FACTORS INFLUENCING THE EFFICIENCY OF ARSENIC EXTRACTION BY PHOSPHATE

A Thesis

by

SU JIN YEAN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2004

Master Subject: Soil Science

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Approved as to style and content by:

Richard H. Loeppert (Chair of Committee)	Timothy Kramer (Member)
Charles Thomas Hallmark (Member)	Mark Hussey (Head of Department)

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ABSTRACT

Factors Influencing the Efficiency of Arsenic Extraction by Phosphate.

(August 2004)

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Chair of Advisory Committee: Dr. Richard H. Loeppert

Extraction with sodium phosphate has been used as a method of accessing arsenic in soils. Arsenic extraction efficiency by phosphate from rice-paddy soils of Bangladesh usually has been low and highly variable between soils. The major objectives of this study were to examine the relationships between phosphate-extractable arsenic and soil iron-oxide composition and to investigate the experimental factors which might influence arsenic-extraction efficiency from rice-paddy soils of Bangladesh by phosphate.

Statistical analysis of approximately 500 surface soils from Bangladesh indicated that phosphate-extractable arsenic was well correlated with total soil arsenic ($r^2 = 0.832$) and oxalate-extractable arsenic ($r^2 = 0.825$), though extraction efficiency varied widely (5 - 54 % of the total soil arsenic). The *thanas* with the lowest arsenic contents generally also had the soils with the lowest arsenic-extraction efficiencies. Quantity of phosphate-extractable arsenic was weakly correlated with the soil iron-oxide content, but extraction efficiency (i.e., the proportion of phosphate-extractable arsenic to total soil arsenic) was not correlated with any iron-oxide parameter.

Arsenic extraction was strongly influenced by reaction variables such as sample grinding, phosphate concentration, principal counterion, reaction pH, and reaction time. The extraction efficiency was impacted by the influence of these individual factors on reaction kinetics and accessibility of arsenic adsorption sites for ligand exchange by phosphate. A portion of the arsenic was readily exchanged during the first few hours of extraction, followed by a much slower subsequent extraction. These results indicate that some of the arsenic is easily exchanged, but for a substantial portion of the arsenic, either the reaction kinetics is very slow or the sites are not accessible for reaction with phosphate. Extraction by phosphate is a useful procedure for the assessment of readily ligand-exchanged arsenic.

ACKNOWLEDGEMENTS

I am deeply grateful for the advice, support, and encouragement of many people during my M.S. program at Texas A&M University. I am truly thankful to Dr. Richard Loeppert who has guided me to achieve my academic accomplishments at Texas A&M and helped me to solve my research problems. I truly appreciate the support and consideration of Dr. Charles Thomas Hallmark who has been a mentor to me and allowed me to teach his undergraduate laboratory classes and Dr. Mysore Mohan in the Chemistry Department who had faith in me and gave me confidence. I am also grateful for the time and help of Dr. Timothy Kramer. I would like to acknowledge the help of many others during the course of my study: Dr. Frank Hons for his encouragement whenever I needed; Dr. Bhajan Biswas for his instruction regarding laboratory techniques; Dr. G. Norman White for his help with X-ray diffraction analysis of the iron oxides; Linda Carpenter for her advice on difficulties that I have faced; Brandon Lafferty for his help on computer usage details and teaching me the English language; Lea Dell Morris for her assistance to find papers and to order laboratory supplies; Fugen Dou and Sattar Abdus for their help with statistical analyses. Without the help of these people, this study would have been very difficult. I also would love to thank all of my family members in Korea who have given me unconditional support and love while I have studied here.

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INTRODUCTION

Phosphate extraction has been a useful method to measure arsenic in soils as a single extractant (Alam et al., 2001; Jackson and Miller, 2000) or as a part of sequential extraction schemes (Lombi et al., 2000). In preliminary extractions of selected surface soils of Bangladesh with pH 4, 0.1 M sodium phosphate, extraction efficiencies ranged from 5 to 54 % of total soil arsenic (Biswas et al., 2003). Although phosphate extraction has been widely used, the causes of its low extraction efficiency and high variability in extraction efficiency between soils are still uncertain. The objectives of this study are to investigate the possible sources of this variability and to better understand phosphate extraction as a tool to assess arsenic in soils.

ARSENIC IN THE ENVIRONMENT

Arsenic has been long recognized as a toxic element but is recently of environmental concern due to its occurrence throughout the world as the result of both geochemical processes and anthropogenic activities. The severe groundwater contaminations in south Asia have recently generated worldwide attention. The origin of the arsenic-contaminated groundwater in West Bengal, India and Bangladesh is geological, from sediments derived from the upland Himalayan catchments (Smedley and Kinniburgh, 2002). The arsenic-affected aquifer sediments were deposited from the Ganges River during the Holocene. In the most highly arsenic-contaminated areas,

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the sediments usually have high organic matter concentrations and are confined to fine-textured subsoil layers. These sediments are subject to reduction, which can result in increasing arsenic mobility (Acharyya et al., 2000; Smedley and Kinniburgh, 2002). The arsenic in groundwater has been reported to derive from three mechanisms: (i) oxidation of arsenic-rich pyrite in the alluvial sediments as water-level drawdown due to heavy groundwater withdrawal for irrigation allows atmospheric oxygen to invade the aquifer during the dry season (Mallick and Rajagopal, 1996; Mandal et al., 1998; Roychowdhury et al., 1999); (ii) reduction of arsenic rich iron oxyhydroxides in anoxic sediments and subsequent release of sorbed arsenic to groundwater (Bhattacharya et al., 1997; Nickson et al., 2000; Nickson et al., 1998); and (iii) anion exchange of sorbed arsenic by phosphate from fertilizer (Acharyya et al., 1999). Arsenic in some soils is naturally released by the weathering of iron-sulfide ore deposits such as arsenopyrite (FeAsS), realgar, and orpiment (Huang, 1994; Tanaka, 1988). The concentrations of arsenic in geological and soil environments are usually less than 6 mg kg^{-1} (Bowen, 1979). Arsenic contamination by human activities is a threat and occurs as a result of mining, smelting, and use of arsenic-based pesticides and fertilizers. The accessibility and availability of arsenic in soils are influenced by sorption, physical occlusion, soil mineralogy, pH, redox potential, and the presence of anions, such as organic anions, hydroxide, bicarbonate, silicate, sulfate, and phosphate, which can act as natural competing ligands at arsenic adsorption sites (Parfitt, 1978).

TOXICITY

The U.S. Environmental Protection Agency (EPA) has adopted a new standard, set the maximum contaminant level goal (MCLG) for arsenic at zero, and proposed to reduce the maximum contaminant level (MCL) for arsenic in drinking water from the current level of 0.050 mg L^{-1} to 0.010 mg L^{-1} starting January 23, 2006 (EPA, 2001).

Arsenate [As (V)] and, if the water is anaerobic, some arsenite [As (III)] are the predominant inorganic arsenic forms in drinking water (Irgolic, 1994). Inorganic arsenic can be methylated to mono-, di-, and possibly tri-methylated metabolites (Styblo et al., 1999). Inorganic arsenicals are generally more toxic than organic arsenicals, and trivalent forms are more toxic than pentavalent forms (Eisler, 1994). Because of the lower toxicity of pentavalent methylated metabolites, methylation has been considered a mechanism of detoxification (Styblo et al., 1999; Styblo et al., 2000); however, it is now known that methylarsonous acid [MMA (III)] is more toxic than arsenite (Petrick et al., 2001; Petrick et al., 2000). Carcinogenic and atherogenic effects on humans are associated with toxic effects of inorganic arsenic after acute or chronic exposures. Carcinogenicity includes arsenic induced skin lesions (e.g., hyperpigmentation, hyperkeratosis, and skin cancers), respiratory cancers (e.g., lung cancer and nasal-cavity cancer), liver cancers (e.g., hepatic angiosarcoma and hepatocellular carcinoma), genitourinary cancers (e.g., bladder cancer, kidney cancer, and prostate cancer), and other internal cancers (e.g., gastrointestinal cancers, hematolymphatic malignancies, and malignant neoplasms of the brain and nervous systems). Atherogenicity consists of peripheral vascular diseases (e.g., blackfoot disease), coronary heart diseases, and cardiovascular diseases (e.g., hypertension and diabetes mellitus) (Chen and Lin, 1994).

ARSENIC CHEMISTRY AND BONDING

A variety of arsenic species has been identified in soil and water (Huang, 1994; Tanaka, 1988); however, the two most common inorganic oxidation states of arsenic in natural environments are arsenite [As (III)] and arsenate [As (V)]. The pK_a values of the arsenite and arsenate species are summarized in Table 1. Arsenic speciation is controlled by both redox potential (Eh) and pH (Bowell, 1994; Ferguson and Gavis, 1972; Smedley and Kinniburgh, 2002). Arsenite and arsenate are predominantly present as the neutral species $H_3AsO_3^{\circ}$ and $H_2AsO_4^{-}$/ $HAsO_4^{2-}$, respectively, under most environmental conditions. Both arsenate and arsenite species are often present in either oxidized or reduced environments due to their slow kinetic transformations (Masscheleyn et al., 1991).

Table 1. Acid-dissociation constants of selected arsenic species.

Arsenic Species	pK_{a1}	pK_{a2}	pK_{a3}
Arsenite	9.22	12.13	13.4
Arsenate	2.20	6.97	11.53

Both arsenate and arsenite have high affinities for Fe oxide (Pierce and Moore, 1982); however, there is an opposite adsorption trend between arsenate and arsenite with regard to the influence of pH (Jain and Loeppert, 2000; Raven et al., 1998). Arsenate is more strongly retained at lower pH values, whereas, arsenite adsorption increases with increasing pH, with maximum adsorption at approximately pH 9. The decrease in arsenate adsorption at higher pH values is caused by electrostatic repulsion between negatively charged iron oxide surface sites and negatively charged arsenate species ($H_2AsO_4^-$, $HAsO_4^{2-}$). The pH at which the adsorption envelopes cross decreases with increasing initial arsenic concentration (Jain and Loeppert, 2000). At equimolar mixtures of arsenate and arsenite, arsenite resulted in a slight decrease in arsenate adsorption at low pH and considerable reduction at high pH, whereas, reduction of arsenite retention was observed in the presence of arsenate over the entire pH range of 4 to 10, with initial arsenate and arsenite concentrations up to 2.08 mmol L^{-1} each. With initial arsenate and arsenite concentrations of 6.94 mmol L^{-1} each, arsenate adsorption was considerably less in the presence compared to the absence of arsenite, whereas, the presence of arsenate did not have an appreciable effect on arsenite adsorption (Jain and Loeppert, 2000).

Arsenate can form inner-sphere bidentate-binuclear complexes with Fe oxides (Figure 1). Extended X-ray absorption fine structure (EXAFS) spectroscopy as well as Fourier transform infrared (FTIR) spectroscopy (Fendorf et al., 1997; Manceau, 1995; Sun and Doner, 1996; Waychunas et al., 1993) have provided direct evidence for inner-sphere adsorption of arsenite and arsenate on Fe oxides. Inner-sphere complexes are defined as direct linkages between the adsorbed ion and the reactive surface, with no water of hydration between the adsorbed ion and the surface structural cation (Sposito, 1984).

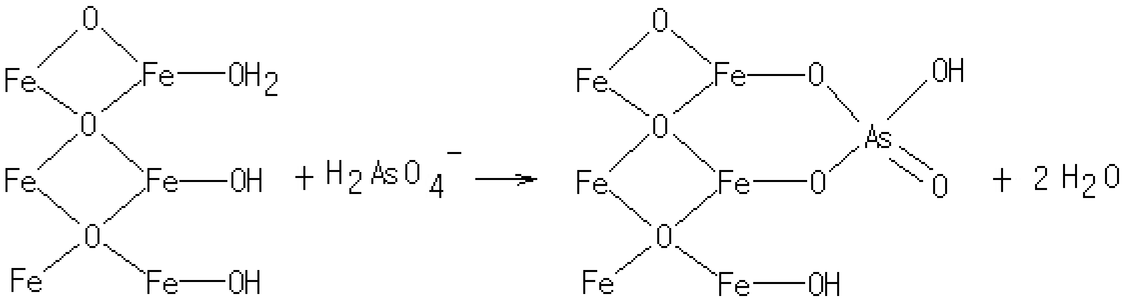

Figure 1. Bidentate, binuclear complex of arsenate on Fe-oxide surface.

Numerous papers have been published which demonstrate that iron oxides have a great affinity for adsorption of both arsenite and arsenate. Only a few studies have examined the adsorption/desorption of arsenic on layer-silicate minerals, although one or more minerals in this group are found in almost every soil environment. A study of layer-silicate minerals indicated that both kaolinite and montmorillonite have high affinities for arsenite and arsenate from landfill leachates (Frost and Griffin, 1977). Adsorption of arsenite and arsenate on kaolinite and montmorillonite had strong pH dependency, and maximum adsorption of arsenate occurred at about pH 5; however, the amount of arsenite adsorption increased with increasing pH (Frost and Griffin, 1977). Lin and Puls (2000) studied the adsorption and desorption of arsenic on several layer-silicate minerals: 1:1 clay minerals (i.e., kaolinite, halloysite), 2:1:1 layered clay (i.e., chlorite), and 2:1 clay minerals (i.e., illite, illite/montmorillonite). They observed that the clay minerals generally exhibited higher arsenate adsorption than arsenite adsorption. Halloysite and chlorite had greater arsenate adsorption than that exhibited by the other clay minerals, and arsenate adsorption on both minerals was little affected by pH (Lin and Puls, 2000). An iron-rich chlorite (containing 4.1 % Fe_2O_3 and 21.3 % FeO) originating from California had a high affinity for arsenate (Post and Plummer, 1972). This mineral is composed of two tetrahedral sheets, one octahedral sheet, and one interlayer hydroxide sheet, which might contribute to the greater arsenate adsorption (Lin and Puls, 2000; Wilson, 1987).

Quantities of arsenite and arsenate desorbed from clay minerals decreased with increasing aging time, which indicates that the long term aging process could result in stronger bonding to clay minerals due to increasing dehydration and arsenic diffusion at the soil-water interface to internal pores of the clay aggregates; therefore, accessibility of arsenic to bulk solution and extractability might both decrease (Lin and Puls, 2000). Also, in this situation, aging could result in iron oxide formation, which could also result in increased arsenic adsorption.

RICE SOILS

Most rice soils, which are commonly found in the alluvial lowlands in humid climates, especially Entisols or Inceptisols, have undergone little soil formation (Kyuma, 1978). A few chronological studies of the mineralogy of rice soils have indicated that the mineral composition of rice soils was almost the same as that of their parent materials (Huizing, 1971; Kawaguchi et al., 1957; Kyuma, 1978). The conclusion of minimum chronological effects on mineral composition of rice soils was corroborated, except in the case of biotite, which was rapidly weathered by seasonal wetting and drying of rice soils (Huizing, 1971). This latter process is very active in Bangladesh. Bangladesh has a tropical monsoon climate, and rice is grown on almost all of the major soils of

Bangladesh, either exclusively or in rotation with dryland crops (Brammer, 1978). Rice soils are affected by alternating reductive and oxidative conditions, resulting in damage to clay lattices and/or chloritization of expanding 2:1 clay minerals (Brinkman, 1970; Kyuma, 1978; Mitsuchi, 1974; Yoshida and Itoh, 1974). A gray colored, less clayey horizon with a lower cation-exchange capacity compared to the underlying layer was observed in seasonally flooded soils in East Pakistan (Brinkman, 1970). This upper layer, resulting from ferrolysis, was impermeable to water percolation. Ferrolysis results in the transformation of partially Fe^{2+}-saturated clay to partial H^+-saturation during the period of oxidation (Brinkman, 1970; Mitsuchi, 1974; Yoshida and Itoh, 1974). Exchangeable H^+ reacts with the clay lattice, resulting in release of Al^{3+} and partial Al^{3+} saturation. Thus, there was partial Al^{3+}- interlayering of the Fe^{2+}-saturated clay during the seasonally wet period. This $Fe^{2+} \rightarrow H^+ \rightarrow Al^{3+}$ replacement induces clay destruction and change in acidity in rice soils (Brinkman, 1970; Mitsuchi, 1974; Yoshida and Itoh, 1974). Another reaction is observed in the rice soils of Bangladesh (personal comments from Dr. Loeppert), i.e., smectite and vermiculite, which have a higher cation-exchange capacity, resulted from the degradation of biotite in sediments which have originated from the Himalayan Mountains.

The mechanical and chemical compositions of rice soils from nine tropical Asian countries (i.e., Bangladesh, Burma, Cambodia, India, Indonesia, Malaysia, Philippines, Sri Lanka, and Thailand) were studied (Kyuma, 1978). The Bangladesh samples generally had a higher silt concentration than the other samples, according to the international grain-size limits (i.e., silt, 0.002 - 0.02 mm), due to sedimentation from the Ganges and the Brahmaputra rivers. Minerals rich in Fe, e.g., hematite (a-Fe_2O_3), goethite (*a*-FeOOH), lepidocrocite (*r*-FeOOH), siderite ($FeCO_3$), jarosite ($KFe_3(SO_4)_2(OH)_6$), and vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$), were identified in rice soils from the nine Asian countries (Kyuma, 1978; Van Breemen, 1976). Minerals rich in Fe often have higher sorbing capacities for AsO_4^{3-} than PO_4^{3-} (Violante and Pigna, 2002). Alternating oxidation/reduction in rice soils might strongly impact mobility and accessibility of arsenic, since the arsenic might be co-precipitated or trapped by iron oxides precipitated during the oxidation of reduced rice soils.

ASSESSMENT OF ARSENIC

Chemical extraction is an important tool to understand bonding, speciation, and solubility of arsenic in soils. A variety of chemical extraction procedures has been utilized to evaluate arsenic in soils. Arsenic release from arsenic-bonding sites results from mineral dissolution or ligand exchange of adsorbed arsenic by a competitive ligand (Loeppert et al., 2002). Some of the predominant methods to assess arsenic in soils are summarized in Table 2. Deionized water and 0.01 M $CaCl_2$ have been used to estimate soluble arsenic in soils (Houba et al., 2000). For this purpose, care must be taken that quantity of dissolved arsenic or concentrations of available surface adsorption sites are not changed during the extraction procedures (Loeppert et al., 2002). For example, concentration of surface sites available for arsenic retention could be altered by the precipitation of dissolved Fe^{2+} during oxidation of reduced soils. Also, substantial changes in arsenic solubility and adsorption behavior could result from oxidation of reactive sulfide minerals (Loeppert et al., 2002). Total arsenic concentrations of soils can be determined following digestion with concentrated mineral acids to facilitate total dissolution of organic and inorganic arsenic. Arsenic has also been extracted by ligand-enhanced dissolution. Reaction of a mineral with an organic complexing agent (e.g., oxalate; citrate; DTPA, diethylenetriaminepentaacetic acid) could result in dissolution of the surface structural cation, e.g., Fe^{3+} on an iron-oxide surface, and subsequent release of adsorbed arsenic (Loeppert et al., 2002; Stumm and Furrer, 1987). In some cases, arsenic can be readsorbed to newly exposed surface Fe^{3+} sites, depending on experimental conditions. Desorption of arsenic by reaction of arsenic-contaminated soil with mineral acids mainly involves H^+-enhanced dissolution. For example, arsenic is released as a result of reaction of hydrochloric acid (0.1 or 1.0 M) with the surface structural cation, e.g., Fe^{3+} of Fe-oxide minerals. Arsenic extraction by OH^--enhanced dissolution of iron oxide involves a reaction with surface structural Fe to form the soluble $Fe(OH)_4^-$ species at high pH. Readsorption is less favorable due to the negative surface charge at the oxide surface at high pH (Jackson and Miller, 2000; Loeppert et al., 2002). Jackson and Miller (2000) have shown that the efficiency of arsenate extraction with 0.1 M NaOH is greater than 70 % from amorphous Fe oxide. Reductive dissolution involves reduction of the surface structural cation (e.g., Fe^{3+}; Mn^{4+}) by reducing reagent (e.g., hydroxylamine hydrochloride in acetic acid; citrate-dithionite). Dissolution of the mineral surface results in arsenic release (Loeppert et al., 2002).

Table 2. Commonly used procedures for evaluation of soil arsenic.

