration is not reliable. Frequently, the lack of the speciation information is the major limitation to our understanding of the biogeochemical cycling of arsenic and its health effects to human beings.

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NaDDC preserves arsenite during soil and sediment extraction.

The identification of different arsenic forms in environmental and biological systems has become an important and challenging research area in environmental and biomedical studies. The separation steps should be considered closely in order to maintain the integrity of arsenic species. As with many other metals, speciation analysis of arsenic involves a complex scheme of operation (Templeton et al., 2000). One of the approaches to study the solid-phase association of elements that has been extensively applied to metals and metalloids is the sequential partial dissolution technique proposed by Tessier et al. (1979). This analytical procedure involves sequential chemical extractions separating trace metals into five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual. Simplified sequential extraction methods have also been developed for practical applications (Aten and Gupta, 1996; Cai et al., 2002; Gomez-Ariza et al., 2000; Gupta et al., 1996; Pansar-Kallio and Manninen, 1997). For example, the three-level evaluation system, which separates metals into mobile, mobilizable, and pseudo total metal fractions, seems to be attractive because of its simplicity and potential application in risk assessment and risk management (Gupta et al., 1996). Although these sequential extraction techniques provide some detailed information about the origin, bioavailability and transport of arsenic in the environment, they do not provide information on arsenic species in different oxidation states, such as inorganic arsenate (As^{V}) and arsenite (As^{III}), the two arsenic forms most commonly encountered in soils and sediments.

A number of studies have investigated the arsenic speciation involving As^{III} and As^{V} in soil and sediment samples using a variety of solvent extraction techniques (Bissen and Frimmel, 2000; Chappell et al., 1995; Ellwood and Maher, 2003; Gomez-Ariza et al., 1998; Manning and Martens, 1997; Pansar-Kallio and Manninen, 1997; Pongratz, 1998; Thomas et al., 1997; Wang et al., 1995). Although these studies provide useful information on the leachability of arsenic species from sediment and soil and the detection techniques for measuring arsenic species, they do not always reflect the original arsenic speciation status from the samples studied. Conversion between arsenic species, especially oxidation of As^{III} to As^{V} during the extraction process have been observed frequently (Ellwood and Maher, 2003; Georgiadis, 2004; Pansar-Kallio and Manninen, 1997; Wang et al., 1995). Extracting arsenic species from sediments while preserving the original arsenic redox integrity has been difficult. Hydrochloric acid extraction was used as a method for removal of arsenic from soil in a form suitable for speciation (Chappell et al., 1995). The strong acidic condition used is probably too aggressive and is suspected to lead to the alternation of arsenic species. Phosphoric acid was also used to extract arsenic species in soil and sediment with (Ellwood and Maher, 2003) or without (Thomas et al., 1997) the presence of hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$). X-ray absorption spectroscopy has also been used for analysis of arsenic oxidation directly in solid phase (Manning et al., 2003). This method, however, is limited by its sensitivity for most real environmental samples.

The primary interest of this study was not to conduct arsenic speciation with complete release of arsenic from soil/sediment, but rather to develop an analytical technique to evaluate the arsenic species in different oxidation states in the more soluble and mobilizable fractions. It is the arsenic in these fractions which is more bioavailable and therefore of greater importance for risk assessment and management. Phosphate solutions have been widely used as an extraction medium for soil arsenic (Loeppert et al., 2002; Manning and Martens, 1997). Extraction of arsenic with phosphate is through ligand exchange that involves the desorption of arsenic by phosphate. Ligand exchange does not dissolve the surface containing the adsorption sites but actively competes for them. Phosphate provides a number of benefits as a choice for chemical speciation of arsenic. It shares many similar chemical properties to arsenate such as ion size and acid dissociation constants (Cai and Braids, 2003; Loeppert et al., 2002) and provides a mild extraction medium which is similar to environmental conditions.

Phosphate was therefore selected as the primary extractant for arsenic speciation for soil and sediment in this study.

