Extraction of Adsorbed Arsenic from IAEA-SOIL-5

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The following parameters influencing the extraction efficiency of adsorbed arsenic (arsenate) from IAEA-SOIL-5 were investigated: (a) sonication or shaking time and temperature and (b) extractant type ($MgCl_2$ or NaH_2PO_4 solution), concentration and pH. Sonication of 250 mg material for 1 h at $< 30°C$ with 10 mL 1 mol L^{-1} phosphate at pH 4.0 yielded a maximum arsenate extraction efficiency of 31.9%. The remainder of the arsenate is probably incorporated in the lattice of minerals and not easily available (exchangeable via ion exchange mechanisms).

Keywords: Arsenate; IAEA-SOIL-5; Extraction; Exchange

INTRODUCTION

Arsenic is a ubiquitous element in the environment with a variety of species, depending on pH, redox potential, microbial activity leading to methylation, etc [1]. The most dominant arsenic species is arsenate (As(V)) and the most toxic arsenic species is arsenite (As(III)); methylation usually leads to detoxification. The arsenic species arsenobetaine, predominantly found in marine animals, is non-toxic. In soils and sediments we mostly find inorganic arsenic (As(III) and As(V)) [2,3] and sometimes a minor organoarsenic fraction, i.e. monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) [4]. Research dealing with this type of speciation usually elaborates on separation of extracted arsenic, whereas the mainstream of research is directed towards binding characteristics of arsenic to soils or sediments and to this end uses Tessier-type sequential extraction schemes [5,6]. In such schemes the use of increasingly stronger extractants, or extractants specific for dissolution of certain soil or sediment constituents, leads to insight into binding characteristics. In most instances it is difficult to establish an extraction situation which does not alter the speciation. For that reason sequential extraction procedures are operationally defined which means that results

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obtained with different procedures are not comparable. The SMT program (BCR) has attempted to bring some unity (harmonization) into sequential extraction procedures by suggesting rugged three-step procedures which were evaluated in round-robin exercises [7,8].

In this work we investigated the extraction of the absorbed arsenic fraction from IAEA-SOIL-5 as a test case for establishing the (bio)available and/or mobile fraction. Insight into the complete picture of arsenic binding (speciation) using sequential extraction (of interest for geologic reasons) is usually unnecessary. By mild extraction using ion exchange mechanisms, in order not to alter the soil constituents or the arsenic species, sufficient information may be obtained to get a better understanding of (bio)availability and/or mobility. To this end we varied a number of 'mild' extraction parameters such as extraction mode, extraction time, extraction temperature, extractant type, extractant concentration and pH to optimize the extraction efficiency related to ion exchange mechanisms.

EXPERIMENTAL

Sample Characteristics

The IAEA (International Atomic Energy Agency) Certified Reference Material SOIL-5 was used in this study. This material is 20 cm topsoil from the Agricultural Experimental Station La Molina in Lima, Peru. It has been ground to pass a 0.16-mm sieve and is thus considered homogeneous, at least for sample weights equal or higher than 100 mg. That was, together with the rather high arsenic content (certified $93.9 \pm 7.5 \, \text{mg kg}^{-1}$ dry weight), a reason to choose this material as a model soil.

Materials

As(III) and As(V) standards were purchased from Merck (Darmstadt, Germany) as As_2O_3 ($1000 \, \text{mg L}^{-1}$ As in 5% nitric acid for ICP analysis) and As_2O_5 ($1.000 \pm 0.002 \, \text{g}$ in H_2O as Titrisol standard), respectively. Both As(III) and As(V) were diluted with $1 \, \text{mol L}^{-1}$ HCl to stock solutions of $10 \, \text{mg L}^{-1}$ As and kept at $4°C$; working solutions with arsenic concentrations of $0.010–0.100 \, \text{mg L}^{-1}$ were prepared from these stock solutions fresh daily. Millipore (Milford, MA, USA) Milli-Q Plus water ($18.2 \, \text{M}\Omega \, \text{cm}$) was used for all preparations of solutions. All chemicals used were at least of analytical reagent grade.