Mechanism	Reaction	Possible extractants
Soluble Arsenic		Deionized water 0.01 M $CaCl_2$
Total Arsenic		Digestion with concentrated mineral acids
Ligand Exchange	Fe-oxide- $AsO_4H + HPO_4^{2-}$ $\rightarrow$ Fe-oxide- $PO_4H + HAsO_4^{2-}$	Phosphate OH^-
Ligand-enhanced Dissolution	Fe-oxide- $AsO_4 + L^- \rightarrow Fe^{3+}$ -L + As_{aq}	Oxalate Citrate DTPA (diethylenetriamine-pentaacetic acid)
H^+ -enhanced Dissolution	Fe-oxide $-AsO_4 + H^+$ $\rightarrow Fe^{3+} + H_2O + As_{aq}$	HCl HNO_3
OH^- -enhanced Dissolution	Fe-oxide $-AsO_4 + OH^-$ $\rightarrow Fe(OH)_4^- + As_{aq}$	OH^- (High pH)
Reductive Dissolution	Fe-oxide $-AsO_4 + e^- + L^-$ $\rightarrow Fe^{2+}$ -L + As_{aq}	0.1 M $NH_2OH{\cdot}HCl$ Citrate-dithionite 0.25 M $NH_2OH{\cdot}HCl$ in 25% Acetic acid

EXTRACTION BY PHOSPHATE

Extraction with phosphate has been used to assess arsenic in soils by ligand exchange. Both phosphorus and arsenic are in Group V of the periodical table, and their respective phosphate and arsenate species have similar chemistries, including ion size and the acid-dissociation constants of the protonated species (Figure 2 - Figure 3).

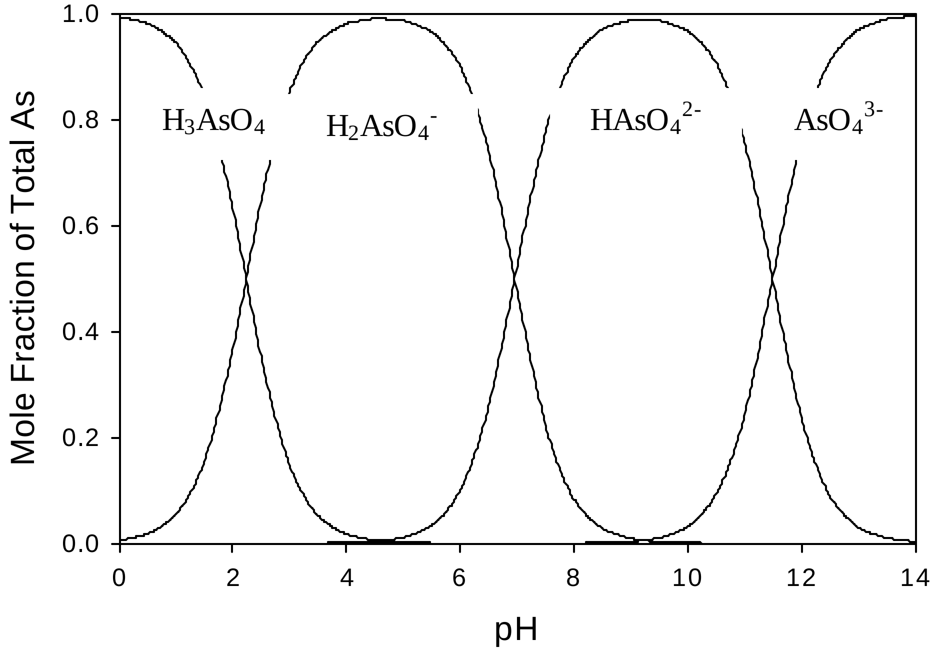

Figure 2. Influence of pH on distribution of inorganic As (V) species.

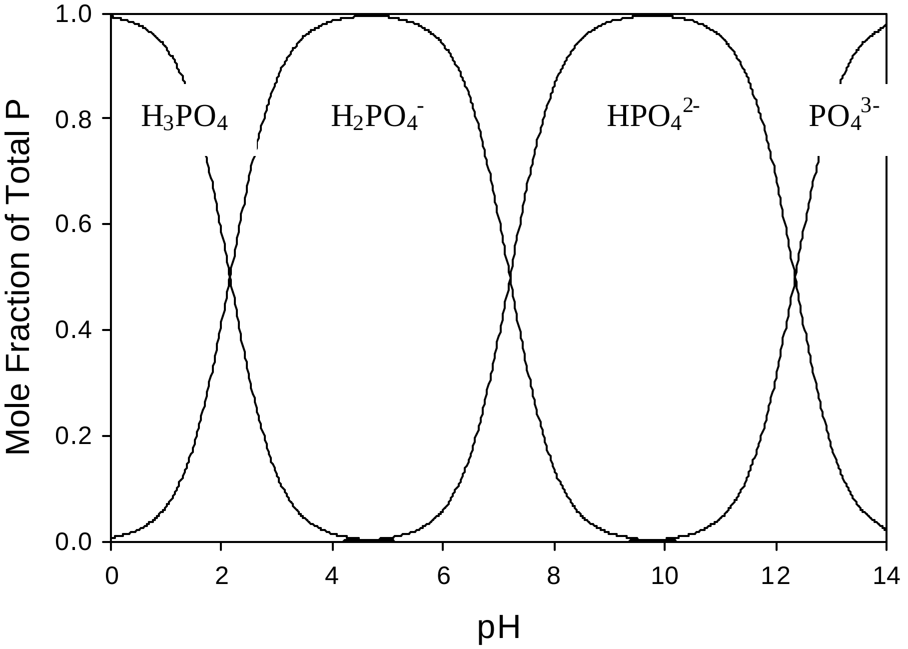

Figure 3. Influence of pH on distribution of inorganic phosphate species.

On ferrihydrite, phosphate and arsenate exhibited similar adsorption behavior, but ferrihydrite moderately preferred arsenate over the entire pH range of 3 to 10 (Jain and Loeppert, 2000). Jackson and Miller (2000) studied the influence of phosphate concentration (i.e., 0.1 M and 0.5 M NaH_2PO_4) and pH (i.e., pH 3 and pH 7) on arsenic extraction. Extraction efficiencies of arsenate and arsenite from both ferrihydrite and goethite were greater at the higher phosphate concentration (i.e., 0.5 M NaH_2PO_4). Desorption behavior of arsenate and arsenite from both iron oxides followed different trends with regard to the influence of pH. Arsenate was more effectively desorbed at the higher pH value (i.e., pH 7), whereas, more arsenite was extracted at the lower pH (i.e., pH 3) (Jackson and Miller, 2000).

Extraction studies of arsenate on a poorly crystalline Fe oxide have indicated that the quantity of arsenic desorbed was increased with increasing phosphate concentration at phosphate concentrations less than 0.9 M at pH 6 (Alam et al., 2001). Phosphate concentration did not substantially influence arsenic desorption at phosphate concentrations of >= 0.9 M.

Violante and Pigna (2002) reported that arsenate sorption on both goethite and gibbsite decreased with increasing initial molar ratio of phosphate to arsenate up to 2. The presence of phosphate resulted in less arsenate sorption on gibbsite than on goethite. This result indicates that goethite (i.e., iron hydroxide) has a greater affinity for arsenate compared to gibbsite (i.e., aluminum hydroxide). When arsenate was added before phosphate, the efficiency of arsenate in suppressing phosphate adsorption on goethite was greater than that of phosphate in inhibiting arsenate adsorption when phosphate was added before arsenate (Liu et al., 2001).

OBJECTIVES OF STUDY

The first objective of this research was to investigate factors impacting the effectiveness of arsenic extraction by phosphate, e.g., the effects of grinding, reaction pH, counterion, reaction time, successive extractions, phosphate concentration, and drying. The second objective was to examine the relationships between phosphate-extractable arsenic and soil factors (e.g., soil Fe-oxide concentration) of approximately 500 rice-paddy soils of Bangladesh, to determine the soil factors which might influence the efficiency of arsenic extraction by phosphate.

MATERIAL AND METHODS

SOILS AND SAMPLING PROCEDURE

Approximately 500 soil samples were collected from boro rice fields in five *thanas* (i.e., smallest political regions) in Bangladesh (Biswas et al., 2003). In summary, 110 samples from Brahmanbaria, 100 samples from Faridpur, 102 samples from Paba, 41 samples from Senbag, and 105 samples from Tala were utilized in the phosphate extraction studies. The sampling sites are summarized in Figure 4. Individual soil samples were collected by the arsenic project partners (i.e., Bangladesh Agriculture University, Bangladesh Agriculture Research Institute, Bangladesh Rice Research Institute, and Bangladesh Institute of Nuclear Agriculture) in Bangladesh. Samples were collected from 0–15 cm depth from a 1 m^2 area to make a composite sample and were homogenized, air-dried, crushed to break soil aggregates, passed through a 2-mm nominal pore-size sieve, thoroughly homogenized again, and stored in polypropylene bottles.

Four soils (i.e., Brahmanbaria 20, Brahamanbaria 90, Paba 76, and Tala 4) were selected from the rice-paddy soils described above and utilized for further studies to evaluate the effects of grinding, counterion, reaction pH, reaction time, sequential arsenic extraction, and phosphate concentration on efficiency of arsenic extraction by phosphate. The characteristics of these soils are summarized in Table 3.

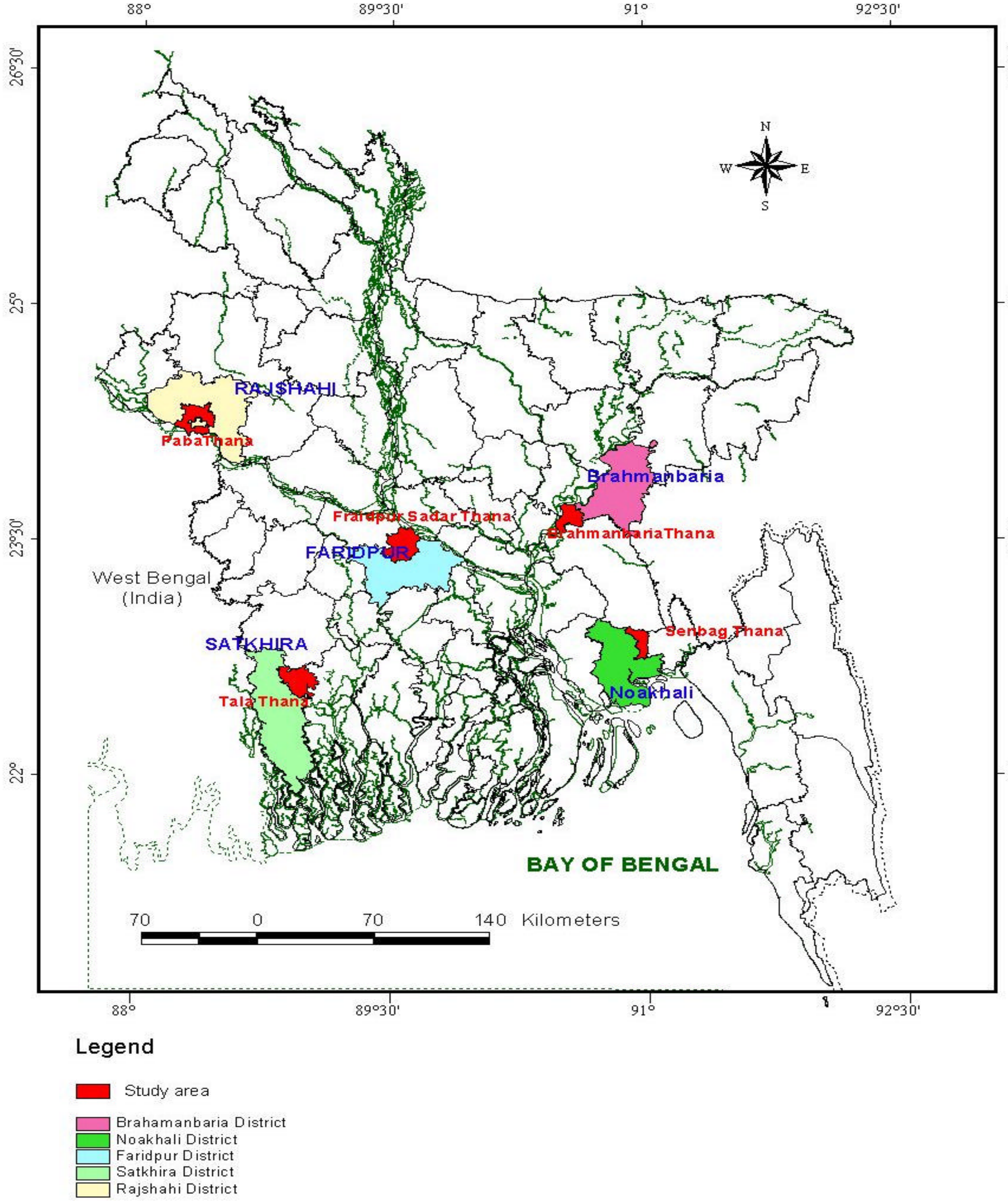

Figure 4. Soil sampling sites in Bangladesh.

Table 3. Characteristics of selected soils.

	Soil			
	Brahmanbaria 20	Brahmanbaria 90	Paba 76	Tala 4
General Soil Type	Non-calcareous grey floodplain soils	Non-calcareous grey floodplain soils	Soil on the upper slopes are calcareous throughout but basin soil are non-calcareous	Calcareous dark grey floodplain soil
USDA Taxonomy	Typic Haplaquept	Typic Haplaquept	-	Aeric Haplaquept
pH	5.33	7.21	7.73	8.24
AEZ	Old Megha floodplain	Old Megha floodplain	High Ganges River Floodplain overlapping with high Barind tract	High Ganges Tidal Floodplain
Texture	Silt loam	Silt loam	Loam	Silty clay
Total iron (mg kg^{-1})	20053	21937	32543	38137
Total free iron (mg kg^{-1})	3549	-	5103	10547
Poorly crystalline iron oxide (mg kg^{-1})	2042	4405	2052	1010
Well crystalline iron oxide (mg kg^{-1})	1506	-	3050	9536
Layer-silicate iron oxide (mg kg^{-1})	16503	-	27440	27590
Total As (mg kg^{-1})	2.32	9.44	12.43	15.75
Phosphate-extractable As (mg kg^{-1})	0.36	2.64	2.48	4.36
Organic matter (%)	1.67	-	1.95	1.98

IRON OXIDE PREPARATION

Two-line ferrihydrite was synthesized using the method described by Schwertmann and Cornell (1991), with slight modifications. Approximately 165 mL of 1 M NaOH were added to 500 mL of a solution containing 20.2 g of $Fe(NO_3)_3 \cdot 9H_2O$, during vigorous stirring with a magnetic stirrer. The pH of the suspension was then adjusted to pH 7.5 by dropwise addition of 1 M NaOH. The suspension was aged for 24 h in the refrigerator at 2 °C and then washed with deionized water until the suspension could no longer be flocculated. Following each washing step, the sample was centrifuged at 2,000 rpm for 20 min and the supernatant was decanted. The oxide was resuspended between each wash by manual agitation. The oxide suspension was dialyzed using deionized water, until electrical conductivity was at 10 – 15 µS cm^{-1} as determined using a Radiometer Copenhagen CDM 3 conductivity meter, The London Company, Cleveland, OH. After dialysis, the suspension was diluted to 1,000 mL final volume and stored in a refrigerator to prevent recrystallization and microbial growth. The ferrihydrite concentration in the final suspension was approximately 2.5 g L^{-1}. X–ray diffraction was used to confirm the presence of 2-line ferrihydrite.

EXTRACTION BY PHOSPHATE

Extractions were performed in 40-mL polypropylene centrifuge tubes, each containing 0.5 g of soil and 20 mL of pH 4, 0.1 M sodium phosphate ($NaH_2PO_4 \cdot H_2O$, FW 137.99) unless stated otherwise. After shaking for 24 h on a reciprocal shaker, samples were centrifuged at 15,000 rpm for 10 min, and the supernatant was decanted, and filtered through a 0.2 µm nominal pore-size membrane filter. The pH of the extract was measured, and then the extract was acidified with 6 M HCl prior to determination of arsenic concentration by flow-injection hydride-generation flame-atomic-absorption-spectroscopy (FI-HG-FAAS).

EVALUATION OF EXTRACTION VARIABLES

Effect of Grinding

Five-gram aliquots of Brahmanbaria 20, Brahmanbaria 90, Paba 76, and Tala 4 soils were ground for 2 min using a disc mill for ground samples. Unground samples were sieved through a 2-mm nominal pore size sieve. Both ground and unground soils (0.5 g) were extracted in triplicate with 20 mL of pH 4, 0.1 M sodium phosphate for 24 h on a reciprocal shaker. Following equilibration, samples were centrifuged at 15,000 rpm for 10 min, the supernatant was filtered through a 0.2 µm nominal pore-size membrane filter, and arsenic concentration was determined by FI-HG-FAAS.

Effect of Counterion and pH

The effect of initial counterion (i.e., Ca^{2+} vs. Na^{+}) on arsenic extraction with phosphate was evaluated because of the possible impact of counterion on strength of arsenic bonding, soil dispersion, and accessibility of phosphate to arsenic-bonding sites. Brahmanbaria 20, Brahmanbaria 90, Paba 76, and Tala 4 soils were used in triplicate.

There was no pretreatment prior to the addition of phosphate in the Ca^{2+} system, because Ca^{2+} is the predominant cation in these soils regardless of whether the soils are calcareous or non-calcareous. The natural Na^{+} concentrations of the soils were negligible. Pretreatments to remove carbonate from the soils and to create a Na^{+} system involved reaction with a pH 5 Na acetate buffer solution, which was made by dissolving 136 g L^{-1} of Na acetate, adjusting pH to approximately 5.0 by adding concentrated HOAc, and diluting to 1 L final volume. To remove carbonate from the soils, 20 mL of Na acetate buffer were added to 0.5 g soil in preweighed polypropylene centrifuge tubes. The samples were stirred thoroughly with a glass-stirring rod, and left to react for 10 min. Then the pH of the suspension was measured, and acetic acid was added dropwise to lower the pH to 5.5 until the pH remained constant. The samples were centrifuged at 2,500 rpm for 10 min, and the supernatant was decanted. The samples were washed twice with 1 M NaCl and twice with 0.1 M NaCl, and centrifuged at 2,500 rpm for 10 min after each treatment. After washing, the final supernate was decanted. Soil suspensions in both counterion systems (e.g., Ca^{2+} and Na^{+}) were treated using the phosphate extraction method described above.

Phosphate solutions with varying pH values (i.e., pH 1- 13) were prepared by adjusting pH with H_3PO_4 and NaOH. Phosphate solutions at approximately pH 1 and pH 13 were prepared as 0.1 M NaH_2PO_4 + 0.2 M HCl and with 0.1 M Na_2HPO_4 + 0.2 M NaOH, respectively. Samples were treated identically using the standard phosphate extraction method described above, but with phosphate solutions with varying pH values.

Effect of Reaction Time

The effect of reaction time on arsenic extraction by phosphate was investigated in batch experiments using 40-mL polypropylene centrifuge tubes. Brahmanbaria 20, Brahmanbaria 90, Paba 76, and Tala 4 soils were extracted at each reaction time in triplicate. Soils (0.5 g) were reacted with 20 mL of pH 4, 0.1 M sodium phosphate on a reciprocal shaker for 0.5, 1, 2, 4, 8, and 24 h. The arsenic desorption was terminated by centrifuging at 15,000 rpm for 10 min, and the supernatant was filtered through a 0.2 µm nominal pore-size membrane filter, acidified with 6 M HCl, and analyzed by FI-HG-FAAS.

Effect of Sequential Arsenic Extraction

Sequential arsenic extraction was used to determine the possible effect of dissolved arsenic during extraction with phosphate on subsequent arsenic extraction. Brahmanbaria 90 and Tala 4 soils were utilized in triplicate for this study. Soils (0.5 g) were shaken on a reciprocal shaker for 2 h in preweighed polypropylene centrifuge tubes with 20 mL of pH 4, 0.1 M sodium phosphate and centrifuged at 15,000 rpm for 10 min. Care was taken during decantation to minimize to loss of soil. The tubes (with soil and solution remaining) were weighed to allow determination of the quantity of arsenic carried to the next extraction stage of the sequential extraction procedure. This procedure was repeated five times. Samples were acidified with 6 M HCl prior to analysis by FI-HG-FAAS.

Effect of Phosphate Concentration

The effect of phosphate concentration was investigated in a batch experiment using the arsenic extraction method described above, with varying phosphate concentrations. The Tala 4 soil was utilized in triplicate for this study. Soil (0.5g) was reacted with 20 mL of sodium phosphate (0.001 - 1.5 mol L^{-1}) at pH 4 on a reciprocal shaker for 24 h. Following equilibration, samples were centrifuged at 15,000 rpm for 10 min, the supernatant was filtered through a 0.2 µm nominal pore-size membrane filter, and arsenic concentration was determined by FI-HG-FAAS.