In this study, an attempt was made to develop a simple scheme that can be used to extract arsenic species from soil and sediment samples while at the same time minimizing the transformation between As^{III} and As^{V} . Our primary objective was to understand the arsenic species that were potentially mobilizable and bioavailable, rather than the total dissolution of arsenic present in the samples. Therefore, we selected a mild extraction media, i.e. phosphate solution (Loeppert et al., 2002). Other additives including ethylenediaminetetraacetic acid (EDTA), $\text{NH}_2\text{OH}\cdot\text{HCl}$, and sodium diethyldithiocarbamate trihydrate (NaDDC) were evaluated in combination with the phosphate solution to determine whether or not they improved arsenic species recoveries. A range of soil and sediment samples were analyzed for As^{III} and As^{V} to examine the validity of the extraction procedures developed on actual environmental samples.

2. Methods and materials

2.1. Chemicals and materials

Standard solutions were made using sodium metaarsenite (As^{III}) (98%, Aldrich, Milwaukee, WI), sodium hydrogen arsenate heptahydrate (As^{V}) (>98%, Aldrich, Milwaukee, WI), monosodium acid methane arsonate sesquihydrate (MMA), (99.5%, Chem Service, Westchester, PA), and cacodylic acid sodium salt (DMA), (98%, Sigma, St. Louis, MO). Arsenic standard stock solutions (As^{III} , As^{V} , MMA, and DMA) (1000 mg/L) were prepared by dissolving appropriate amounts of the individual arsenic standard in deionized distilled (DDI) water. Appropriate dilutions of the stock solutions were made for working standards and spiking solutions. Phosphate stock solution (1.0 M) for soil extraction was prepared by dissolving appropriate amounts of K_2HPO_4 and KH_2PO_4 in DDI water resulting in a solution of 0.5 M K_2HPO_4 and 0.5 M KH_2PO_4 . Additional solutions used to augment removal by phosphate were prepared from NaDDC (A.C.S. Reagent, >99%, Sigma-Aldrich, St. Louis, MO), $\text{NH}_2\text{OH}\cdot\text{HCl}$ (Certified A.C.S., 97.6%, Fisher Scientific, Fair Lawn, NJ), and EDTA disodium salt (99%, Sigma-Aldrich, St. Louis, MO). All chemicals were used upon receipt without further purification.

Phosphate mobile phase for HPLC analysis was prepared by dissolving appropriate amounts of potassium phosphate monobasic (KH_2PO_4) in DDI water to make a 1.5 mM solution. This solution was then adjusted to pH 5.8 with the addition of the 1.5 mM of potassium phosphate dibasic (K_2HPO_4) solution while monitoring with a pH meter.

DDI water was prepared by passing tap water through two deionization filters (US Filter Service, Warrendale, PA) and then distilling the water using a distiller (Barnstead Fistream™ GlassStill, Barnstead/Thermolyne, Dubuque, Iowa).

2.2. Selection of soil/sediment

Currently, soil or sediment standard reference materials (SRM) for arsenic speciation are not available. An alternative was to use one of the reference materials in which the total arsenic concentration is known and to spike the reference with different arsenic species if necessary. The SRM chosen for this study was PACS-2, a marine sediment reference material for trace metals and other constituents (National Research Council Canada (NRCC), Ontario, Canada). This particular SRM was chosen due to its elemental composition. The certified concentration of total arsenic in PACS-2 is $26.2 \pm 1.5 \mu\text{g/g}$. This level should be sufficiently high for total arsenic analysis even at relatively low extraction efficiency, as well as speciation of different arsenic forms, if any, present in the sample. Other important elements which are known to

influence the retention of arsenic are iron, aluminum, and manganese. Iron (Fe), aluminum (Al), and manganese (Mn) in PACS-2 are found at $4.09 \pm 0.06\%$, $6.62 \pm 0.32\%$, and $440 \pm 19 \mu\text{g/g}$, respectively, as reported by NRCC. For the purpose of comparison, a soil sample with high concentration of organic matter (40.7%) and low contents in Fe ($2473 \pm 71 \mu\text{g/g}$), Al ($6470 \pm 621 \mu\text{g/g}$), and Mn ($9.03 \pm 0.62 \mu\text{g/g}$) was collected from the Florida Everglades. PACS-2 and the Everglades soil were used for method development.