Extraction Procedures

In most experiments $250 \pm 0.5 \, \text{mg}$ of IAEA-SOIL-5 was exactly weighted in a polypropylene conical centrifugation vial with screw cap to which $10 \, \text{mL}$ of extractant was added; for some experiments the extractant volume/soil mass (V/M) ratio was varied. For extraction of arsenic the vials were subjected to sonication of shaking. After sonication or shaking the samples were centrifuged at 3000 rpm for 10 min, decanted and the extracts immediately filtered through a 0.2-μm syringe filter (PVDF, 25 mm diameter, Whatman). Extracts were kept frozen till analysis. Prior to analysis most of the extracts were diluted $1 + 2$ with water.
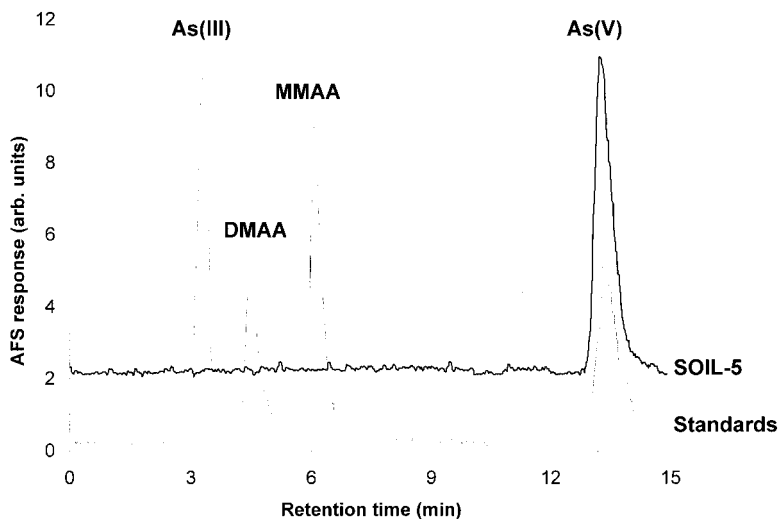
FIGURE 1   HPLC–HGAFS measurement of arsenic compounds in a phosphate extract of IAEA-SOIL-5 against standards (0.050 mg kg^{-1} of As(III), DMAA, MMAA and As(V)). Extractant: 0.01 mol L^{-1} phosphate, pH = 6.0; $V/M = 40$. The IAEA-SOIL-5 chromatogram is shifted for 2 arbitrary units for reasons of clarity.

Measurement

Arsenic compounds in extracts were identified and quantified using anion exchange chromatography combined with on-line hydride generation and atomic fluorescence spectrometry (HPLC–HGAFS). Experimental details can be found in [9]. Figure 1 shows a typical anion exchange chromatogram for a soil extract and a standard solution with inorganic (As(III) and As(V)) and organoarsenic (MMAA and DMAA) compounds. Since only arsenate was found in soil extracts, for all further analyses total arsenic was determined with the much simpler flow injection setup, i.e. the same system as above with omission of the HPLC column [10].

RESULTS AND DISCUSSION

In this work we varied several extraction parameters to get insight into extraction of adsorbed arsenic (arsenate) from IAEA-SOIL-5 in order to optimize the extraction efficiency. We only investigated extraction of adsorbed arsenic using so-called mild extractants (magnesium chloride and phosphate solutions) at supposedly "friendly" pH values and temperatures leaving the soil matrix intact and only leading to extraction of ion exchangeable arsenate as a measure of (bio)available and/or mobile arsenate.

Extraction Mode, Time and Temperature

In Fig. 2 the arsenate extraction efficiency from IAEA-SOIL-5 with 1 mol L^{-1} phosphate (pH 6.0) at a V/M ratio of 40 is given as a function of extraction mode (shaking or sonication), time and temperature. For shaking at 25°C a plateau was reached within 16 h with a yield of about 30%. Sonication gave a much higher plateau
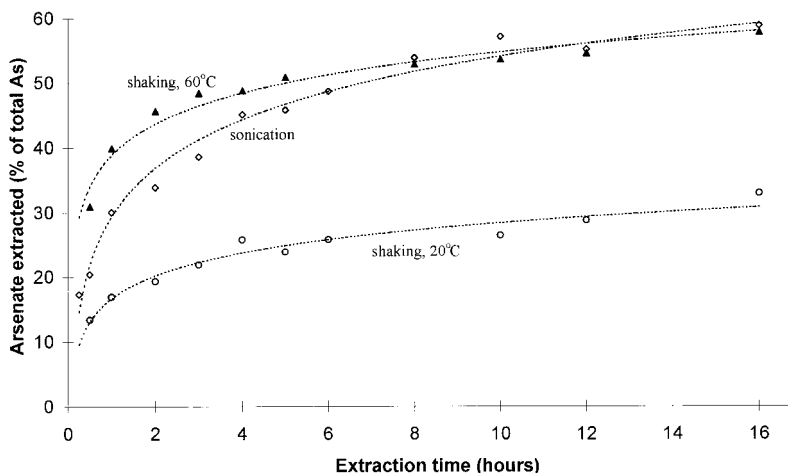
FIGURE 2   Extraction efficiency of arsenate from IAEA-SOIL-5 using $1 \, mol \, L^{-1}$ phosphate (pH $= 6.0$) as a function of extraction time in two different modes (shaking or sonication) and at two different temperatures (20 or $60°C$); $V/M = 40$.