Effect of Drying on Adsorption/Desorption of Arsenic in a Pure Fe-oxide System with Variable Amounts of Sand

The effect of drying on adsorption/desorption of arsenic by ferrihydrite in the presence of varying amounts of sand was studied to investigate whether physical occlusion might be an important factor that impacts the low efficiency of arsenic extraction by phosphate. A stock solution of arsenate (from As_2O_5) was prepared at a concentration of 13.4 mmol of As L^{-1} without addition of NaOH. A stock suspension of ferrihydrite was diluted to 1 g Fe L^{-1} in preweighed 40-mL polypropylene centrifuge tubes. Centrifuge tubes also contained aliquots of air-dried, acid washed quartz sand ranging from 0 to 8 g. The suspensions were pretreated by three different methods (Figure 5). In the first method, arsenic was added to the suspension so that the Fe : As molar ratio was 50 : 1 (i.e., 17.9 mmol L^{-1} of Fe and 0.358 mmol L^{-1} of arsenate). The samples were equilibrated for 24 h on a reciprocal shaker, centrifuged at 15,000 rpm for

30 min, decanted to remove the supernatant, and oven-dried (60 ± 5 °C) for 12 h. Upon the completion of drying, 15 mL of pH 4, 0.1 M sodium phosphate were added, the suspension was equilibrated for 24 h on a reciprocal shaker and centrifuged at 15,000 rpm for 30 min, and the supernatant was filtered through a 0.2 µm nominal pore size membrane filter and analyzed for arsenic by FI-HG-FAAS. In the second method, the samples were pretreated as above except they were not dried prior to extraction with phosphate. In the third method, samples were treated as with the first method, except that ferrihydrite was oven-dried (60 ± 5 °C) for 12 h before addition of arsenic.

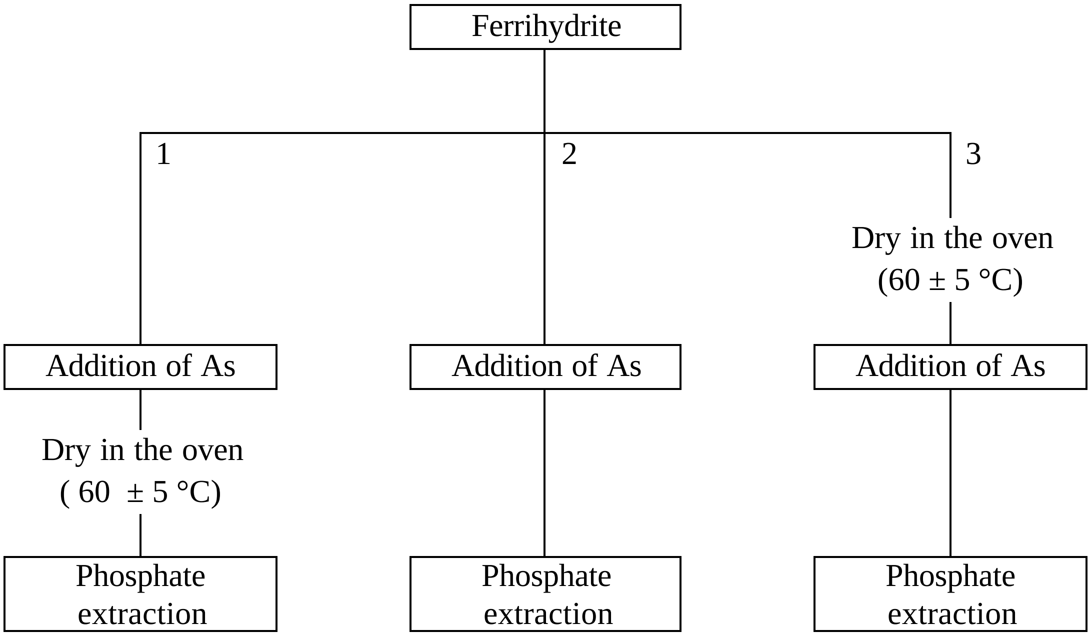

Figure 5. Experimental scheme for evaluating the effect of sample drying on extraction of arsenic from ferrihydrite.

ARSENIC ANALYSIS

Arsenic was analyzed using flow-injection hydride-generation flame-atomic-absorption spectroscopy (FI-HG-FAAS). The hydride generation technique, which is based on the conversion of the analyte to its volatile hydride using sodium borohydride ($NaBH_4$) as the reductant in acidic medium, is widely used to determine arsenic at trace levels (Agterdenbos and Bax, 1986; Burguera and Burguera, 1997). The reaction of arsenic with $NaBH_4$ in acid medium to generate the arsine is summarized in Equation [1].

$$H^+ + BH_4^- + H_3AsO_4 \rightarrow AsH_3 + H_2O + H_3BO_3 \qquad [1]$$

$$BH_4^- + 3\ H_2O + H^+ \rightarrow H_3BO_3 + 4H_2 \qquad [2]$$

$$2\ AsH_3 \rightarrow 2\ As + 3\ H_2 \qquad [3]$$

A peristalitic pump separately transports the arsenic solution in 5 M HCl and 1.5 % $NaBH_4$ (in 0.5 % NaOH) to a reaction chamber where the arsine generation occurs. The excess $NaBH_4$ is decomposed by the acid solution (Equation [2]). A constant flow of carrier gas (i.e., Ar) brings liquid and gaseous reaction products to a gas-liquid separator, from which the resulting gas mixture of arsine (AsH_3) and hydrogen (H_2) is carried to the heated quartz cell (Equation [3]). In the quartz cell, arsenic from the dissociation of the molecular hydride species is analyzed by flame-atomic-absorption spectroscopy. A continuous signal is observed with this procedure (Agterdenbos and Bax, 1986; Agterdenbos et al., 1985; Pierce et al., 1976). The arsenate [As (V)] has to be reduced to arsenite [As (III)] to produce the corresponding arsine (Carrero et al., 2001; Howard, 1997). The formation of arsine with $NaBH_4$ is sensitive to pH, because the arsenic species must be fully protonated before they can be converted to arsine. The formation of arsine from arsenate is slower than that from arsenite because of the time-dependent reduction of arsenate to arsenite (Ikeda, 1985). In the current studies, samples were preacidified (1 part 6 M HCl : 1 part sample) to lower the pH in solution to improve the rate of formation of arsine, since arsenate was considered to be the predominant arsenic species in these air-dried soils.

STATISTICAL ANALYSIS

Statistical analysis (mean, median, standard deviation, quartiles) of the distribution of phosphate-extractable arsenic both within and between *thanas* was performed using boxplots and descriptive statistical routines in SPSS. The one-way ANOVA test was conducted to compare differences in mean between *thanas*. Additionally, Kolmogorove-Smirnov and Shapiro-Wilk tests were used to evaluate normality at the 5 % level. Spearman's coefficient between phosphate-extractable arsenic and other arsenic parameters (i.e., total arsenic, oxalate-extractable arsenic) was obtained from bivariate correlation tests. Also, linear regression between phosphate-extractable arsenic (as a dependent factor) and other arsenic parameters (as independent factors) was evaluated. Correlations between phosphate-extractable arsenic and soil iron parameters (i.e., total iron, total free iron, poorly crystalline iron, well crystalline iron, and layer-silicate iron) were tested using Spearman's coefficient. The same tests were utilized to evaluate correlation between the proportion of phosphate-extractable arsenic to total arsenic and soil iron parameters.

RESULTS AND DISCUSSION

EFFECT OF GRINDING

The results of grinding studies are shown in Figure 6 and Figure 7. The two figures are similar except that the concentration of arsenic desorption by phosphate on a soil basis with and without the grinding treatment are shown in Figure 6, while the efficiency of arsenic extraction by phosphate is shown in Figure 7.

The quantity of arsenic desorbed by phosphate decreased as follows: Tala 4 > Brahmanbaria 90 >= Paba 76 > Brahmanbaria 20 (Figure 6), while the efficiency of arsenic extraction decreased as follows: Brahmanbaria 90 > Tala 4 >= Paba 76 > Brahmanbaria 20 (Figure 7). The effectiveness of arsenic extraction by phosphate following grinding was at least 2 % lower than with the sieving treatment, except for Tala 4.

The results of the paired t-test (Table 4) indicate significant differences between treatments with Paba 76 and Brahmanbaria 90, because the p-values were < 0.05; however, no significant differences were indicated with Brahmanbaria 20 and Tala 4. The decrease in arsenic extraction upon grinding might be attributable to readsorption of desorbed arsenic on newly exposed sites that were exposed with the grinding treatment. These results were not expected, since it was initially anticipated that grinding would result in increased exposure of adsorbed or occluded arsenic and hence greater ease of extraction of soil arsenic. The observations of this experiment are indicative of the complexity of the processes that contribute to overall extraction efficiency.

Table 4. P-values and standard errors from the paired t-test to investigate the difference in arsenic extracted with and without the grinding treatment.

Sample	Std. Error	P-value[†]
Brahmanbaria 90	0.12	0.02
Paba 76	0.04	0.01
Brahmanbaria 20	0.03	0.12
Tala 4	0.06	0.61

[†] A p value < 0.05 indicates that the quantities of phosphate-extractable arsenic with and without grinding are significantly different at the 0.05 confidence level.

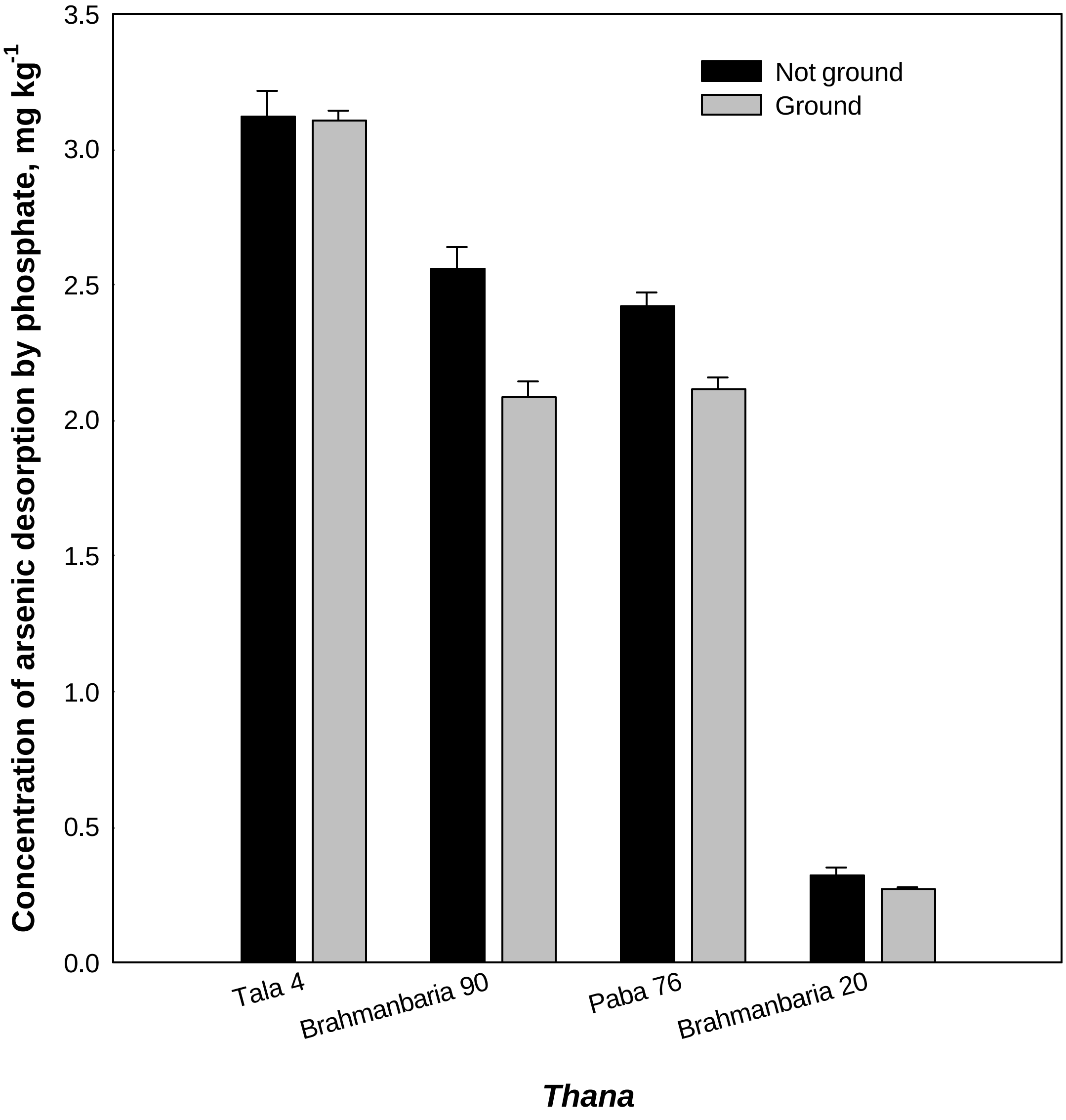

Figure 6. The influence of soil grinding on concentration of arsenic extracted by sodium phosphate. Experimental conditions included 0.5 g of soil, 20 mL of pH 4, 0.1 M sodium phosphate, and 24-h extraction time with continuous shaking at room temperature.

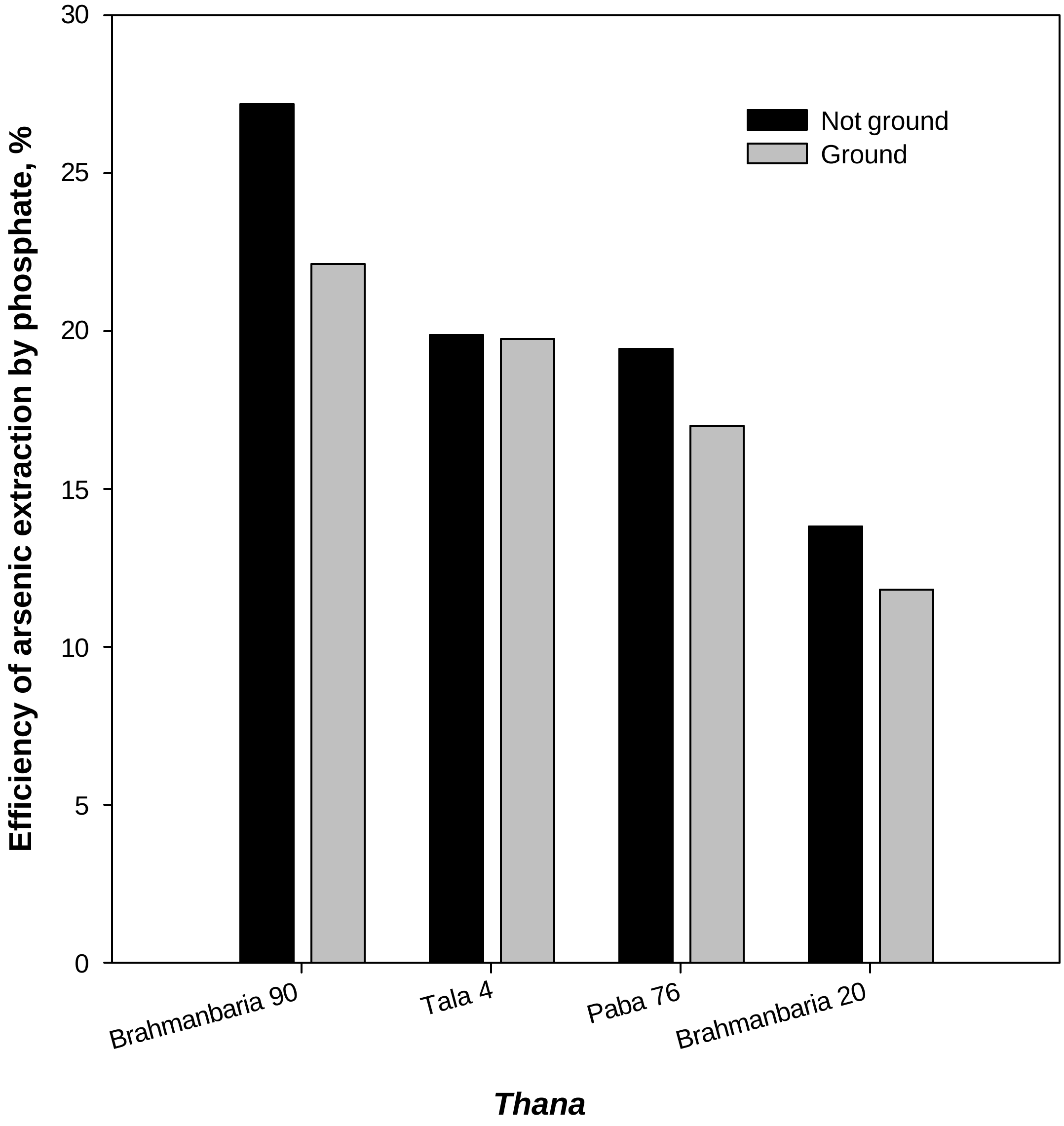

Figure 7. The influence of soil grinding on efficiency of arsenic extraction by sodium phosphate. Experimental conditions included 0.5 g of soil, 20 mL of pH 4, 0.1 M sodium phosphate, and 24-h extraction time with continuous shaking at room temperature.

EFFECT OF pH

In both the Ca^{2+} and Na^{+} systems, higher efficiencies of arsenic extraction by phosphate were observed at extreme pH values (i.e., pH 1 and pH 13), and the highest overall efficiencies of arsenic extraction by phosphate were at pH 1. The efficiency of arsenic extraction decreased towards intermediate pH values (Figure 8 - Figure 9). In the Ca^{2+} system, the lowest efficiencies of arsenic desorption by phosphate were at pH 9 (Figure 8). Arsenic extraction from Brahmanbaria 90 was greater than from the other soils, whereas, arsenic extraction from Brahmanbaria 20 was relatively low over the entire pH range of 1 to 13. At pH 9, the extraction of arsenic from Brahmanbaria 20 was negligible. With the Na^{+} systems, the lowest efficiencies of arsenic extraction by phosphate from Brahmanbaria 20 and Paba 76 were at pH 5, whereas, the lowest efficiencies of arsenic desorption by phosphate from Brahmanbaria 90 and Tala 4 were at pH 9 (Figure 9).

Arsenate [As (V)] was the predominant arsenic species in these air-dried soils. The impact of pH on arsenic extraction could be strongly influenced by the effect of pH on both mineral dissolution and mineral surface charge. The oxide surface is negatively charged at pH values above the point of zero charge (PZC). For example, the PZCs of iron oxides are at approximately pH 8 - 8.5 (Dzombak and Morel, 1990; Sadiq, 1997; Sposito, 1984), which indicates that the mineral surface sites are more negatively charged at pH values above the PZC. Therefore, it is reasonable that the higher efficiency of arsenic extraction by phosphate at high pH is influenced by the electrostatic repulsion of negatively charged arsenate by negatively charged surface sites (Jackson and Miller, 2000; Jain and Loeppert, 2000). Also, Manning and Goldberg (1996) suggested that the

PZCs of edge sites of layer-silicate minerals (i.e., kaolinite, illite, and montmorillonite) are at approximately pH 8 – 8.5. Another explanation for the higher arsenic-extraction efficiency at high pH could be the higher concentration of OH^- and its increased competition as an exchange ligand at the oxide surface (Loeppert et al., 2002). Also, OH^--enhanced dissolution of iron oxides might contribute to the extractability of arsenic. OH^--enhanced dissolution (Equation [4]) involves a reaction with surface structural Fe to form the soluble $Fe(OH)_4^-$ species at high pH, which will likely result in the desorption of adsorbed arsenic (Loeppert et al., 2002).

$$\text{Fe-oxide}-AsO_4 + OH^- \rightarrow Fe(OH)_4^- + As_{aq} \qquad [4]$$

At the extreme low pH (i.e., pH 1), arsenate is fully protonated and positive charges are predominant on the Fe-oxide surface sites (Mott, 1981). Consequently, there is less impact of electrostatic attraction on arsenic retention. The observation of higher efficiencies of arsenic extraction by phosphate at extreme low pH suggests that ligand exchange could be catalyzed as a result of oxygen protonation by available hydrogen ions, which results in the weakening of Fe--O-As bonds at the Fe oxide surface (Mott, 1981). Also, H^+-enhanced dissolution (Equation [5]) might also be an important extraction mechanism at low pH (Loeppert et al., 2002).

$$\text{Soil}-AsO_4 + H^+ \rightarrow \text{Soil} + H_2O + As_{aq} \qquad [5]$$

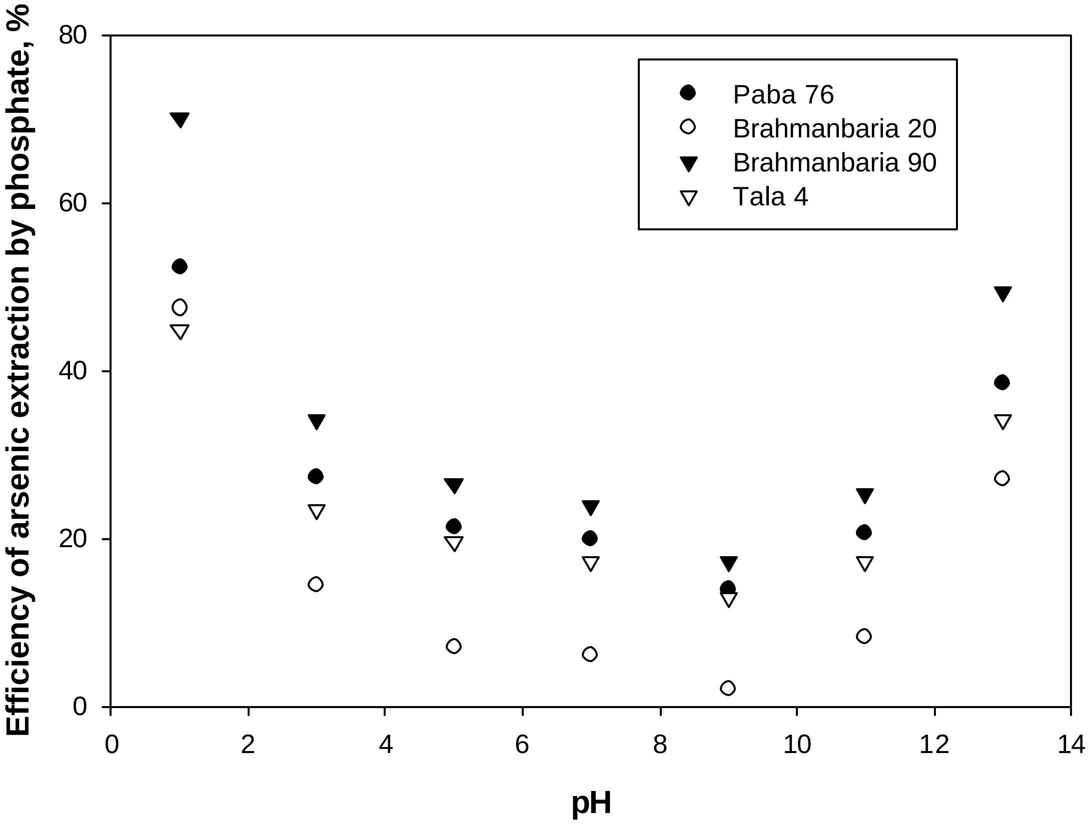

Figure 8. Effect of pH of the Ca^{2+}system on efficiency of arsenic extraction by sodium phosphate. Experimental conditions included 0.5 g of soil, 20 mL of 0.1 M sodium phosphate, and 24-h extraction time with continuous shaking at room temperature.