A range of soil samples were selected to validate the procedures developed. Several types of soils chosen, including uncoated sand, naturally coated sand, naturally coated sand with 10% (v/v) peat (Canadian sphagnum peat moss) were well characterized and have been studied for use in golf course putting green construction (Snyder, 2003). Uncoated sands and naturally coated sands are the normal substrates for golf course putting greens. The uncoated sand used was common quartz sand, light gray or colorless, and did not have clay-sized coatings. Naturally coated sands, collected from Lake County, Florida, had a reddish-brown hue due to oxidized Fe in the clay-sized fraction of the coating. It consisted of quartz and clay fractions including hydroxy-interlayered vermiculate ($(\text{Mg}, \text{Fe}^{++}, \text{Al})_3(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), goethite ($\text{FeO}(\text{OH})$) and gibbsite ($\text{Al}(\text{OH})_3$). The cation exchange capacities of sands and naturally coated sands were 0.1 and 4–5 cmol/kg, respectively as measured by Snyder (2003). There is evidence that organic matter may influence arsenic mobility (Redman et al., 2002; Xu et al., 1988) so an experiment was conducted to evaluate the proposed extraction procedure on arsenic stability in the presence of organic matter. The experiment was conducted using naturally-coated sand with the addition of 10% peat by volume. A carbonate soil obtained from local rock mining activities within South Florida was also chosen. The percent organic matter in the carbonate soil was <1%.

2.3. Instrumentation

Separation of the individual arsenic species was conducted using an HPLC (SpectraSYSTEM P4000, Thermo Finnigan, CA, USA) with a 100 μL injection loop for sample introduction. This HPLC system was coupled with an atomic fluorescence detection unit (PS Analytical Millenium System, PS Analytical, UK). The mobile phase (1.5 mM phosphate, pH 5.8) was pumped isocratically at 1 mL/min through a polymeric guard column (Hamilton PRP-X100) and an analytical anion exchange column (Hamilton Company, NV, USA). Trace metal grade hydrochloric acid (12.5%, v/v) and sodium borohydride solution (1.4%, w/v) were pumped at half speed (roughly 5 mL/min) generating arsine gas which was detected by the AFS. The HPLC and HG-AFS operating settings and experimental conditions were reported elsewhere (Georgiadis, 2004; Khan et al., 2004). With this instrumental set up, all major species present in the soil/sediment samples including As^{III} , As^{V} , monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) could be detected. Total arsenic and other metal analyses were performed using an inductively coupled plasma mass spectrometer (ICP-MS) (HP4500 PLUS, Hewlett-Packard Co., Wilmington, DE, USA). The experimental settings for ICP-MS were reported previously (Cai et al., 2002; Georgiadis, 2004).

Extraction of soil and sediment samples was conducted using an orbital shaker (Model DS-500, VWR International, West Chester, PA). Digestion of soils and sediments for total metal analysis was performed using a closed vessel microwave digestion system (CEM Mars5, CEM Co., Mathews, NC). The digestion procedure followed the EPA standard method 3051.

2.4. Extraction procedures

Before extraction, the bottles were thoroughly rinsed and filled with 10% HCl (v/v) and left to soak overnight. They were then rinsed three times with DDI water. Typically, 0.5 g of soil or sediment was extracted in washed 60 ml HDPE bottles (Nalgene). Sample extraction was conducted in triplicate for each of the experimental conditions tested. Soil/sediment was spiked

if necessary with appropriate amounts of either As^{III}, or As^V. Extraction was immediately carried out without waiting for adsorption equilibrium because of the purpose of these experiments were to preserve As speciation during extraction. Extraction solution (20 mL) with or without the presence of the arsenic species preserving reagents was placed in each bottle. Samples were placed on an orbital shaker and allowed to shake at a speed of 300 rpm for a pre-determined period of time (generally 1, 3, 5, 12 and 24 h or as otherwise noted). A portion of the solution was transferred to a 10 mL plastic tube and centrifuged at 5000 rpm for 5 min. The supernatant was then filtered through a 0.45 µm PVDF Acrodisc[®] syringe filter into a 2 mL HPLC vial and immediately analyzed by HPLC-HG-AFS.