(*ca.* 60%) in the same time; however, the temperature increased to $60°C$ in about 3–4 h and stayed on the same level for the remainder of the sonication. If shaking is performed at $60°C$ (thermostatted water bath) the same plateau is reached as for sonication although the initial extractability is higher since shaking was at $60°C$ from the onset. Under similar temperature regimes shaking and sonication seem to be able to release the same amounts of arsenate from IAEA-SOIL-5. However, sonication is more efficient in terms of extraction time and ease of operation as in 1 h the same arsenate yield was obtained as in 16 h of shaking at $25°C$. Relative standard deviations for two parallel extractions and duplicate injection of each extract were from 3.5 to 6.9%. In further experiments sonication for 1 h was used as a standard procedure; the extractant temperature remained $< 30°C$ which circumvented unwanted temperature-promoted arsenate dissolution.

Extractant Type, Concentration and pH

Tessier-type extractants for extraction of exchangeable metals ions from soil include $MgCl_2$, $CaCl_2$, etc. [5,11]. Using $1 \, mol \, L^{-1}$ $MgCl_2$ at a pH of 7.0 with a V/M ratio of 8 [12] we extracted 0.7% of the total arsenic present in the soil. Increasing the V/M ratio to 40 and 200 gave extraction efficiencies of 2.2 and 6.7%, respectively. This indicates that the V/M ratio is a critical parameter, especially related to mild extractants, and probably less critical for extractants which work by e.g. dissolution of a certain matrix constituent. However, a very high V/M ratio leads to a low concentration of the analyte and thus inaccuracy, so a sensible compromise between extractability and sensitivity has to be made. In the literature V/M ratios of 8 [12], 18 [13], 25 [6,14,15], 40 [7] and 100 [16] are reported. We have chosen a V/M ratio of 40 as a good compromise for the remainder of the work.