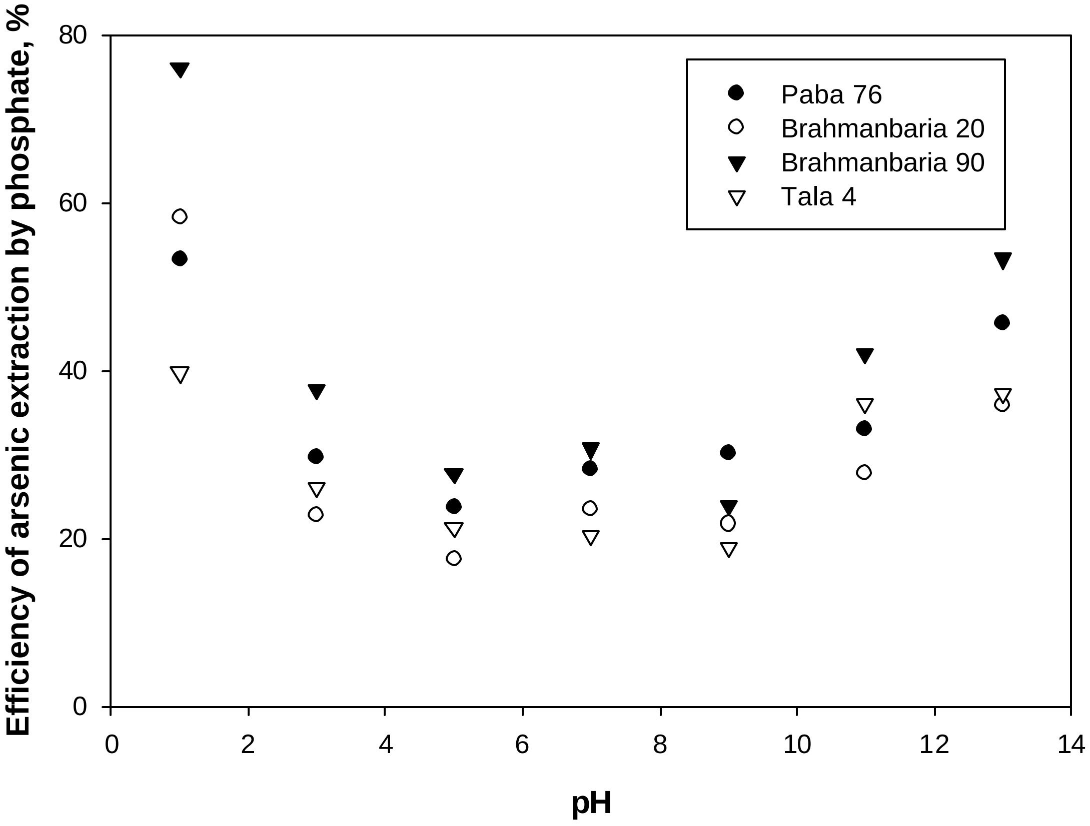

Figure 9. Effect of pH of the Na^+ system on efficiency of arsenic extraction by sodium phosphate. Experimental conditions included 0.5 g of soil, 20 mL of 0.1 M sodium phosphate, and 24-h extraction time with continuous shaking at room temperature.

EFFECT OF COUNTERION

The effects of counterion are summarized in Figure 10 - Figure 13. In each case, the efficiency of arsenic extraction by phosphate was lower with the Ca^{2+} system than with the Na^+ system over the entire pH range of 1 to 13. At pH =< 5, desorption behavior of arsenic by phosphate in Na^+ versus Ca^{2+} systems was similar; however, at pH >= 7, arsenic extraction efficiency in the Ca^{2+} systems was considerably lower compared to the Na^+ systems.

Freeman and Rowell (1982) suggested that arsenate might be occluded as a result of co-precipitation with Ca phosphate at high pH. Another explanation for the lower efficiency of arsenic extraction in the Ca^{2+} systems could be a greater ease of bonding of arsenic in the presence of Ca^{2+} versus Na^+ in the diffuse double layer (McBride, 1994). Counterions with lower charge result in increased electrical double layer thickness of negatively charged clays as well as increased electrostatic repulsion between the negatively charged surface and anions (Bolt, 1976; McBride, 1994; Tan, 1982). The relationship between electrical double layer thickness and counterion valence is expressed in Equation [6],

$$\kappa = A \cdot z\,(n_0/ekT)^{1/2} \qquad [6]$$

where κ is the reciprocal of diffuse double-layer thickness, A is a constant, z is the counterion valence, n_0 is the electrolyte concentration, *e* is the dielectric constant of the solvent, k is the Boltzmann constant, and T is temperature (K) (McBride, 1994). With the higher valence counterion, i.e., Ca^{2+} vs. Na^+, specifically adsorbed anions such as arsenate can be attracted to the surface more readily due to the more rapid decay in negative electrical potential with distance from the surface. This phenomenon could have a positive impact on arsenate adsorption and a negative impact on extraction. Also, enhanced flocculation of colloids in the presence of Ca^{2+} could result in trapping of adsorbed ions and decreased extraction efficiency.

EFFECT OF REACTION TIME

The rate of arsenic extraction by phosphate decreased with longer reaction times, after an initially rapid desorption (Figure 14). The extraction efficiency decreased in the following order: Brahmanbaria 90 > Paba 76 = Tala 4 > Brahmanbaria 20. In each case, the total efficiency of arsenic desorption by phosphate increased with reaction time and was less than 30 % after the 24-h reaction time. The results indicate that a considerable amount of arsenic was still retained on soil retention sites after the 24-h extraction.

In a previous study (O'Reilly et al., 2001), arsenate desorption from goethite by 6 mM phosphate at pH 6 was rapid within the first 24 h and then proceeded slowly for up to 7 mo. Total desorption increased with time and the efficiency of total arsenate desorption was approximately 65 % after 5 mo. Willett et al. (1988) reported that phosphate adsorption on soils also increased with increasing reaction time. An initially rapid phosphate adsorption occurred during the first 6 d, and phosphate adsorption rate slowed considerably with longer reaction times.

The initially rapid and subsequently slow desorption of arsenate by phosphate in the current study might result from differences in ease of accessibility of sites and

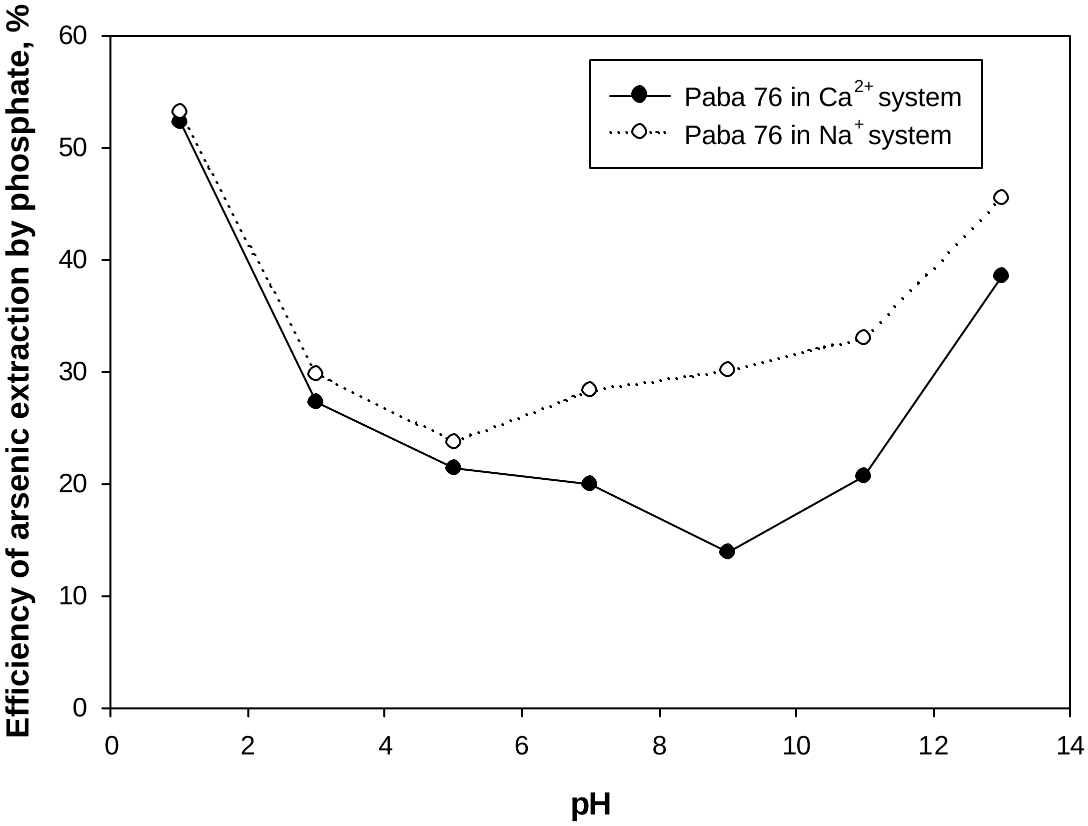

Figure 10. Effect of counterion on arsenic desorption from Paba 76 soil by sodium phosphate in the pH range of 1 and 13. Experimental conditions included 0.5 g soil, 20 mL pH 4, 0.1 M sodium phosphate, and 24-h extraction time with continuous shaking at room temperature.

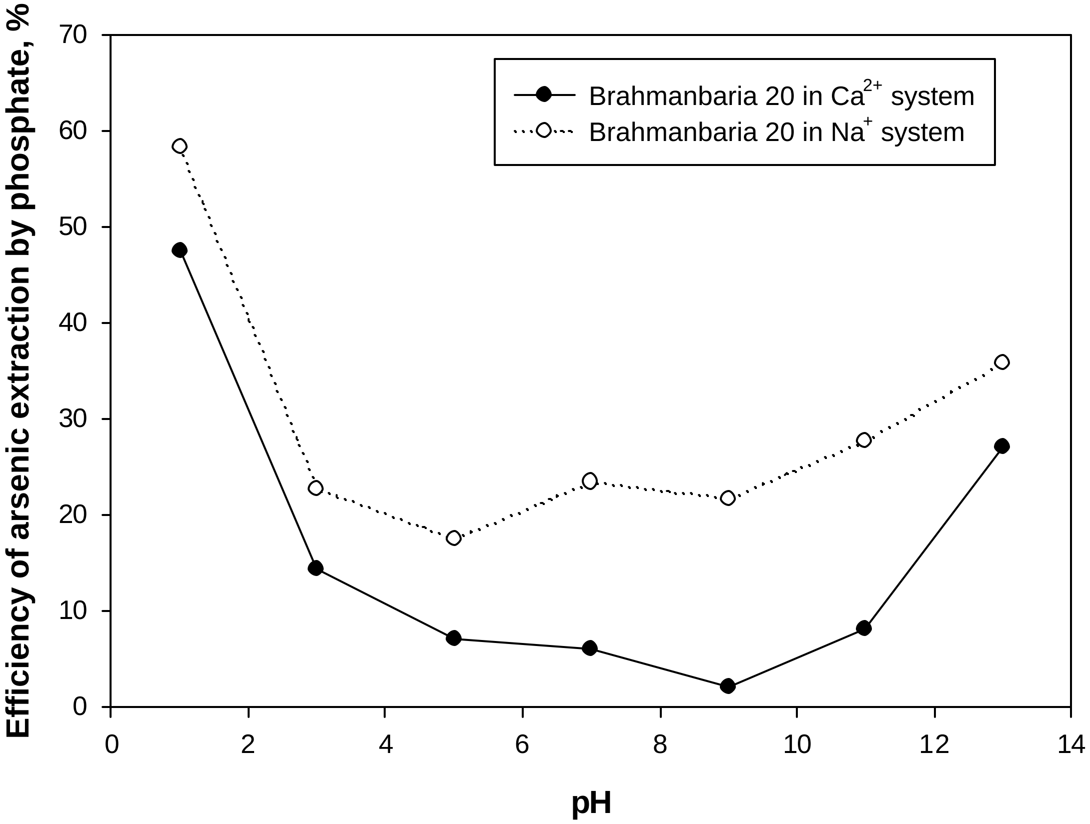

Figure 11. Effect of counterion on arsenic desorption from Brahmanbaria 20 soil by sodium phosphate in the pH range of 1 and 13. Experimental conditions included 0.5 g soil, 20 mL pH 4, 0.1 M sodium phosphate, and 24-h extraction time with continuous shaking at room temperature.

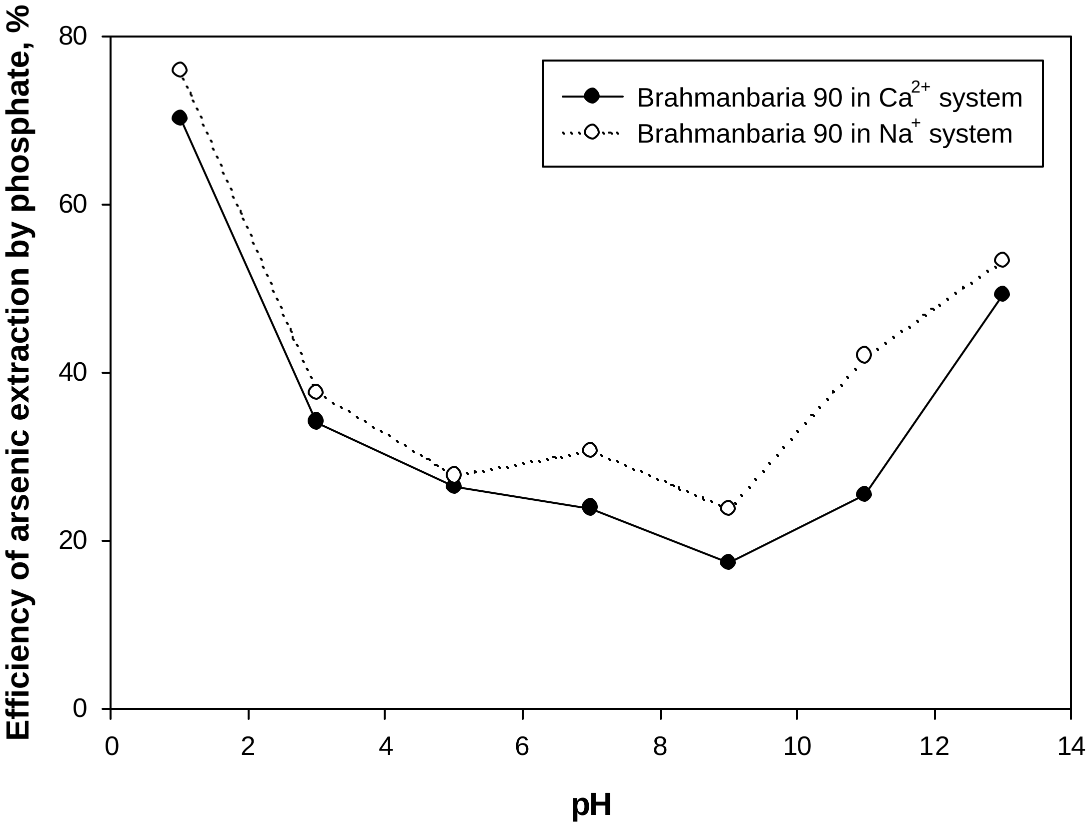

Figure 12. Effect of counterion on arsenic desorption from Brahmanbaria 90 soil by sodium phosphate in the pH range of 1 and 13. Experimental conditions included 0.5 g soil, 20 mL pH 4, 0.1 M sodium phosphate, and 24-h extraction time with continuous shaking at room temperature.

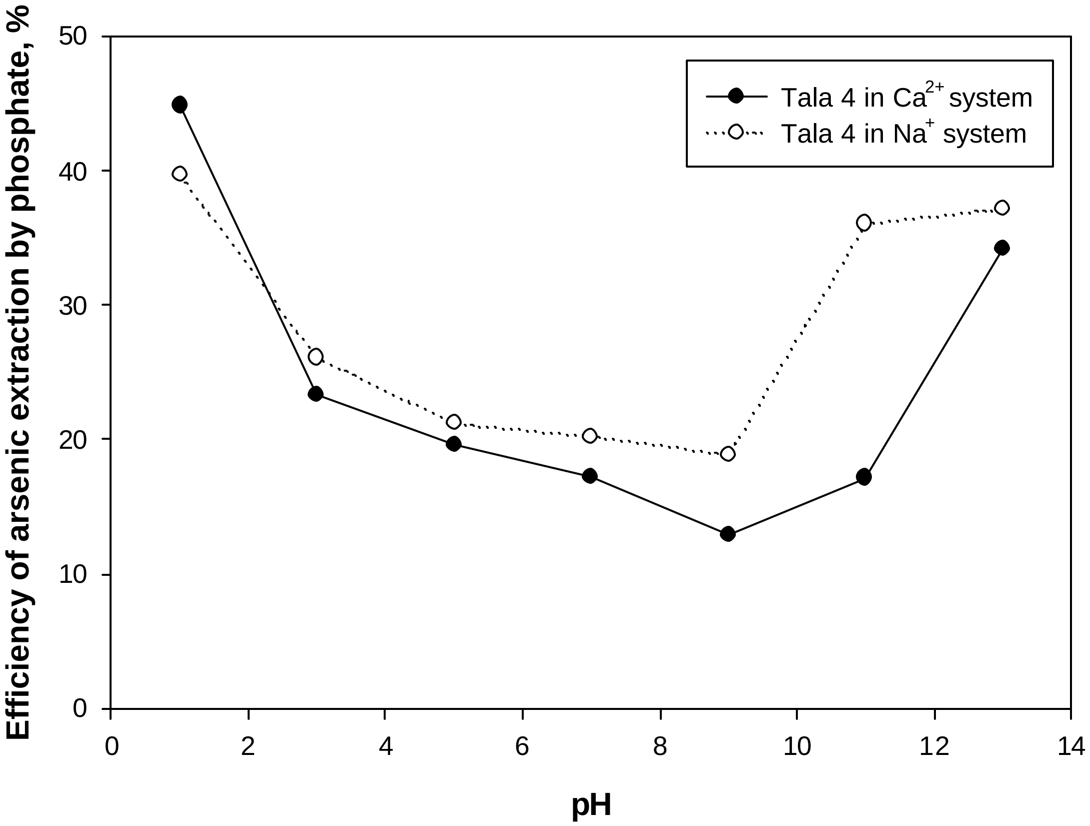

Figure 13. Effect of counterion on arsenic desorption from Tala 4 soil by sodium phosphate in the pH range of 1 and 13. Experimental conditions included 0.5 g soil, 20 mL pH 4, 0.1 M sodium phosphate, and 24-h extraction time with continuous shaking at room temperature.

diffusion processes within the aggregates. Also, arsenic might be too strongly adsorbed to some adsorption sites on soils to be easily displaced by phosphate.