For the experiments with the presence of NaDDC in extraction media, several modifications were made before analysis using HPLC-HG-AFS. As^{III}-NaDDC complexes could not be analyzed using HPLC under our experimental conditions. Therefore, an aliquot (5 ml) of the supernatant was acidified with 50 µL of 6 M HCl to break the complex formed between NaDDC and As^{III}. The pH was then adjusted with a small amount of 6 M NaOH (approximately 10 µL) to about pH 7. These samples were then ready for analysis by HPLC-HG-AFS.

3. Results and discussion

Several chemicals including EDTA, NH₂OH-HCl, and NaDDC, were selected as additives to the phosphate solution in an effort to prevent the oxidation of As^{III} to As^V. EDTA has been successfully used in water analysis to preserve the re-distribution of arsenic species by chelating metal cations, buffering the sample pH, and reducing microbial activity (Bednar et al., 2002, 2004). However, the ability of EDTA in preserving arsenic species integrity in soil extract has not been tested. NH₂OH-HCl has been added to 0.5 M phosphoric acid as a “sacrificial oxidant” in an effort to reduce the oxidation of As^{III} to As^V during soil extraction but without reducing As^V to As^{III} (Ellwood and Maher, 2003). NaDDC is a good complexing agent for As^{III} extraction from water samples (Alfassi and Wai, 1992). However, its ability in preventing arsenic species redistribution in soil extraction has never been evaluated.

3.1. Soil extraction with phosphate alone

It should be pointed out that the analytical technique employed in this study, HPLC-HG-AFS, determines the hydride-forming arsenic species, i.e. As^{III}, As^V, MMA, and DMA, which are the major arsenic forms in soils and waters (Frankenberger, 2002). Only two arsenic species, As^{III} and As^V were detected in the soils tested in this study. A typical chromatogram for the analysis of PACS-2 extract is shown in Fig. 1. To ensure that HPLC-HG-AFS could identify all arsenic forms present in the soil extract, the total arsenic concentration in the soil extract was also measured using ICP-MS. For one hour triplicate extraction, the total As concentrations were 1.88 ± 0.06 µg/g for ICP-MS and 1.90 ± 0.08 µg/g for HPLC-HG-AFS. For 24 h extraction, the total As concentrations were 2.38 ± 0.09 and 2.48 ± 0.44 µg/g for ICP-MS and HPLC-HG-AFS, respectively. The results for ICP-MS were in good agreement with the sum of concentrations of As^{III} and As^V detected using HPLC-HG-AFS. This confirmed that the two hydride-forming arsenic species, As^{III} and As^V composed the majority of arsenic present in the soil extract. Thus, the results from HPLC-HG-AFS analysis were used throughout the discussion.

When optimizing the phosphate concentration for soil extraction, 0.5 g PACS-2, 20 ml of phosphate solution, and 5 h of extraction time were used. The amounts of total arsenic (As^{III} + As^V) extracted using 10 mM (1.55 µg/g) to 50 mM (1.49 µg/g) phosphate were found to be similar. Although a significantly larger amount of arsenic (2.20 µg/g) was extracted at higher phosphate concentrations, such high concentrations (>50 mM) were not preferred due to the deterioration of peak shape in the analytical process. A 10 mM phosphate solution was therefore utilized in the following experiments. The focus of this research was to develop a method to

preserve the integrity of As species during extraction. Method for maximizing the total As extracted from soil has been reported elsewhere (Georgiadis, 2004).