For the extraction of arsenate, also phosphate [14–16] or phosphoric acid [2,17] is used with good effect as a result of similarity in chemical properties between arsenate and phosphate and thus boosted ion exchange behavior. In Fig. 3(A) the phosphate
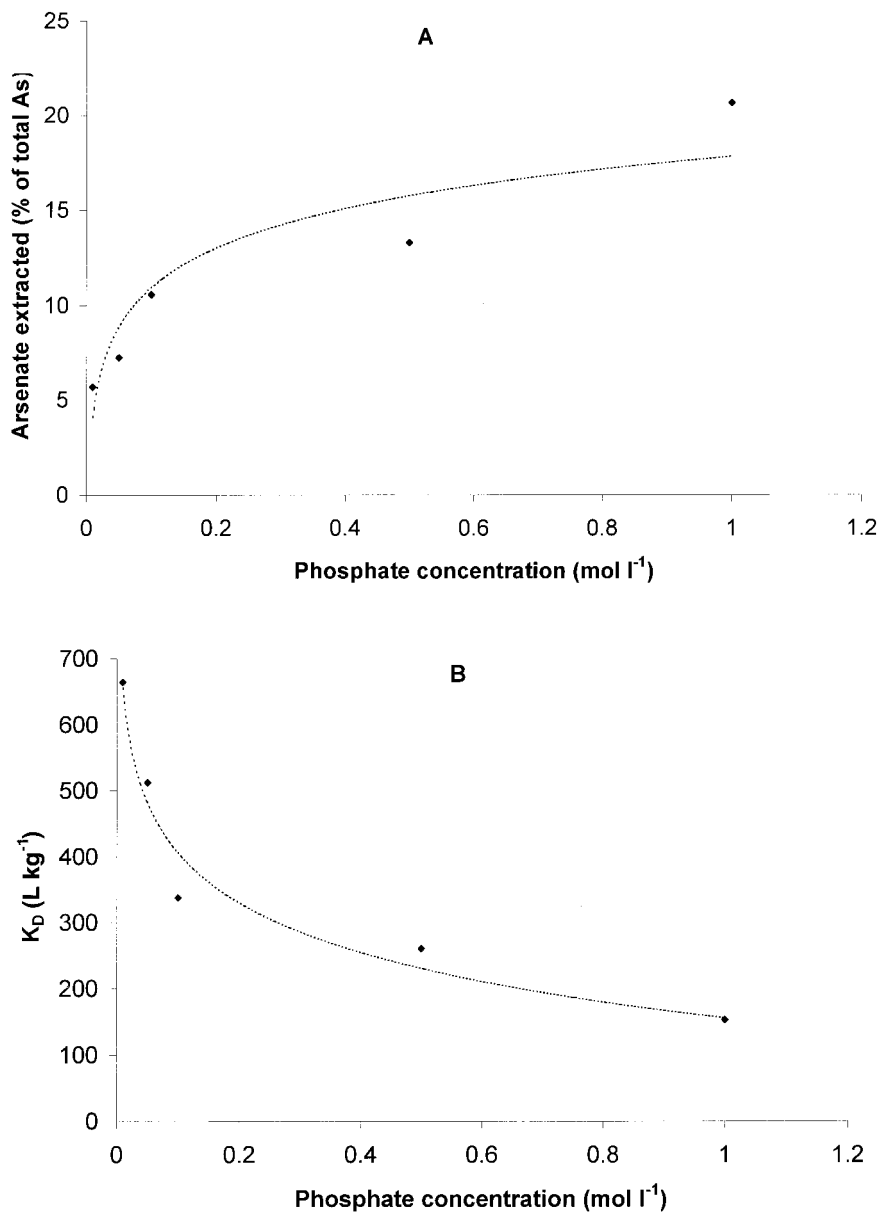
FIGURE 3 Extractability of arsenate from IAEA-SOIL-5, expressed as % of total As present (A) and distribution coefficient K_D (B), as a function of the phosphate concentration (pH 6.0); $V/M = 40$; 1 h sonication at $< 30°C$.

concentration is varied at fixed pH (6.0) and shows that the arsenate extraction efficiency at a phosphate concentration of $1 \, mol \, L^{-1}$ is a mere 20.7% indicating that the majority of arsenic is not easily available (exchangeable). The distribution coefficient K_D ($L \, kg^{-1}$) defined as the ratio between arsenic concentration remaining in soil $(mg \, kg^{-1})/$ arsenate concentration in extract ($mg \, L^{-1}$) is phosphate dependent due to ion exchange between arsenate and phosphate. Figure 3(B) shows this relationship

with K_D values decreasing from 665 to 153 when the phosphate concentration increases from 0.01 to $1 \, mol \, L^{-1}$. A phosphate concentration of $1 \, mol \, L^{-1}$ was used in further experiments with only one variable left to be optimized, viz. pH.