The rate data in Figure 14 were evaluated to determine whether arsenic desorption from soils by phosphate follows first order reaction kinetics (Figure 15). The first order reaction, in which the rate of desorption is dependent on the concentration of adsorbate C, is expressed in Equation [7] (McBride, 1994; Sawyer et al., 1994):

$$-\frac{dC}{dt} = kC \qquad [7]$$

Integration of this equation over a time interval gives

$$\log_{10}\frac{C}{C_0} = -\frac{kt}{2.303} = -k't\ , \qquad [8]$$

where C_0 is the initial concentration of arsenic adsorbed on surface adsorption sites, C is the concentration of arsenic adsorbed on the sites at time t, k' is the rate constant for the reaction and the slope for the reaction when a plot of $\log_{10}(C/C_0)$ versus t, and k is also a rate constant for the reaction and can be calculated by multiplying the slope k' of the plotted line by -2.303.

Desorption of arsenic from the soils by phosphate did not follow first order kinetics, since the plot of $\log_{10}(C/C_0)$ versus time did not yield a straight line for any of the soils (Figure 15). The results of the current study indicate that rate of extraction of arsenic by phosphate was not proportional to the concentration of arsenic adsorbed on surface sites. This phenomenon might be attributable to multiple arsenic adsorption sites with several arsenic bonding strengths or to arsenic adsorption sites to which phosphate was not readily accessible.

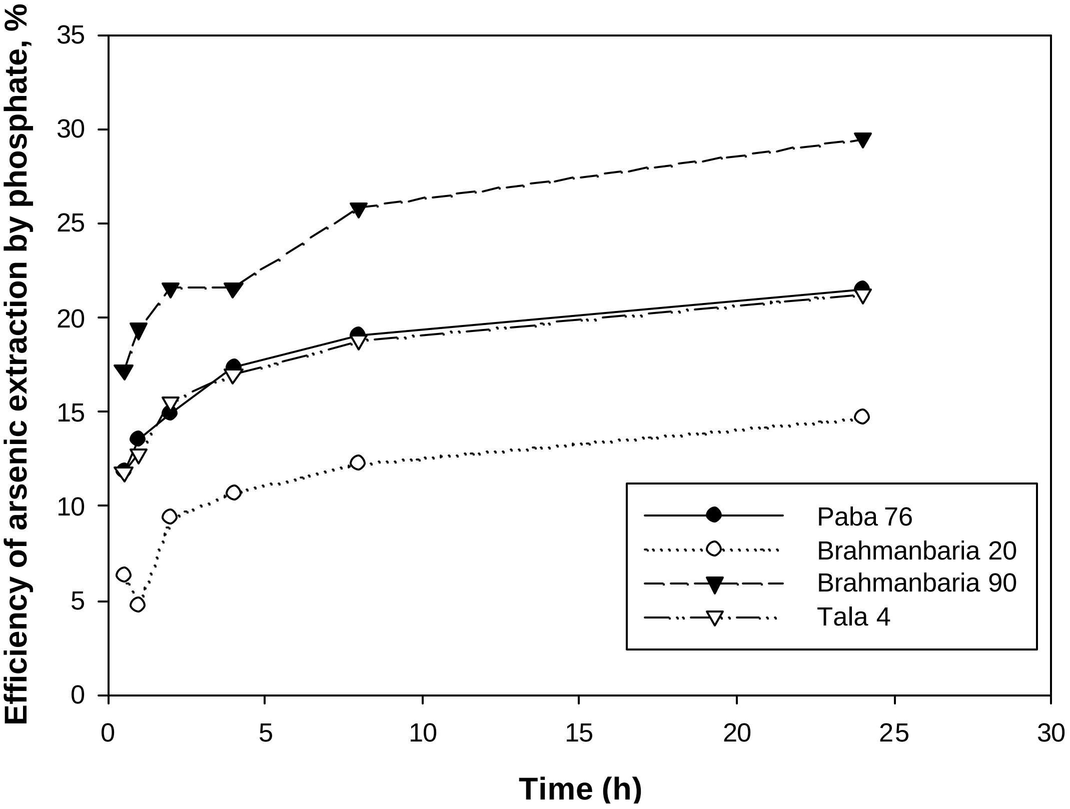

Figure 14. Effect of reaction time on arsenic extraction by sodium phosphate. Experimental conditions included 0.5 g of soil, 20 mL pH 4, 0.1 M sodium phosphate, and various extraction times (e.g., 0.5 – 24 h) with continuous shaking at room temperature.

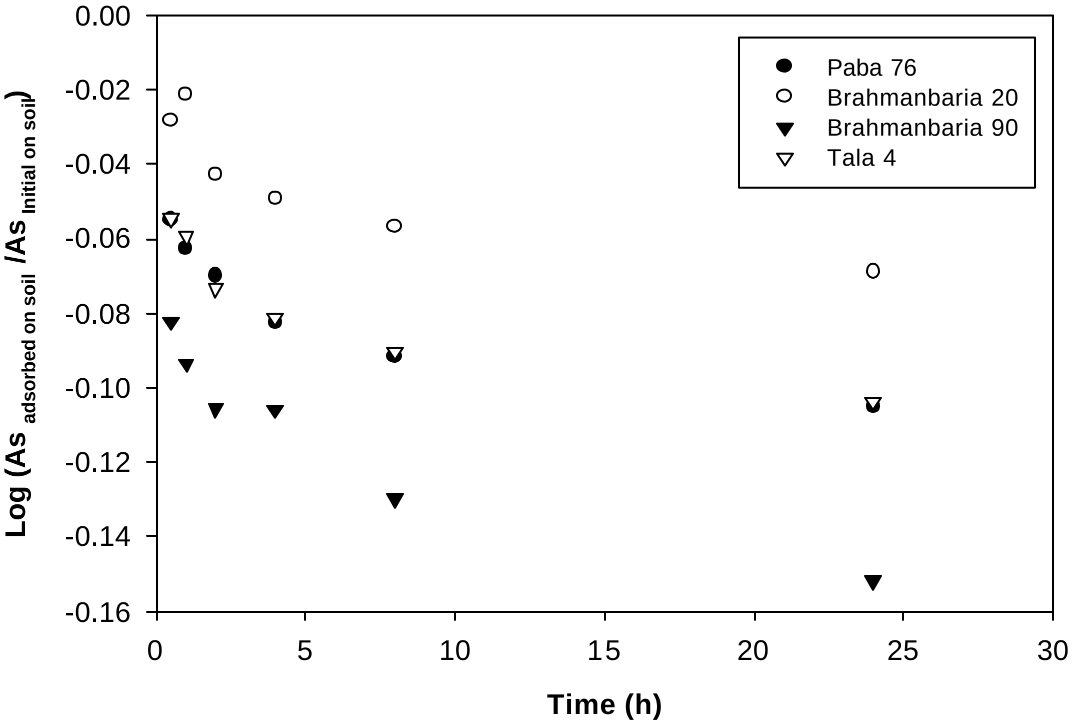

Figure 15. First order plot of arsenic extraction by sodium phosphate. Experimental conditions included 0.5 g of soil, 20 mL pH 4, 0.1 M sodium phosphate, and various reaction times (e.g., 0.5 – 24 h) with continuous shaking at room temperature.

EFFECT OF SEQUENTIAL ARSENIC EXTRACTION

During sequential extraction, the quantity of arsenic extracted decreased with each successive extraction (Figure 16). Arsenic desorption from both soils decreased considerably between the first and second arsenic extractions, and the quantity of arsenic extracted was negligible at the fifth sequential arsenic extraction. With the Brahmanbaria 90 soil, there were no appreciable differences between the quantities of arsenic extracted by sequential extraction versus continuous extraction (Figure 17). With the Tala 4 soil (Figure 18), there was an indication of a slightly higher extraction efficiency by sequential extraction. This higher extraction efficiency was influenced by the additional 30 min contact time for each step of the sequential extraction during sample centrifugation. Taken together, these results indicate that the presence of dissolved arsenic during continuous extraction with phosphate did not appreciably impact the subsequent arsenic extraction.

In previous studies, McBride (1994) reported that adsorption of metal cations (e.g., Pb^{2+} and Cu^{2+}, that were adsorbed strongly by soil organic matter) was relatively rapid, whereas, desorption of these metal cations from surfaces was several orders of magnitude slower than adsorption. Desorption of inner-sphere multidentate complexes occurs slowly because large activation energies might be needed to break the strong bonds (McBride, 1994). The observations of the current study indicate that arsenic desorption by phosphate is a very slow process that might be influenced by strong adsorption of arsenic on iron oxides as an inner-sphere complex. Also, phosphate might not be readily accessible to arsenic on retention sites, because arsenic might be trapped by soil aggregates.

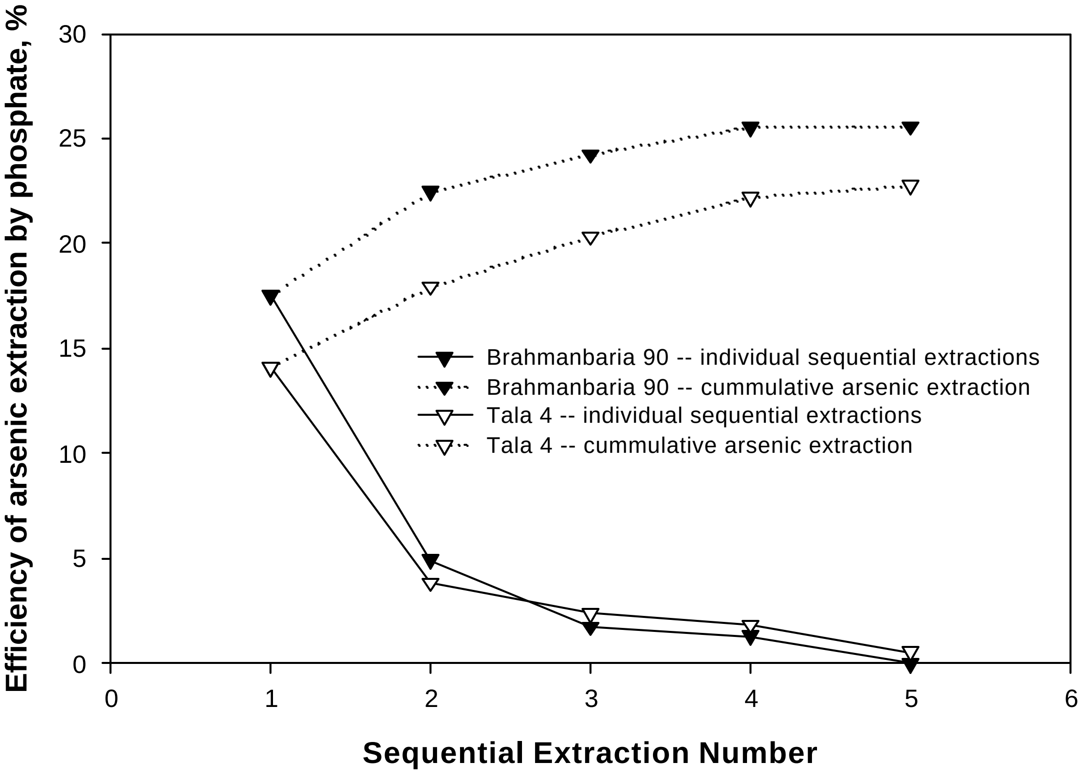

Figure 16. Sequential extraction of arsenic by sodium phosphate. Experimental conditions included 0.5 g soil, 20 mL pH 4, 0.1 M sodium phosphate, and 2 h extractions with continuous shaking at room temperature.

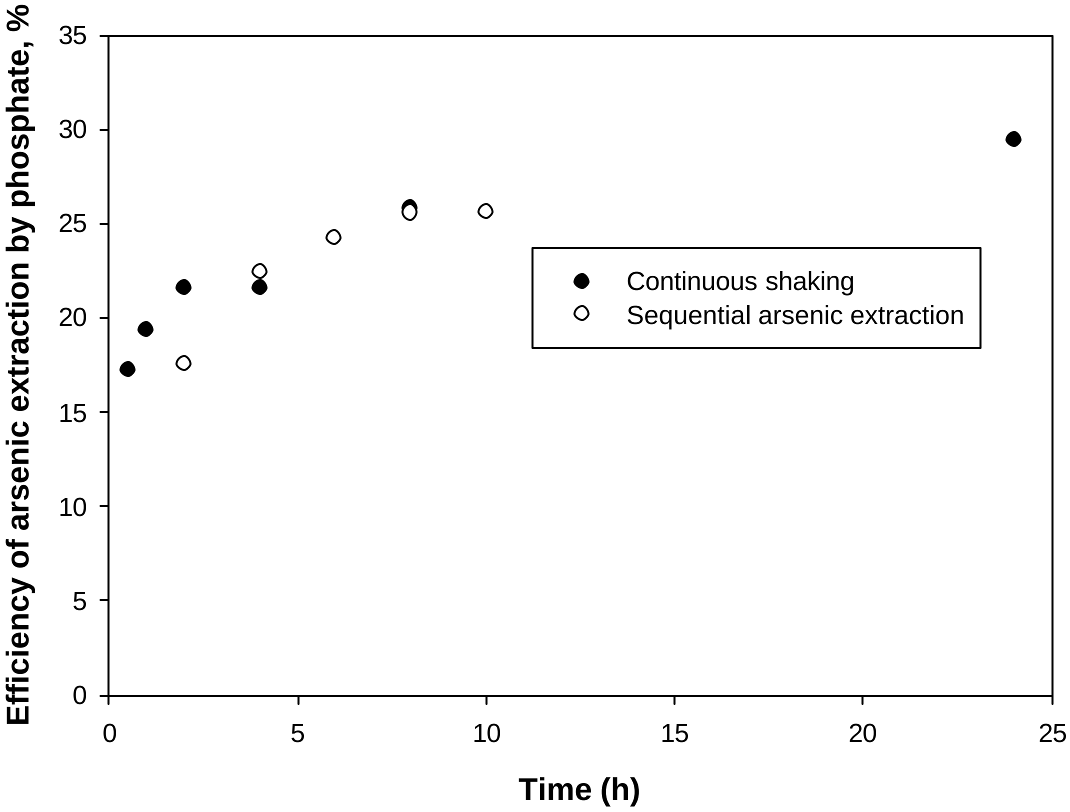

Figure 17. Comparison of the efficiencies of arsenic extraction from the Brahmanbaria 90 soil by sodium phosphate with sequential 2 h arsenic extractions and continuous shaking. Experimental conditions included 0.5 g soil, 20 mL pH 4, 0.1 M sodium phosphate, and continuous shaking or sequential extraction at room temperature.

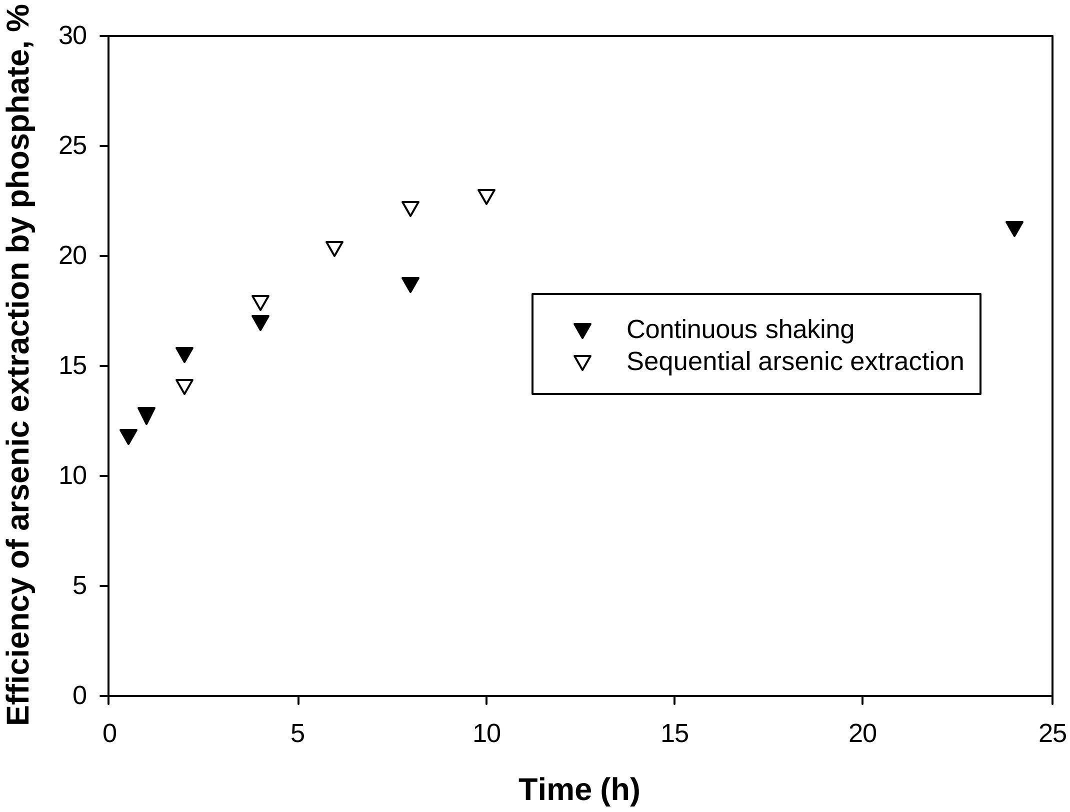

Figure 18. Comparison of the efficiencies of arsenic extraction from the Tala 4 soil by sodium phosphate with sequential 2 h arsenic extractions and continuous shaking. Experimental conditions included 0.5 g soil, 20 mL pH 4, 0.1 M sodium phosphate, and continuous shaking or sequential extraction at room temperature.

EFFECT OF PHOSPHATE CONCENTRATION

Arsenic extraction from soils by phosphate increased with increasing phosphate concentration (Figure 19). For example, the efficiency of arsenic desorption increased from approximately 9 % with 0.001 M sodium phosphate to 45 % with 1.5 M sodium phosphate at pH 4.

Alam et al. (2001) also reported that extraction of arsenate from a poorly crystalline Fe oxide increased with increasing phosphate concentration. Jain and Loeppert (2000) observed a reduction in arsenate adsorption on ferrihydrite with increasing initial molar ratio of phosphate to arsenate. The effect of phosphate on arsenate adsorption was greater at high pH than at low pH. At a $\mathrm{mol}_P : \mathrm{mol}_{As}$ ratio of 50 : 1, < 10 % of the arsenic adsorption maximum was achieved across the pH range of 3 to 11. The results of this previous study indicate that during adsorption, phosphate is highly competitive for arsenic adsorption sites.

The current desorption experiments indicate that considerable arsenic was still retained when phosphate concentration was 1.5 M (P : As molar ratio = $2.86 \times 10^5 : 1$). The strong dependence of arsenic desorption efficiency on initial phosphate concentration indicates that mass action and diffusion processes might impact arsenic desorption from poorly accessible arsenic adsorption sites. Apparently, some sites have very strong affinity for arsenic and slow desorption kinetics even at high phosphate concentrations and high P : As molar ratios.