With the selection of 10 mM as the phosphate concentration for extraction, the effect of extraction time on arsenic release from PACS-2 was investigated. As shown in Fig. 2A, As^{III} concentrations decreased sharply after 1 h extraction while As^V concentrations remained constant throughout a 12 h time period with a significant increase at 24 h. It is plausible that the rapid decrease in As^{III} concentration with extraction time was caused by conversion of As^{III} to As^V during extraction. Rapid conversion from As^{III} to As^V during soil, sediment and fly ash extraction has been observed in other studies (Ellwood and Maher, 2003; Wang et al., 1995). This transformation could be facilitated in the presence of some microorganisms (Ahmann et al., 1997; Cummings et al., 1999; Turpeinen et al., 1999; Wilkie and Hering, 1998) and in the presence of hydroxides of Fe, Al, and Mn (Driehaus et al., 1995; Manning et al., 2002; Matera et al., 2003; Mucci et al., 2000; Raven et al., 1998; Scott and Morgan, 1995; Takamatsu et al., 1985; Tournassat et al., 2002). PACS-2 contains fairly high concentrations of Fe ($4.09 \pm 0.06\%$), Al ($6.62 \pm 0.32\%$), and Mn ($440 \pm 19 \mu\text{g/g}$). The presence of these elements on the surface of soil particles or in the solution may enhance/catalyze the transformation of As^{III}, which could increase the concentration of As^V with time. It is also possible that the soil could have released more As^V with time, so the extent to which As^{III} conversion contributed to the increase of As^V is difficult to determine from these results. In order to further confirm the arsenic extraction patterns observed, a similar extraction procedure was applied to PACS-2 spiked with $4 \mu\text{g/g}$ As^{III}. Similar patterns were observed in the distribution of As^{III} and As^V during the 24 h extraction time period (Fig. 2B).

To compare the stability of As^{III} during extraction from soils with lower contents of Fe, Al, and Mn, a soil sample from the Florida Everglades was chosen. Relative to PACS-2, the Everglades soil contained low levels of As ($1.94 \pm 0.03 \mu\text{g/g}$), Fe ($2473 \pm 71 \mu\text{g/g}$), Mn ($9.03 \pm 0.62 \mu\text{g/g}$), and Al ($6470 \pm 621 \mu\text{g/g}$) and high levels of total organic matter (40.7%). The Everglades soil sample, spiked with $4 \mu\text{g/g}$ of As^{III}, was extracted with 10 mM phosphate for time periods ranging from 1 to 24 h. The results (Fig. 3) indicated that the As^{III} concentrations remained constant from 1 to 5 h of extraction, then decreased and again remained constant for the remainder 12 to 24 h. Compared to the results obtained with PACS-2, the rate of decrease in As^{III} concentration during the extraction of soil sample from the Everglades was slower, indicating that the soil characteristics played an important role in the As^{III} transformation. For example, As^{III} recovered was reduced to $2.55 \mu\text{g/g}$ after 24 h extraction from the Everglades's soil spiked at $4 \mu\text{g/g}$, while for PACS-2 spiked at $4 \mu\text{g/g}$ As^{III} extracted was $1.1 \mu\text{g/g}$ for the same extraction time. Nevertheless, oxidation of As^{III} to As^V during extraction seemed to occur for both soil types evaluated.

3.2. Soil extraction in the presence of EDTA

With the assumption that conversion is occurring due at least in part to the oxidation processes, an effort was made to stabilize arsenic species by sequestering possible metals which promote oxidation. EDTA has been successfully used in water analysis for the preservation of arsenic and selenium species in the presence of iron (Bednar et al., 2002; Gallagher et al., 2001; Garrabrants and Kosson, 2000). The premise is that EDTA will chelate with metals such as Fe and Mn thereby minimizing oxidation. Experiments were conducted to extract PACS-2 using 10 mM phosphate in the presence of 50 mM EDTA. The selection of 50 mM of EDTA was based on the observation that no significant difference was observed between 10 to 50 mM EDTA when PACS-2 was extracted with 10 mM phosphate for 5 h (data not shown). As^{III} concentrations still showed a steady decrease throughout a 24 h extraction time period for As^{III} spiked sample (Fig. 4A). The decrease in As^{III} concentration correlated with an increase in its respective As^V concentration.