Since we look at mild extraction of arsenate only, the pH is varied in a rather narrow range (4–10) so as not to promote dissolution of matrix constituents. The pH may
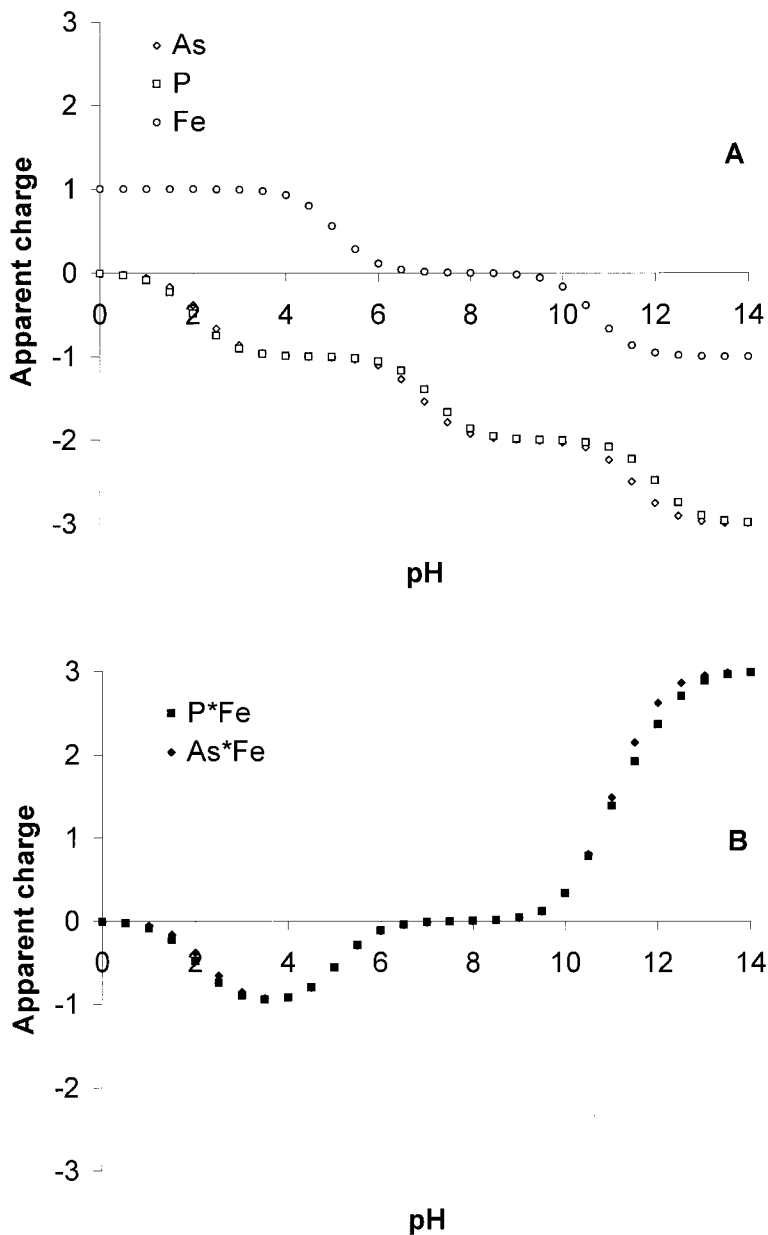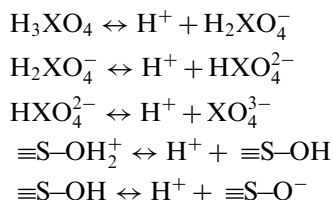

FIGURE 4   Apparent charge on: (A) arsenate (As), phosphate (P) and ferrihydrite (Fe) and; (B) the combination of phosphate and ferrihydrite (P*Fe) and arsenate and ferrihydrite (As*Fe); for arsenate: $pK_{a_1} = 2.24$, $pK_{a_2} = 6.96$, $pK_{a_3} = 11.50$; for phosphate: $pK_{a_1} = 2.148$, $pK_{a_2} = 7.198$, $pK_{a_3} = 2.18$ [19].

significantly influence the extraction efficiency since arsenate/phosphate and soil typi-
cally have amphoteric properties:

$$H_3XO_4 \leftrightarrow H^+ + H_2XO_4^-$$
$$H_2XO_4^- \leftrightarrow H^+ + HXO_4^{2-}$$
$$HXO_4^{2-} \leftrightarrow H^+ + XO_4^{3-}$$
$$\equiv S\text{--}OH_2^+ \leftrightarrow H^+ + \ \equiv S\text{--}OH$$
$$\equiv S\text{--}OH \leftrightarrow H^+ + \ \equiv S\text{--}O^-$$