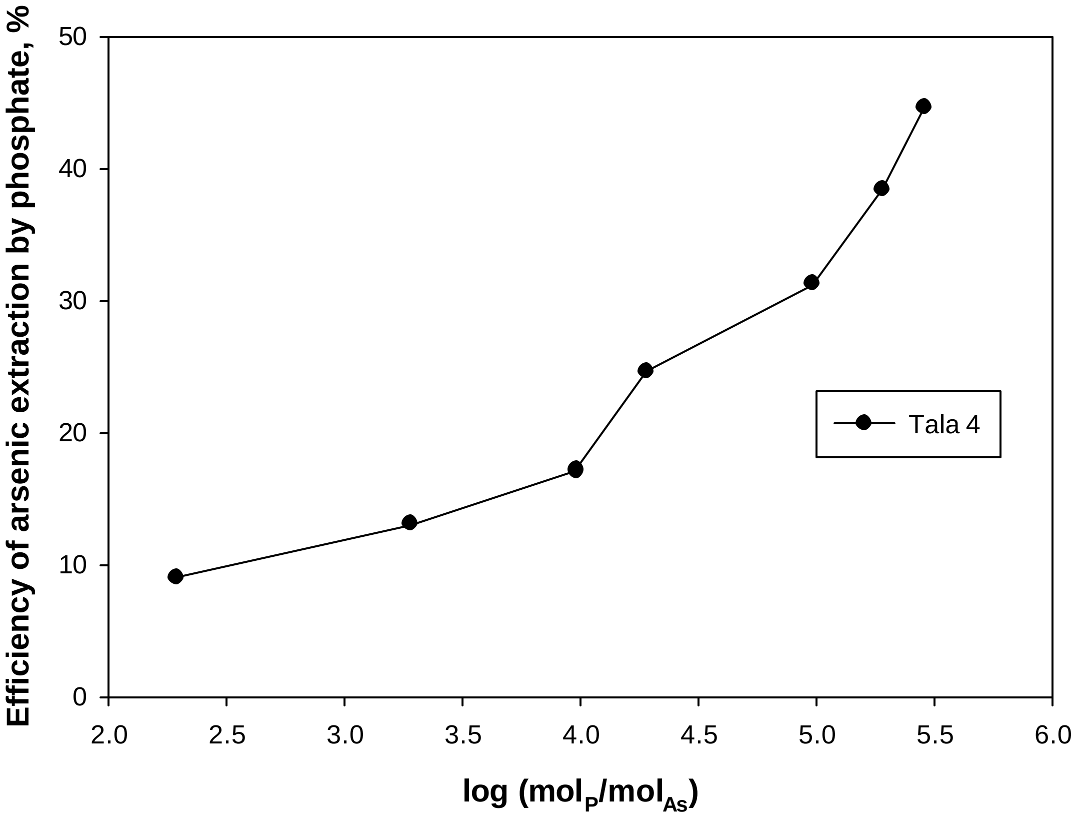

Figure 19. Effect of phosphate concentration on arsenic desorption from the Tala 4 soil. Experimental conditions included 0.5 g soil, a range of initial pH 4 sodium phosphate concentrations from 0.001 to 1.5 mol P L^{-1} (1.92 x 10^2 to 2.86 x 10^5 mol$_P$/mol$_{As}$), and a 24-h extraction time with continuous shaking at room temperature.

EFFECT OF DRYING

The 1 g L^{-1} Fe suspensions containing aliquots of air-dried, acid-washed sand ranging from 0 to 8 g were pretreated by three different methods. In treatment # 1, arsenic was added to the suspensions so that the molar ratio of Fe : As is 50 : 1. The samples were equilibrated, centrifuged, decanted and dried in the oven (60 ± 5 °C). Upon the completion of drying, pH 4, 0.1 M sodium phosphate was added, equilibrated, centrifuged, filtered, and stored to analyze arsenic. In treatment # 2, the samples were pretreated as above, except they were not dried prior to extraction with phosphate. In treatment #3, samples were treated as with the first method, except that ferrihydrite was oven-dried (60 ± 5 °C) before addition of arsenic.

The quantities of arsenic desorbed by phosphate were generally similar for treatment # 2 (non-drying) and treatment # 3 (addition of arsenic after drying ferrihydrite) (Figure 20). For treatment # 1 (drying after addition of arsenic and ferrihydrite), the efficiency of arsenic extraction by phosphate was generally lower than with the other treatments, but increased with increasing amount of sand. Complete extraction of arsenic was not obtained in any case.

With treatment # 1, the positive relationship between sand content and arsenic extraction efficiency might be due to the influence of sand on ferrihydrite aggregation. The flocculated ferrihydrite is probably coating the sand particles. Hence the thickness of the ferrihydrite coatings and aggregation of ferrihydrite are strongly impacted by sand content and surface area. Therefore, a higher sand content would also favor a higher exposed surface area of flocculated ferrihydrite. The higher arsenic-extraction efficiency at the higher sand content might be attributable to the greater accessibility of adsorption sites on ferrihydrite.

With treatment # 3, the negative relationship between sand content and arsenic extraction efficiency might be attributable to a positive influence of sand on the availability of Fe oxide surface sites for adsorption of arsenic, i.e., arsenic was more readily retained against extraction by phosphate with a greater availability of potential arsenic adsorption sites. With treatment # 2, the negative relationship between sand content and arsenic-extraction efficiency cannot be readily explained, unless the presence of sand negatively influenced Fe-oxide flocculation, with resulting positive influence on the accessibility of potential arsenic adsorption sites for retention against desorption by phosphate. SEM might be beneficial to understand the flocculation behavior of ferrihydrite in the presence of sand.

The results in present studies indicate that some arsenate might be very strongly retained on iron oxide and arsenate adsorbed on some sites might be less accessible to extraction by phosphate. Also, desorption of strongly bound arsenate by phosphate might be a relatively slow process.

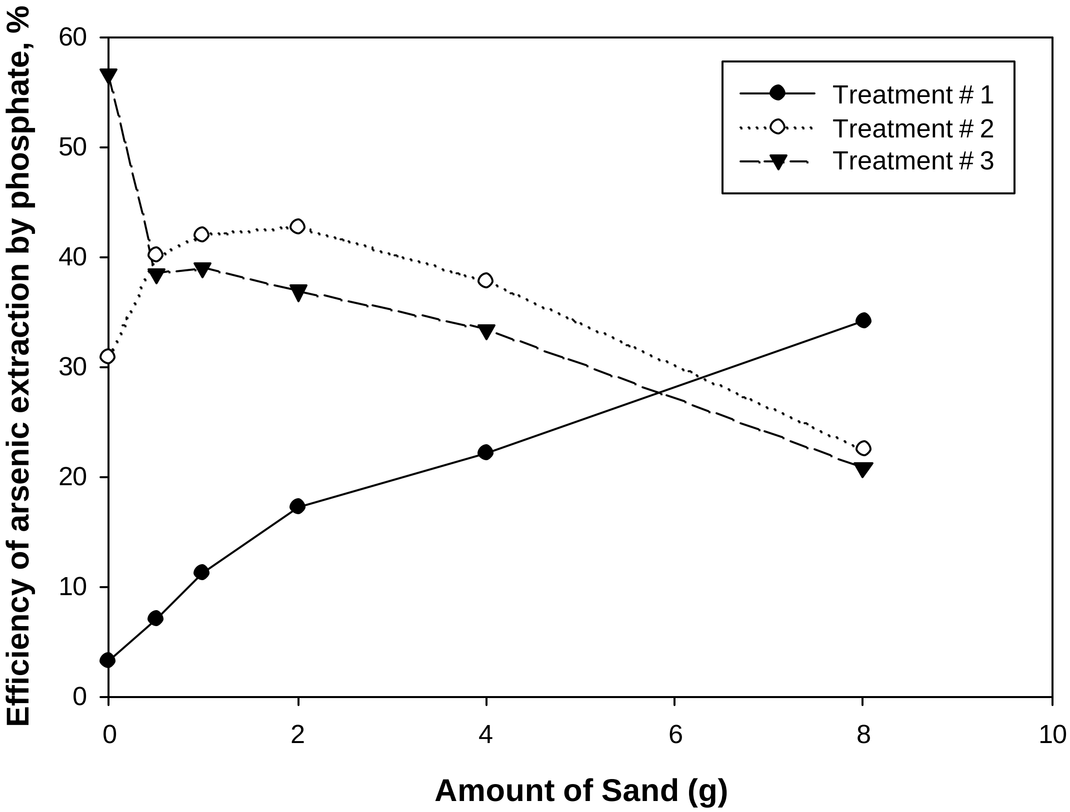

Figure 20. Effect of sand content and drying treatment on desorption of arsenic from ferrihydrite by pH 4, 0.1 M sodium phosphate, at 1 g L^{-1} ferrihydrite, and 26.8 mg As L^{-1} as arsenate. Treatment # 1, ferrihydrite dried after addition of arsenate; treatment # 2, ferrihydrite not dried after addition of arsenate; treatment # 3, ferrihydrite dried before addition of arsenate.

PHOSPHATE-EXTRACTABLE ARSENIC CONCENTRATIONS IN FIVE *THANAS* OF BANGLADESH

The concentrations of total arsenic and phosphate extractable arsenic of Bangladesh soils were highly variable both within and between *thana(s).* The concentrations of total arsenic ranged from 2.89 to 17.8 mg As kg^{-1} in Paba *thana*, 0.772-38.5 mg kg^{-1} in Brahmanbaria, 4.30 to 51.8 mg kg^{-1} in Tala, 2.08 to 9.33 mg kg^{-1} in Senbag, and 4.98 to 66.0 mg kg^{-1} in Faridpur (Biswas et al., 2003; Appendix). Phosphate extractable arsenic concentrations ranged from 0.435 to 4.52 mg As kg^{-1} in Paba *thana*, 0.120 to 10.6 mg kg^{-1} in Brahmanbaria, 0.779 to 14.8 mg kg^{-1} in Tala, 0.314 to 2.14 mg kg^{-1} in Senbag, and 0.995 to 20.8 mg kg^{-1} in Faridpur (Appendix).

The boxplots of phosphate-extractable arsenic (Figure 21) indicate that Paba and Senbag soils have relatively low mean and median phosphate-extractable arsenic, whereas, mean and median phosphate-extractable arsenic were high in Faridpur and Tala *thanas*. More outliers were observed with the Brahmanbaria soil, compared to the other *thanas*. The mean phosphate-extractable arsenic concentration decreased as follows: Faridpur >= Tala > Brahmanbaria > Paba > Senbag (Table 5). The median phosphate-extractable arsenic concentrations decreased in the order: Tala > Faridpur > Brahmanbaria > Paba > Senbag (Table 5). The standard deviations of phosphate extractable-arsenic followed the following trend: Faridpur (3.452) > Tala (2.343) > Brahmanbaria (2.051) > Paba (0.632) > Senbag (0.377). The results of multiple mean comparisons indicated that the difference in mean between Faridpur and Tala *thanas* was not significant at the 5 % level (Table 6). The Tamhane T2 test of all other combinations showed that mean differences were significantly different at the 5 % level.

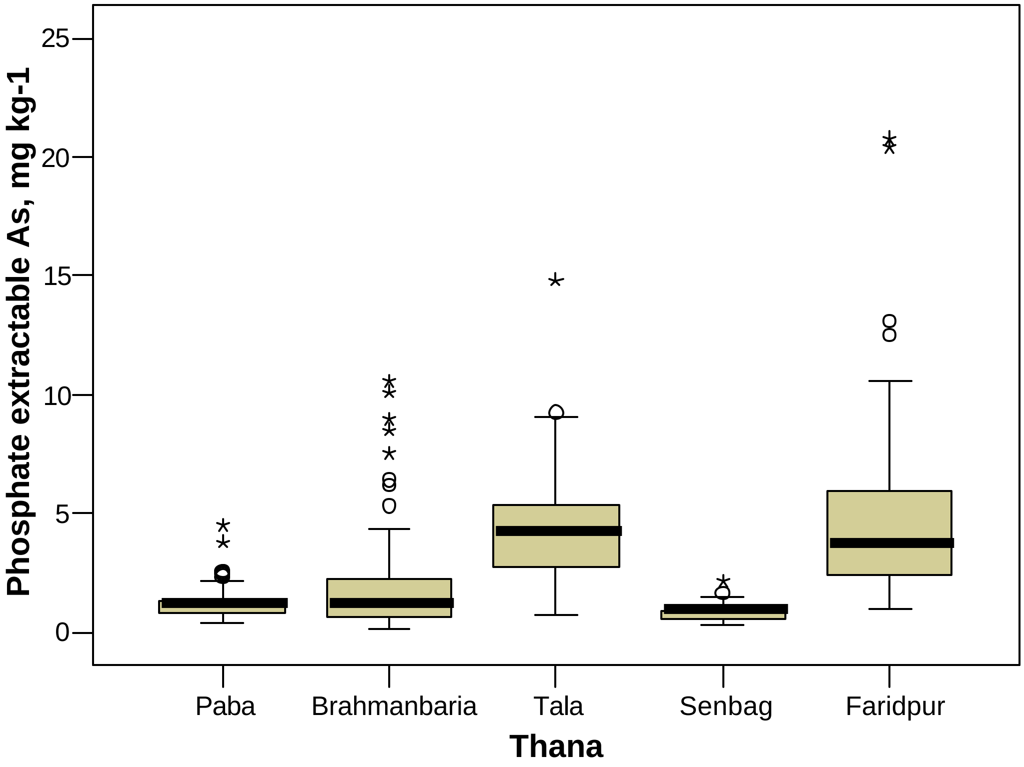

Figure 21. Boxplots of phosphate extractable arsenic for the various *thanas*.

Table 5. Descripiton of phosphate extractable arsenic among the five *thanas*.

	Paba	Brahmanbaria	Tala	Senbag	Faridpur
Mean	1.192	1.821	4.281	0.823	4.679
Median	1.083	1.117	4.065	0.783	3.566
Std. Deviation	0.632	2.051	2.343	0.377	3.452
Minimum	0.435	0.120	0.779	0.314	0.995
Maximum	4.519	10.58	14.804	2.142	20.77

Table 6. Multiple comparisons between *thanas* using the Tamhane T2 test. The dependent variable is phosphate-extractable arsenic.

Thana		Mean Difference	Std. Error	Significance
Paba	Brahmanbaria	-0.629	0.205	0.026*
	Tala	-3.089	0.237	0.000*
	Senbag	0.369	0.086	0.000*
	Faridpur	-3.487	0.351	0.000*
Brahmanbaria	Tala	-2.460	0.301	0.000*
	Senbag	0.997	0.204	0.000*
	Faridpur	-2.858	0.397	0.000*
Tala	Senbag	3.458	0.236	0.000*
	Faridpur	-0.398	0.414	0.984
Senbag	Faridpur	-3.856	0.350	0.000*

* The mean difference is significant at the 0.05 level.

The results indicate that Faridpur and Tala *thanas* have relatively high phosphate-extractable arsenic concentrations and that phosphate extractable arsenic concentration is more highly distributed in Faridpur compared to the other *thanas*. The soils from Senbag have relatively low phosphate-extractable arsenic concentrations and a relatively low distribution of values.

The high variability in arsenic concentration both within and between *thana(s)* could be influenced by (i) sediment mineralogy, (ii) arsenic source factors such as original arsenic concentration of the sediment and addition of arsenic by irrigation with arsenic-contaminated water, or (iii) loss factors such as leaching of arsenic through the soil profile and arsenic volatilization. The results of the two normality tests for each *thana* (Table 7) indicated that the phosphate-extractable arsenic concentrations in each *thana* were not normally distributed, as indicated by the p-values < 0.05.

Table 7. Tests of normality with Kolmogorov-Smirnov test and Shapiro-Wilk test.

Thana		Kolmogorov-Smirnov		Shapiro-Wilk	
		df	Significance†	df	Significance†
Phosphate extractable As mg kg^{-1}	Paba	102	0.000	102	0.000
	Brahmanbaria	110	0.000	110	0.000
	Tala	105	0.026	105	0.000
	Senbag	41	0.014	41	0.002
	Faridpur	100	0.000	100	0.000

† Populations are normally distributed when P > 0.05 at the 0.05 level.

CORRELATION BETWEEN PHOSPHATE-EXTRACTABLE ARSENIC AND OTHER ARSENIC PARAMETERS (i.e., OXALATE-EXTRACTABLE ARSENIC, TOTAL ARSENIC)

Spearman's coefficient between phosphate-extractable arsenic and total arsenic in each *thana* indicated that phosphate-extractable arsenic was positively correlated with total arsenic (Table 8 and Figure 22 - Figure 27). The Spearman's coefficient between phosphate-extractable arsenic and total arsenic decreased as follows: Brahmanbaria (0.935) > Faridpur (0.835) > Tala (0.778) > Senbag (0.569) > Paba (0.556). The results from the linear regression of phosphate-extractable arsenic versus total arsenic indicated that the slope, which is an indication of extraction efficiency, decreased in the following order: Faridpur (0.312) > Brahmanbaria (0.309) > Tala (0.257) > Paba (0.173) > Senbag (0.112) (Table 9). For each *thana*, the extraction efficiency (as indicated from the linear regression slope) was less than 32 %. For the Senbag *thana* soils, the extraction efficiency was only 11 %. The *thanas* with the lowest arsenic contents (i.e., Paba and Senbag) also had the soils with the lowest arsenic-extraction efficiency. The Spearman's coefficient between proportion of phosphate-extractable arsenic to total arsenic and total arsenic decreased as follows: Faridpur (0.425) > Brahmanbaria (0.336) > Tala (0.074) > Senbag (-0.135) > Paba (-0.265) (Table 10). The proportion of phosphate-extractable arsenic in Paba and Senbag soils were negatively correlated with total arsenic. Also, the results of linear regression of proportion of phosphate-extractable arsenic to total arsenic and total arsenic indicated that the r^2 values were very low in all cases and the slopes of the Paba and Senbag data were negative (Table 11).

Phosphate-extractable arsenic was positively correlated with oxalate-extractable arsenic in each of the five *thanas* (Table 12 and Figure 28 - Figure 33). The Spearman's coefficient between phosphate-extractable arsenic and oxalate-extractable arsenic decreased as follows: Brahmanbaria > Faridpur > Tala > Paba > Senbag. Oxalate-extractable arsenic represents the portion of arsenic that is associated with the poorly crystalline Fe-oxide component.

Table 8. Spearman's coefficient between phosphate-extractable arsenic and total arsenic.

	Phosphate-extractable arsenic					
	Paba	Brahmanbaria	Tala	Senbag	Faridpur	Total
Total arsenic	0.556**	0.935**	0.778**	0.569**	0.835**	0.897**

** Correlation is significant at the 0.01 level.

Table 9. Slope and r^2 of linear regression of phosphate-extractable arsenic versus total arsenic.

		Phosphate-extractable arsenic					
		Paba	Brahmanbaria	Tala	Senbag	Faridpur	Total
Total arsenic	Slope	0.173	0.309	0.257	0.112	0.312	0.277
	r^2	0.502	0.926	0.691	0.177	0.782	0.832

Table 10. Spearman's coefficient between proportion of phosphate-extractable arsenic to total arsenic and total arsenic.

	Proportion of phosphate-extractable arsenic to total arsenic					
	Paba	Brahmanbaria	Tala	Senbag	Faridpur	Total
Total arsenic	-0.265**	0.336**	0.074	-0.135	0.425**	0.212**

** Correlation is significant at the 0.01 level.

Table 11. Slope and r^2 of linear regression of proportion of phosphate-extractable arsenic to total arsenic versus total arsenic.

		Proportion of phosphate-extractable arsenic to total arsenic					
		Paba	Brahmanbaria	Tala	Senbag	Faridpur	Total
Total arsenic	Slope	-0.004	0.003	0.001	-0.008	0.002	0.002
	r^2	0.026	0.055	0.003	0.026	0.060	0.042

Table 12. Spearman's coefficient between phosphate-extractable arsenic and oxalate-extractable arsenic.