The experiments showed that the addition of EDTA to the extraction media did not effectively prevent the decrease in As^{III} concentration with extraction time, in contrast to the results obtained for water samples where EDTA was shown to be useful in protecting As^{III} species (Bednar et al., 2002; Gallagher et al., 2001; Garrabrants and Kosson, 2000), strong matrix effects from the high metal concentrations in PACS-2 extracts is one possible reason for the inability of EDTA solution to preserve As^{III} . The Everglades soil was also spiked with $2 \mu\text{g/g}$ As^{III} and extracted with 10 mM phosphate in the presence of 50 mM of EDTA. Results indicated that the As^{III} concentrations did not vary significantly at the beginning, but decreased after 5 h (Fig. 4B). The slower decrease in As^{III} concentration during extraction for the Everglades soil suggests that the high concentrations of Fe and Mn hydroxides present in PACS-2 may have enhanced the conversion of As^{III} to As^{V} .

3.3. Soil extraction in the presence of $\text{NH}_2\text{OH}\cdot\text{HCl}$

$\text{NH}_2\text{OH}\cdot\text{HCl}$ could serve two functions for these experiments. One is to provide a mild reducing environment which in theory may facilitate retaining arsenic in its As^{III} oxidation state. Another function is through its effectiveness in dissolving iron oxy/hydroxide surfaces which are known to be strong adsorption sites for arsenic (Matera et al., 2003; Tessier et al., 1979). Experiments were first conducted to evaluate whether $\text{NH}_2\text{OH}\cdot\text{HCl}$ would facilitate the reduction of As^{V} to As^{III} . To do this, $50 \mu\text{g/L}$ As^{V} were prepared with 10 mM phosphate solution with and without the presence of 1% (w/v) $\text{NH}_2\text{OH}\cdot\text{HCl}$. The results indicated that a 1% solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 10 mM phosphate did not convert As^{V} to As^{III} over a 41 h time period (Georgiadis, 2004). Subsequent experiments thus utilized 10 mM phosphate and 1% $\text{NH}_2\text{OH}\cdot\text{HCl}$. Results show that up to a period of 12 h As^{III} concentration was conserved but again decreased at extended periods of 24 to 72 h (Fig. 5). As^{V} concentrations increased sharply for the periods of 48 to 72 h. Apparently the $\text{NH}_2\text{OH}\cdot\text{HCl}$ tends to limit As^{III} oxidation initially but the effectiveness was gradually reduced with time after 12 h extraction, causing an increase in As^{III} conversion. The significant increase in As^{V} after 24 h of extraction could be attributed, in part, to the decrease in As^{III} . It should also be noted that larger amounts of As^{III} were extracted from PACS-2 in the presence of 1% $\text{NH}_2\text{OH}\cdot\text{HCl}$ compared to those obtained without $\text{NH}_2\text{OH}\cdot\text{HCl}$ (see Fig. 2B for without $\text{NH}_2\text{OH}\cdot\text{HCl}$), indicating that $\text{NH}_2\text{OH}\cdot\text{HCl}$ enhanced the release of arsenic bound to sediment. It was expected that extraction with $\text{NH}_2\text{OH}\cdot\text{HCl}$ would yield higher total As concentrations since $\text{NH}_2\text{OH}\cdot\text{HCl}$ has been used to dissolve the iron oxy/hydroxide bound arsenic in soil and sediment (Gomez-Ariza et al., 1998; Tessier et al., 1979; Xiao-Quan and Bin, 1993). Ellwood and Maher (2003) have recently tested the effects of a number of sacrificial oxidants on arsenic species conversion during extraction with phosphoric acid. The best results for preventing As^{III} from oxidation were achieved when $\text{NH}_2\text{OH}\cdot\text{HCl}$ was used. They observed a slight increase in As^{V} concentration for all but one reference sediment spiked with As^{III} , thereby suggesting that little As^{III} was converted to As^{V} during the extraction process. Unfortunately, the sediments were extracted for only 1 h and no time effect was evaluated in that study (Ellwood and Maher, 2003). Nevertheless, these results showed that $\text{NH}_2\text{OH}\cdot\text{HCl}$ could be used to effectively prevent As^{III} from oxidation during soil/sediment extraction in combination with either phosphoric acid or phosphate buffer solution. It should be kept in mind, however, that the effectiveness of $\text{NH}_2\text{OH}\cdot\text{HCl}$ could decrease at extended extraction times.