with $X = As$ or P and $\equiv S\text{--}OH$ denoting the characteristic functional groups on the sur-
face of the soil, e.g. $\equiv Fe\text{--}OH$. Changing pH results in a subtle interaction between
arsenate and phosphate species with soil functional groups. Since arsenate and phos-
phate have very similar pKa values they behave similarly with regard to apparent
charge as a function of pH (Fig. 4(A)). As the IAEA-SOIL-5 properties are unknown,
pK_a values are unknown as well. When we assume $\equiv S\text{--}OH$ to be ferrihydrite, pK_a
values are 5.1 and 10.7, respectively [18]. Plotting the apparent charge on ferrihydrite
as a function of pH in Fig. 4(A) as well as we can get a notion about sorption phenom-
ena comparing the apparent charges on ferrihydrite with these on the phosphate. As
phosphate competes with arsenate for sorption sites, the enormous excess of phosphate
leads to displacement of arsenate when the apparent charges between ferrihydrite and
phosphate are opposite. By multiplying the ferrihydrite and phosphate apparent charge
graphs (Fig. 4(B)) it is obvious that by changing the pH from 4 to 8 the arsenate
displacement gets less when approaching pH 8, the zero apparent charge point of
ferrihydrite. At a pH above 8 the apparent charges of phosphate and ferrhydrite are
no longer opposite so that there is no longer displacement of arsenate by phosphate
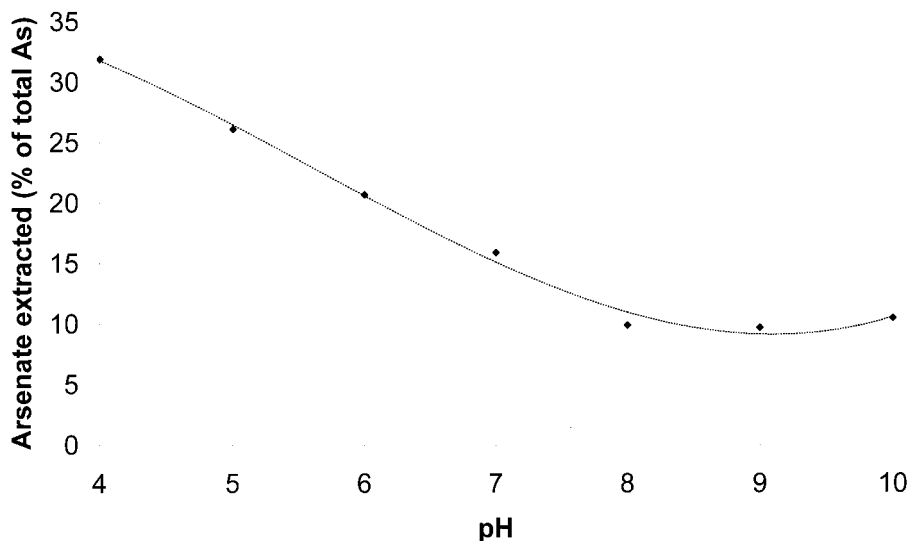but another sorption mechanism comes into action, namely the repulsion of arsenate

FIGURE 5 Extraction efficiency of arsenate from IAEA-SOIL-5 as a function of pH using $1\,mol\,L^{-1}$
phosphate; $V/M = 40$; 1 h sonication at $< 30^\circ C$.

by the ferrihydrite as a result of equal charge signs. By multiplying the ferrihydrite and phosphate apparent charge graphs (Fig. 4(B)) we can visualize this behaviour, so by changing the pH from 8 to 10 the repulsion and thus the desorption increases. The qualitatively deducted arsenate desorption behaviour from apparent charges *vs* pH values is in good agreement with experimental findings for desorption *vs* pH values (Fig. 5). Although rather speculative the soil functional groups may reflect the presence of ≡Fe–OH functional groups, the more that the Fe content of IAEA-SOIL-5 is very high (4.45 wt.%). However, the presence of other (combined) soil functional groups giving similar apparent charge *vs* pH profiles should not be ruled out. A more theoretical treatment of sorption of arsenate on ferrihydrite can be found in the literature [18,20].

CONCLUSIONS

The extraction efficiency of adsorbed arsenate from IAEA-SOIL-5 as a function of a range of variables has a maximum of 31.9% of the total arsenic present. Since mild extraction conditions were applied in order not to dissolve soil matrix constituents this fraction may be attributed to exchangeable and thus (bio)available and/or mobile arsenate. Phosphate enhances the extraction efficiency considerably due to chemical resemblance with arsenate and thus the potential for effective exchange with soil surface bound arsenate. Furthermore, the pH was a variable significantly influencing the extraction behaviour. By simple mathematical deduction, using pK_a values to derive apparent charges on arsenate, phosphate and soil functional groups, the desorption of arsenate as a function of pH could be explained.

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