	Phosphate-extractable arsenic					
	Paba	Brahmanbaria	Tala	Senbag	Faridpur	Total
Oxalate-extractable arsenic	0.544**	0.930**	0.750**	0.262	0.832**	0.897**

** Correlation is significant at the 0.01 level.

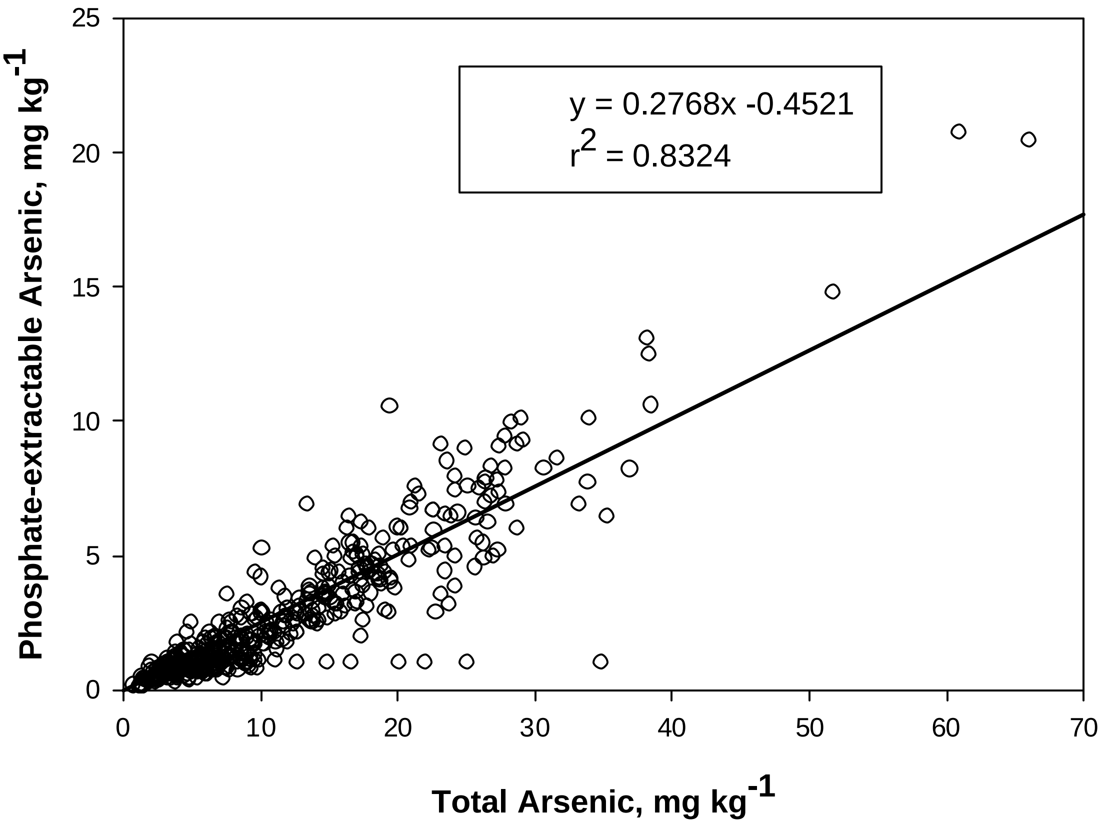

Figure 22. Relationship between phosphate-extractable arsenic and total arsenic of soils from the five *thanas.*

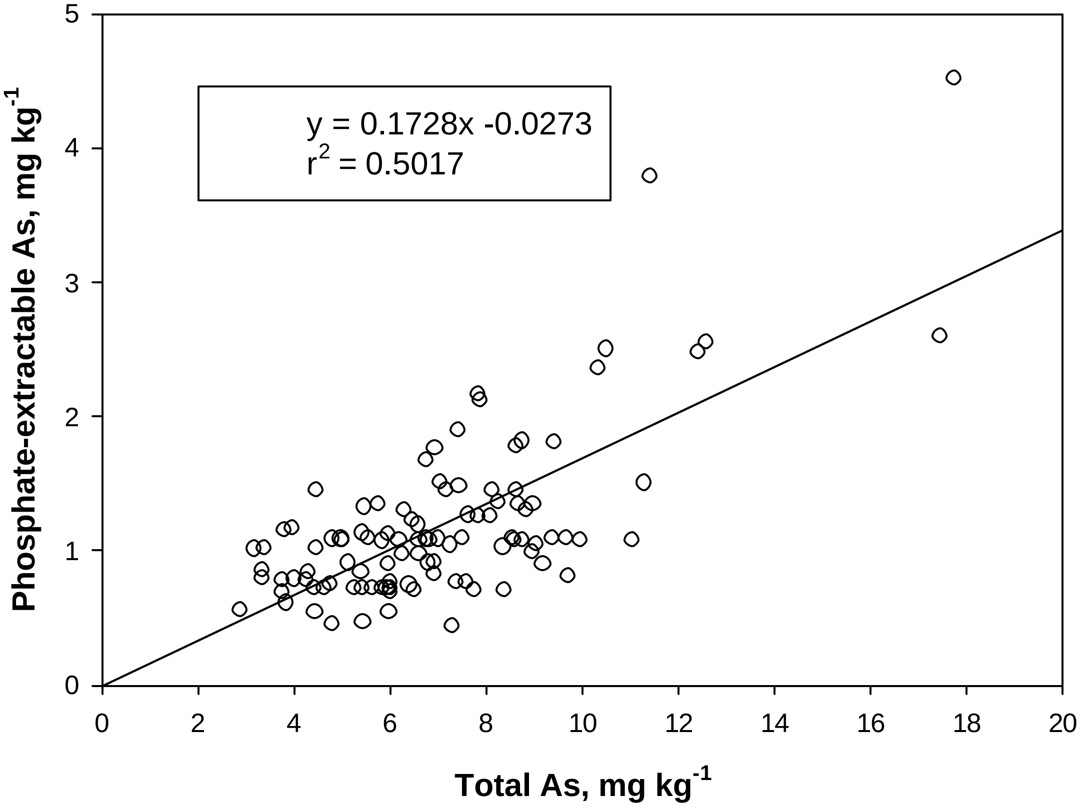

Figure 23. Relationship between phosphate-extractable arsenic and total arsenic of soils from Paba *thana*.

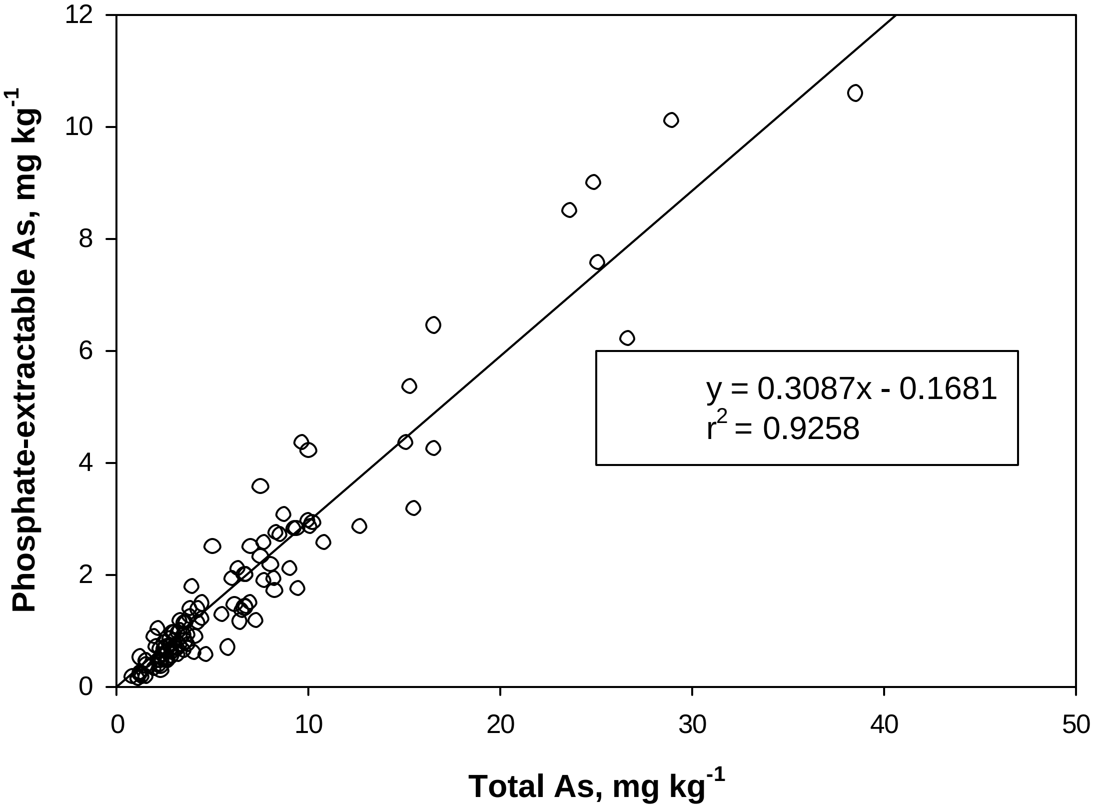

Figure 24. Relationship between phosphate-extractable arsenic and total arsenic of soils from Brahmanbaria *thana*.

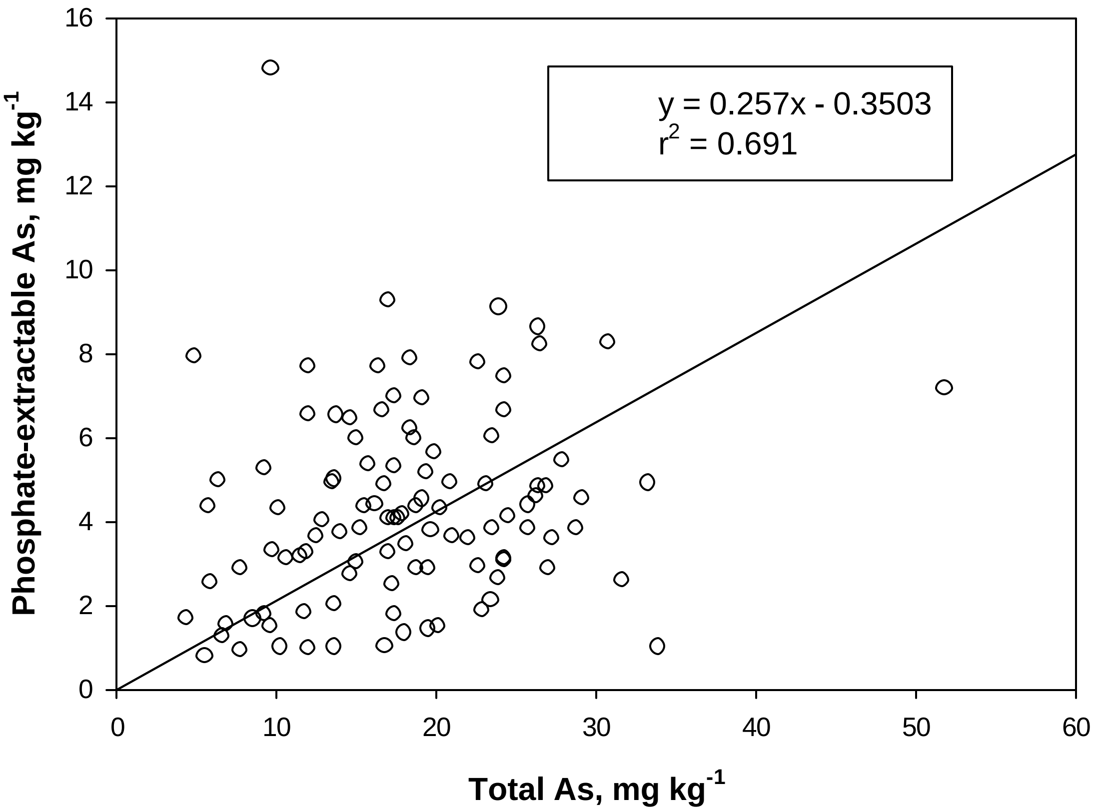

Figure 25. Relationship between phosphate-extractable arsenic and total arsenic of soils from Tala *thana*.

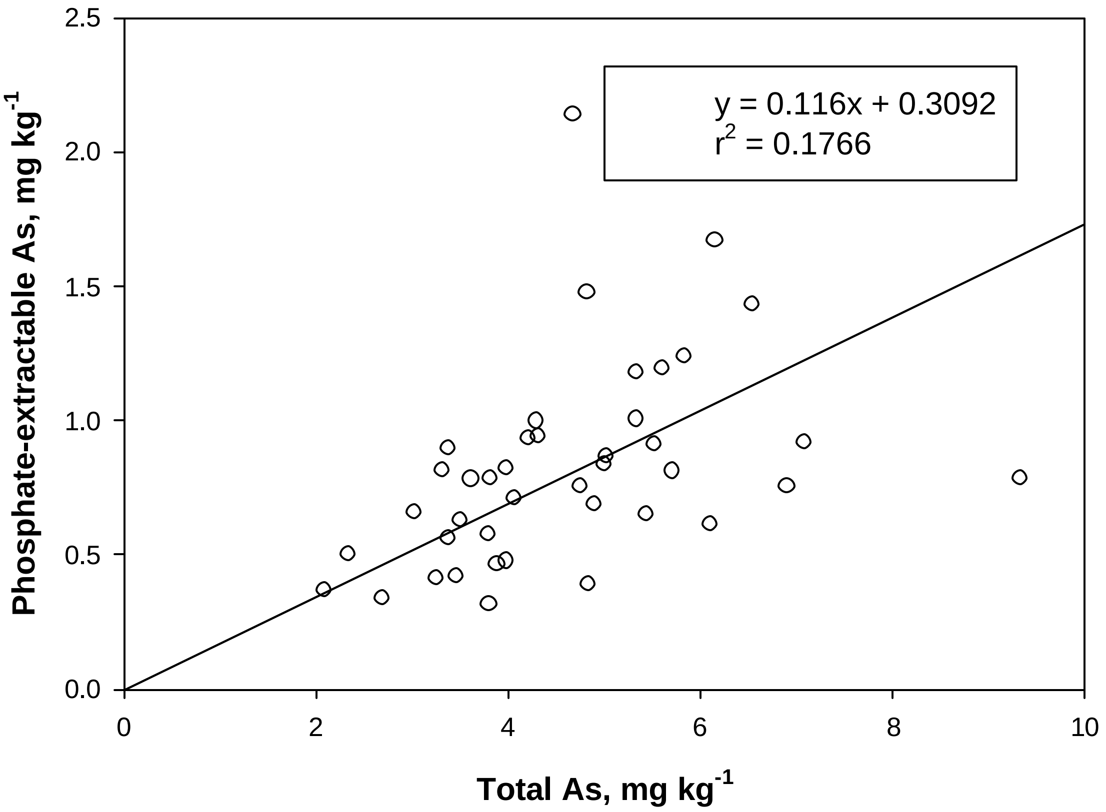

Figure 26. Relationship between phosphate-extractable arsenic and total arsenic of soils from Senbag *thana*.

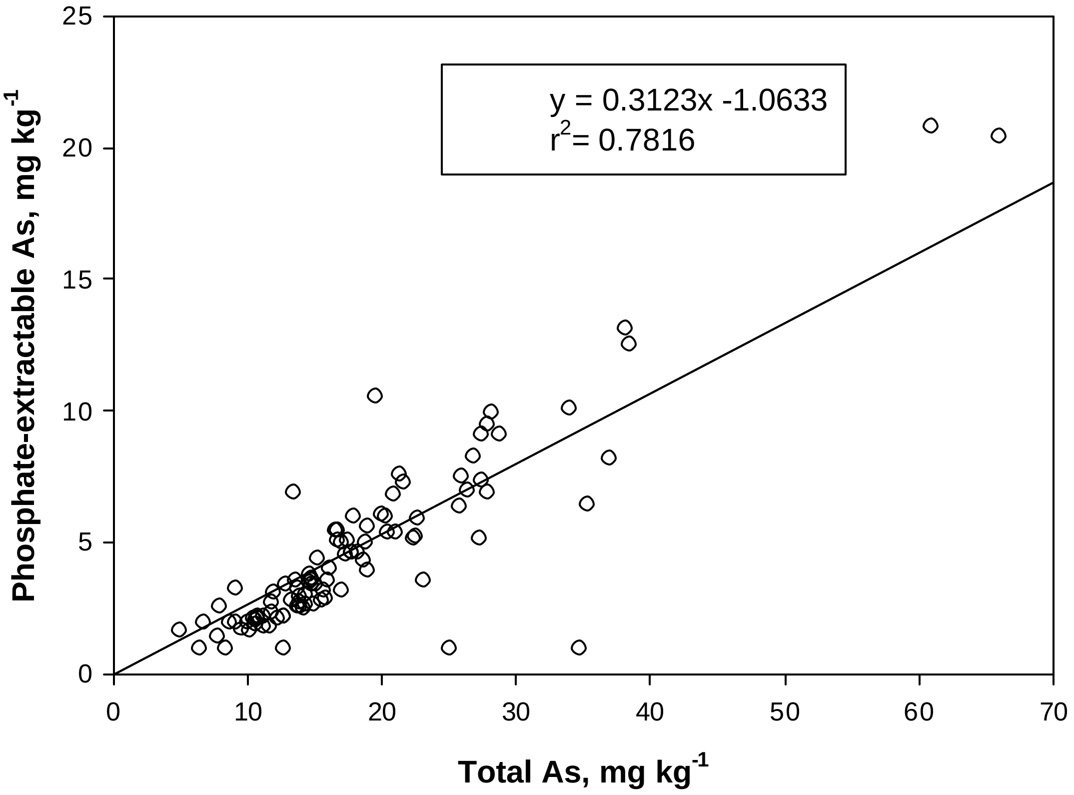

Figure 27. Relationship between phosphate-extractable arsenic and total arsenic of soils from Faridpur *thana*.

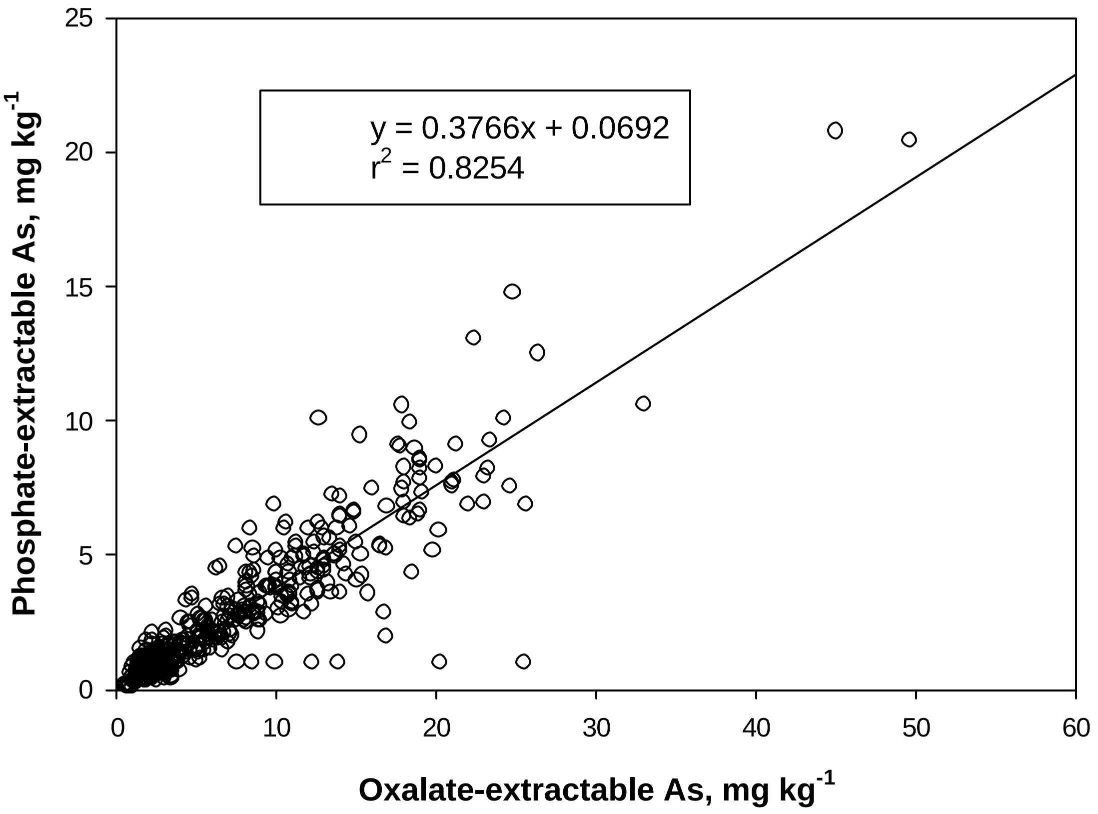

Figure 28. Relationship between phosphate-extractable arsenic and oxalate-extractable arsenic of soils from the five *thanas*.

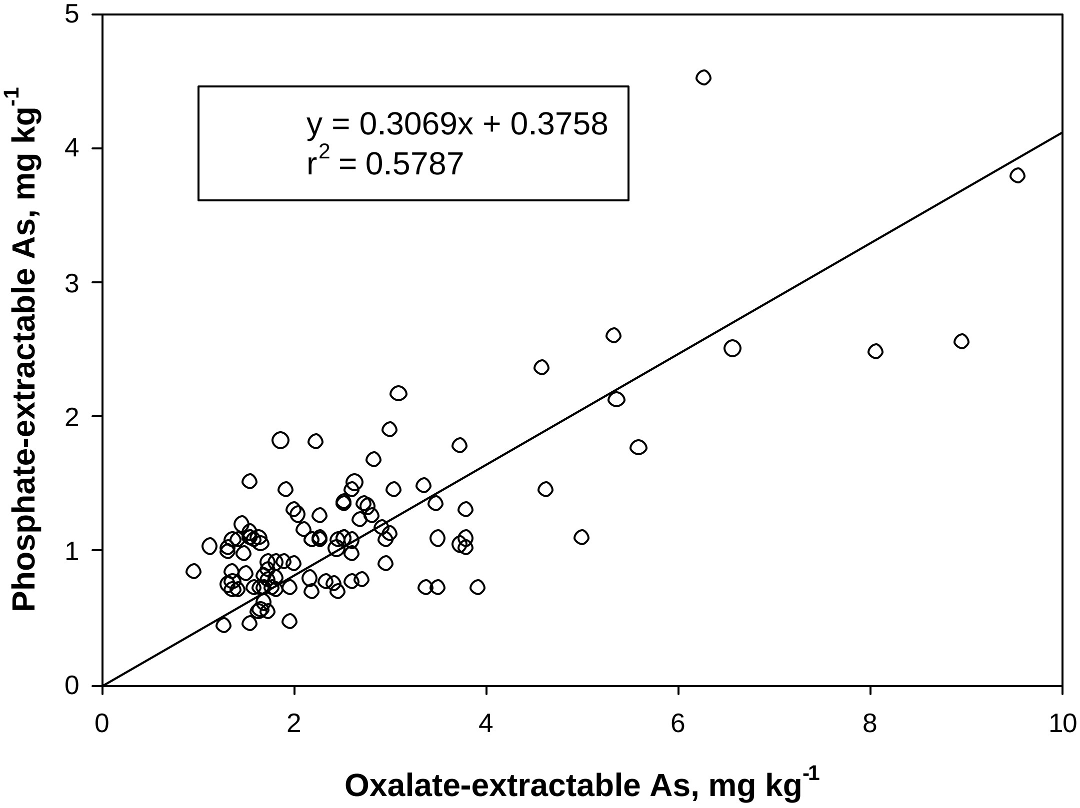

Figure 29. Relationship between phosphate-extractable arsenic and oxalate-extractable arsenic of soils from Paba *thana*.