3.4. Soil extraction in the presence of NaDDC

In addition to the above two strategies that were evaluated to prevent As^{III} from oxidation during soil and sediment extraction (through reducing the reactive metal content via complexation with EDTA, and through providing a mild reducing environment using $\text{NH}_2\text{OH}\cdot\text{HCl}$ as a sacrificial oxidant), we proposed a novel strategy in an effort to find an agent that forms a complex with As^{III} directly during extraction, thereby preventing oxidation of As^{III} to As^{V} . Dithiocarbamate compounds have been used for metal chelation and its

applications can be readily found in the literature. They have been used for chelation therapy such as the British AntiLewisite Agent (Bal) in World War II and dimercaprol (ATSDR, 1990). These compounds have also been widely used as pre-concentration agents in metal analysis (Alfassi and Wai, 1992; Chakraborti et al., 1987; Rodriguez et al., 1994). Dithiocarbamates contain two thiol groups which can bind to metals with a particular oxidation state. NaDDC can bind to many metals including arsenic in its +3 oxidation state at a molar ratio of 3:1 (Alfassi and Wai, 1992; Andres et al., 1994; Chakraborti et al., 1987; Garje and Jain, 2003; Rodriguez et al., 1994). The expectation was that NaDDC would complex with As^{III} thereby minimizing conversion to As^{V} .

Experiments were first conducted to evaluate the binding capability of NaDDC to As^{III} . Initial results from these experiments found that amounts of NaDDC (0.5%, w/v), in excess of the 3:1 ratio as indicated in the complexation stoichiometry, were needed for quantitative formation of the complex (Georgiadis, 2004). Concentrations greater than 0.5% NaDDC were not used due to the deterioration of chromatographic peaks. Thus, PACS-2 was extracted with 10 mM phosphate with the presence of 0.5% NaDDC (Fig. 6). Results show that NaDDC preserves As^{III} during extraction over a period of at least 24 h.

In addition to NaDDC, other dithiocarbamate compounds, such as pyrrolidinedithiocarbamate ammonium salt (APDC) can also form a relatively stable complex with As^{III} (Alfassi and Wai, 1992). These dithiocarbamate compounds are very different in their stability under different pH values. For example, the half-life times for NaDDC and APDC at pH <2 are 7 s and 63 min, respectively. For pH of 5 for NaDDC and 7.3 APDC, the half-life times are 87 min and 170 days. Ideally the most stable agent would be selected for the experiment. However, this was limited by the subsequent HPLC separation of the arsenic species. The APDC- As^{III} complex is much more stable than NaDDC- As^{III} and interfered with the analytical process used, which required that the complex be decomposed before HPLC separation. The decomposition of NaDDC- As^{III} complex was easily carried out at pH 1–2 after separation of the supernatant. This was usually accomplished by adding 50–100 μL of 6 M HCl to 5 mL of supernatant. Similar experiments were conducted using APDC. It was found that rapid decomposition of APDC- As^{III} complex was not easily accomplished, therefore making the subsequent analysis using HPLC-HG-AFS impossible.

3.5. Arsenic species in different soils extracted with phosphate + NaDDC

The results for the extraction of the phosphate + NaDDC extractant for the test soils are presented in Fig. 7. Extractions of phosphate alone were conducted to provide a reference for comparison with extractions conducted with 10 mM phosphate + 0.5% NaDDC. Since phosphate extractable arsenic concentrations in these soils were below detection limit (0.04 $\mu\text{g/g}$ calculated based on the three times of the baseline noise), the soils were spiked with 4 $\mu\text{g/g}$ As^{III} . When As^{III} was spiked into the soils, adsorption to soil particles could also occur in addition to the potential oxidation to As^{V} . It can be seen that the recoveries of As^{III} were clearly improved with the presence of 0.5% NaDDC for all soils tested. The relatively low As^{V} concentrations found in the extracts for all soils is another indication that conversion to As^{V} was minimized because of the presence of NaDDC. This was true for all soil types tested including the soil sample containing 10% peat by volume. It appears that the addition of peat did not alter the results obtained with naturally coated sand. It seems that the spiked As^{III} could be adsorbed more in the presence of carbonate soil compared to other soils. The reason for this to happen is currently not clear. Slight increase in total As concentrations when NaDDC was used was probably caused by the fact that the addition of NaDDC not only protected As^{III} from oxidation, but also reduced its adsorption on soil particles because of the formation of the As^{III} -DDC complex.

4. Conclusions

Rapid conversion of As^{III} to As^V during extraction of soils was observed with 10 mM of phosphate. Efforts were made to preserve the oxidation of As^{III} to As^V by using several additives to the phosphate solution, including EDTA as complexing agent for metals in the soil extract, NH₂OH·HCl as a sacrificial oxidant, and NaDDC as a complexing agent for As^{III}. The addition of EDTA to the phosphate solution did not prevent As^{III} from oxidizing probably because of the high concentrations of metals present in the soil extract. While promising results were shown when 1% NH₂OH·HCl was added, conversion of As^{III} began to occur with extended extraction time (>12 h). Good results were achieved using 10 mM phosphate and 0.5% NaDDC with minimized reductions in As^{III} concentrations in both original and As^{III} spiked sediment and soil samples. Experiments were conducted to test the applicability of 10 mM phosphate and 0.5% NaDDC to preserve As^{III} in the extract of several soil samples. The results indicated that the procedure successfully preserved the As^{III} concentration in all soil types tested. Recoveries of As^{III} spiked into these samples ranged from 80–120% and the As^V concentrations remained constant.

Results from this study indicate that phosphate solutions with 0.5% NaDDC could be used to extract arsenic species while at the same time minimizing the transformation between As^{III} and As^V from the soil and sediment samples used. Although this method should be further tested for its application for a broad range of soil and sediment samples, the results obtained in this study are promising.

Acknowledgements

This study was partially supported by funding from the National Institute of Environmental Health Science (S11 ES11181). We would like to thank Dr. George Snyder and Dr. John Cisar from University of Florida for providing the golf course soil samples and Tomoyuki Shibata from the University of Miami for collecting the carbonate soil.

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Fig. 1. Typical chromatogram of arsenic species extracted from PACS-2 using 10 mM phosphate.

Fig. 2. As^{III} and As^V extracted from PACS-2 with 10 mM phosphate at varying extraction time periods. 2A: PACS-2; 2B: PACS-2 spiked with 4 µg/g of As^{III}.

Fig. 3.
Arsenic species extracted with 10 mM phosphate from the Florida Everglades soil spiked with 4 µg/g As^{III}.

Fig. 4. Concentrations of As^{III} and As^{V} in A) PACS-2 spiked with 4 $\mu\text{g/g}$ of As^{III} and B) in the Everglades soil spiked with 2 $\mu\text{g/g}$ of As^{III} , extracted with 10 mM phosphate +50 mM EDTA.

Fig. 5. Arsenic extracted from PACS-2 spiked with 4 µg/g of As^{III} with 10 mM phosphate +1% NH₂OH·HCl.

Fig. 6.
Arsenic extracted from PACS-2 with 10 mM phosphate +0.5% NaDDC.

Fig. 7.

Comparisons of As^{III} extracted from soils spiked with 4 µg/g As^{III} using 10 mM phosphate with or without 0.5% NaDDC for 12 h. Phosphate extractable arsenic concentration in the unspiked soils was less than detection limit (0.04 µg/g calculated based on the three times of baseline noise). The uncoated sand, naturally coated sand, and naturally coated sand + peat have been used in Florida Golf courses. The high carbonate soil has been used in a study evaluating arsenic leaching from a deck constructed of wood treated with chromated copper arsenate.