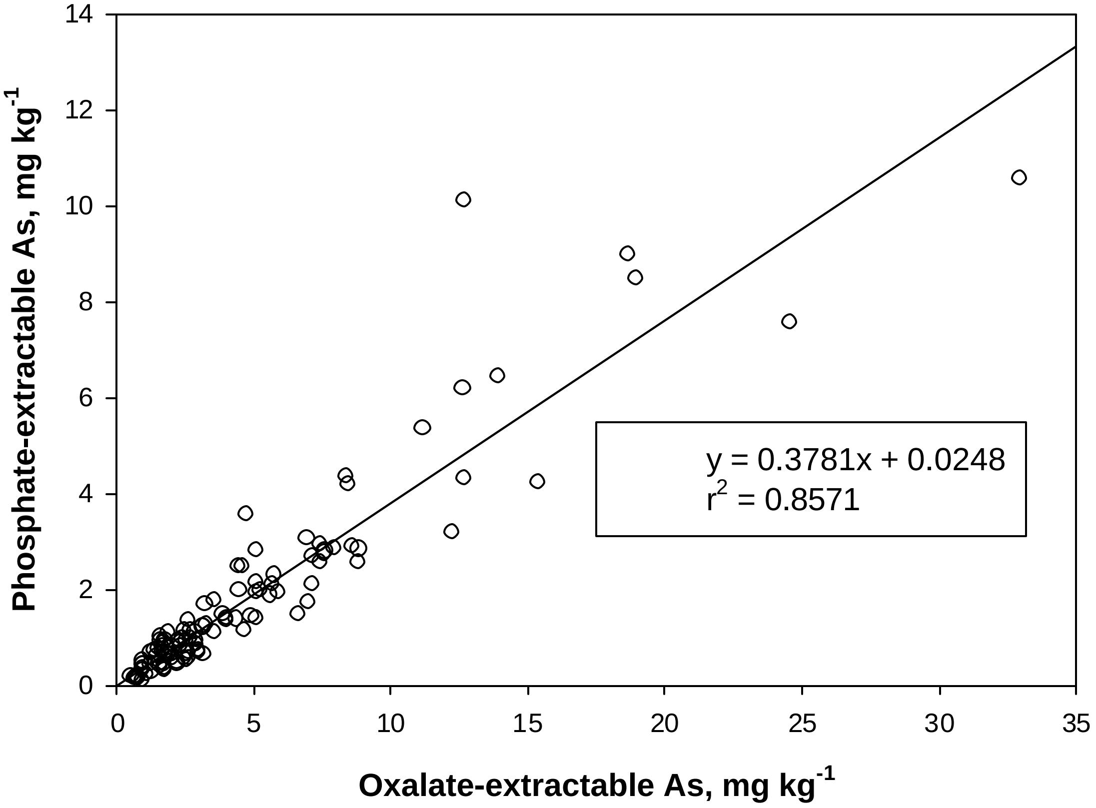

Figure 30. Relationship between phosphate-extractable arsenic and oxalate-extractable arsenic of soils from Brahmanbaria *thana*.

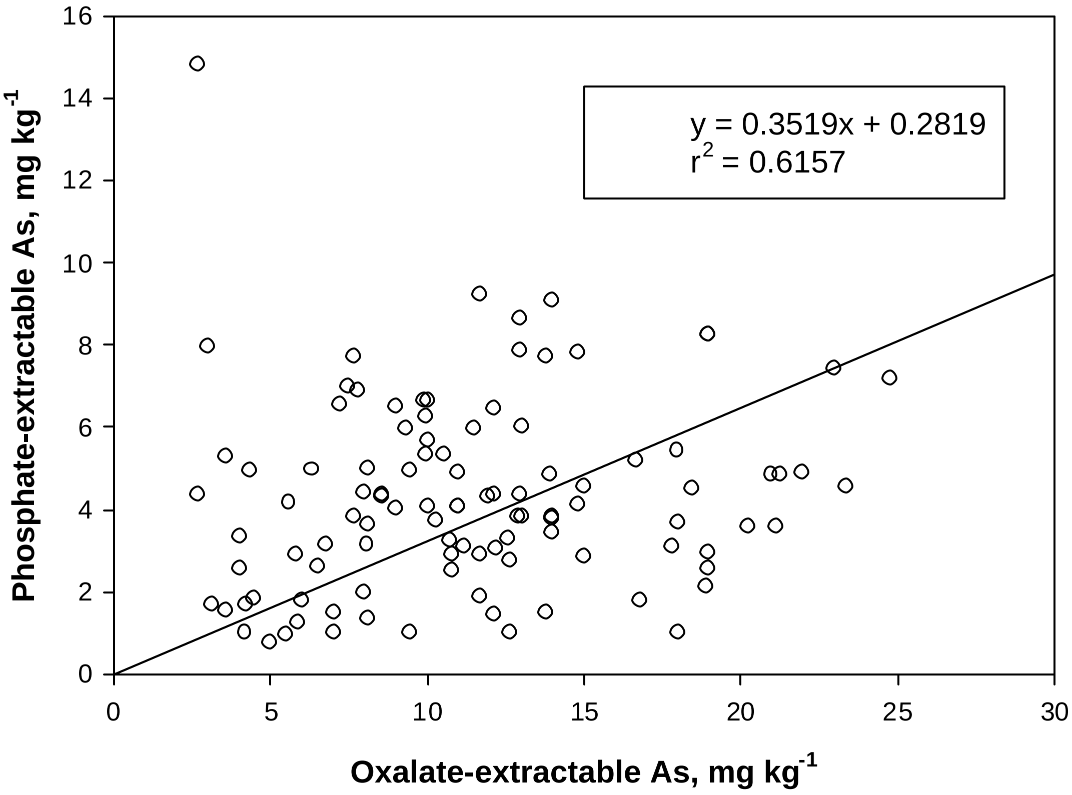

Figure 31. Relationship between phosphate-extractable arsenic and oxalate-extractable arsenic of soils from Tala *thana*.

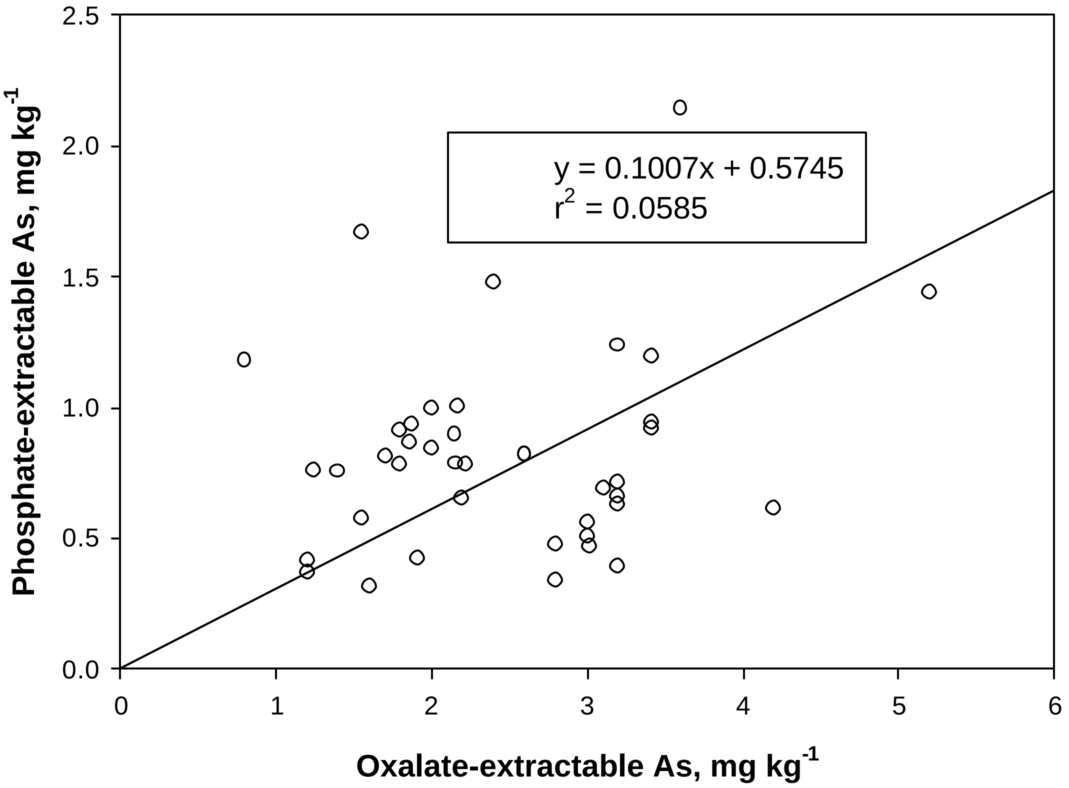

Figure 32. Relationship between phosphate-extractable arsenic and oxalate-extractable arsenic of soils from Senbag *thana*.

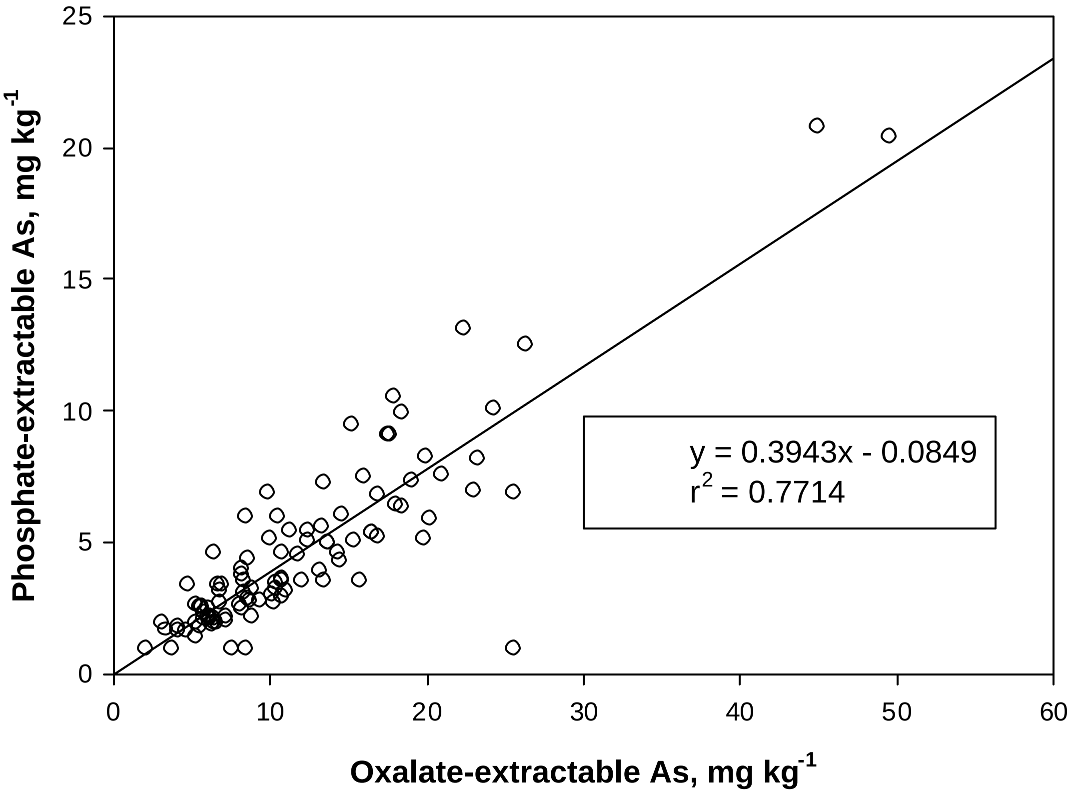

Figure 33. Relationship between phosphate-extractable arsenic and oxalate-extractable arsenic of soils from Faridpur *thana*.

RELATIONSHIP BETWEEN PHOSPHATE-EXTRACTABLE ARSENIC AND SOIL IRON PARAMETERS

Spearman's coefficients between phosphate-extractable arsenic and soil iron parameters are shown in Table 13. The results indicate that phosphate-extractable arsenic was correlated with total soil iron oxide and amorphous iron oxide contents in the Brahmanbaria and Faridpur *thanas*, but was either not correlated or very weakly correlated in the other *thanas*. Phosphate-extractable arsenic was significantly correlated with each soil iron parameter when data from the five *thanas* was considered together. In all cases, the correlation coefficients were relatively low (i.e., < 0.56) (Table 13). These results are indicative of the important role of soil iron oxide in arsenic retention. The relatively weak correlation coefficients are indicative of the complex source factors (e.g., arsenic content of the parent material, irrigation-water arsenic content, and sediment depositional patterns) and loss factors (e.g., leaching and volatilization) that contribute to arsenic balance. There was no significant correlation between proportion of phosphate-extractable arsenic to total arsenic and the any of soil iron parameters because values were negligible (Table 14).

Table 13. Spearman’s coefficients between phosphate-extractable arsenic and various iron parameters.

	Phosphate-extractable arsenic					
	Paba	Brahmanbaria	Tala	Senbag	Faridpur	Total
Total Soil Fe	0.204	0.252^{**}	0.182^{*}	0.098	0.072	0.502^{**}
Total Free Fe Oxide	0.023	0.350^{**}	0.081	0.237	0.306^{**}	0.553^{**}
Poorly Crystalline Fe Oxide	0.040	0.334^{**}	0.140^{*}	0.206	0.274^{**}	0.108^{*}
Well Crystalline Fe Oxide	-0.027	0.212^{*}	0.019	0.116	0.249^{*}	0.494^{**}
Layer-silicate Fe Oxide	0.201^{*}	0.195^{*}	0.186^{*}	0.062	-0.020	0.494^{**}

*, ** Correlation is significant at the 0.05 and 0.01 levels, respectively.

Table 14. Spearman’s coefficients between proportion of phosphate-extractable arsenic to total arsenic and different iron parameters.

	Proportion of phosphate-extractable arsenic compared to total arsenic					
	Paba	Brahmanbaria	Tala	Senbag	Faridpur	Total
Total Fe	-0.207^{*}	-0.004	-0.250^{*}	0.018	-0.177	-0.069
Total Free Fe Oxide	0.086	0.063	-0.247^{*}	-0.003	-0.080	0.070
Poorly Crystalline Fe Oxide	0.154	0.037	0.065	0.007	0.158	0.179^{**}
Well Crystalline Fe Oxide	0.003	0.020	-0.275^{**}	-0.017	-0.128	0.014
Layer-silicate Fe Oxide	-0.215^{*}	0.014	-0.136	0.092	-0.180	-0.090

*, ** Correlation is significant at the 0.05 and 0.01 levels, respectively.

CONCLUSIONS

The observations of the current study indicate the complexity and ambiguity of processes that contribute to arsenic extraction from soils by sodium phosphate. Arsenic extraction was strongly impacted by extraction variables, including sample grinding, phosphate concentration, principal counterion, reaction pH, and reaction time. Upon grinding, the quantity of arsenic desorption by phosphate decreased compared to that with the sieving treatment, and statistically significant differences between treatments were observed. These results upon grinding might be attributed to readsorption of desorbed arsenic on newly exposed sites that were created by the grinding treatment.

Arsenic extraction by phosphate was highly dependent on pH and initial counterion. The effectiveness of arsenic extraction by phosphate was lower with the Ca^{2+} system than with the Na^+ system over the entire pH range studied. In both the Ca^{2+} and Na^+ systems, the efficiency of arsenic extraction by phosphate was higher at extreme pH values (i.e., pH 1 and pH 13) and decreased towards intermediate pH values. The relationship between pH and the efficiency of arsenic extraction was strongly influenced by the charge characteristics of both the Fe oxide surface and the arsenic species. At high pH, the higher efficiency of arsenic extraction results from electrostatic repulsion between the negatively charged arsenic species (i.e., arsenate) and negatively charged oxide surfaces. Also, arsenic readsorption on oxide surfaces is less favorable due to increased OH^- concentration and increased competition for ligand-exchange sites. At the extreme low pH (i.e., pH 1), arsenate is fully protonated and positive charges are predominant on the Fe oxide sites (Mott, 1981). Consequently, there is less impact of electrostatic attraction on arsenic retention. Also, the rate of ligand exchange would be enhanced by protonation of oxygen at the Fe-O-As sites, resulting in reduced strength of arsenate bonding at the iron oxide surface. Desorption behavior of arsenic by phosphate in the Na^+ and Ca^{2+} counterion systems was similar at low pH; however, arsenic extraction in the Ca^{2+} system was considerably lower compared to the Na^+ system at high pH. These differences in arsenic desorption trends with low versus high valence counterion could be related to the diffuse electrical double layer (McBride, 1994). With the higher valence counterion, specifically adsorbed anions (e.g., arsenate) can be attracted to the surface more readily due to the more rapid decay in negative electrical potential with distance from the surface.

After an initially rapid arsenic desorption, the rate of arsenic extraction by phosphate decreased with either increasing reaction time or sequential extraction. Arsenic desorption did not follow first order reaction kinetics, which indicates that arsenic desorption rate was not directly dependent on the concentration of adsorbed arsenate. These results indicate possible differences in ease of accessibility of adsorption sites or different arsenic bonding strengths at different adsorption sites.

Arsenic-extraction efficiency by phosphate increased with increasing phosphate concentration; however, the total efficiency of arsenic extraction was less than 50 % with 1.5 M phosphate concentration. This result agrees with results of previous studies (e.g., Alam et al., 2001). The findings of the current study indicate that arsenic-desorption efficiency is highly dependent on initial phosphate concentration but that considerable arsenic is still retained in the presence of high phosphate concentration. These results suggest that competition between arsenic and phosphate is influenced by mass action and diffusion of phosphate concentration; however, desorption of arsenic from some adsorption sites occurs very slowly, even at high phosphate concentration. Also, some arsenic adsorption sites might not be readily accessible to phosphate.

Complete ligand exchange between phosphate and arsenic did not occur in any of the studies performed. The efficiency of arsenic desorption by pH 4, 0.1 M sodium phosphate was usually less than 30 % after the 24-h reaction time.

The low efficiency of arsenic extraction from soils by phosphate and the high variability between soils could be influenced by several factors, including soil mineralogy, variable accessibility of arsenic, bonding-site heterogeneity, bonding mechanism, and extraction kinetics. These studies indicate that low arsenic-extraction efficiency by phosphate could be attributed to both a slow kinetics of arsenic exchange and very strong retention of some arsenic at adsorption sites. Also, poor accessibility of arsenic, which might be trapped by soil aggregates, could also influence the low efficiency of arsenic extraction.

Statistical analysis of the approximately 500 surface soils from Bangladesh indicated that phosphate-extractable arsenic was positively correlated with total soil arsenic and oxalate (in the dark) extractable arsenic. Phosphate-extractable arsenic was highly variable both within and between *thana(s).* Phosphate-extractable arsenic was correlated with several soil iron-oxide parameters, including total free iron oxide content, indicating the importance of iron oxide in the retention of soil arsenic. Arsenic extraction efficiency was not correlated with any soil iron-oxide parameter.

Arsenic extraction by phosphate is not suited for the assessment of total soil arsenic, due to the relatively low extraction efficiencies, though the highest extraction efficiencies were obtained at the pH extremes, i.e., pH 1 and 13, and high phosphate concentration. Extraction by phosphate is suited for assessment of the portion of arsenic that is readily displaced by ligand exchange.

Further spectroscopic and spatial analytical studies will be required to more fully assess the bonding mechanisms that contribute to the readily exchangeable and poorly exchangeable arsenic components.

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APPENDIX

Total arsenic and phosphate extractable arsenic concentrations of Bangladesh soils.

Sample ID	Total As (mg kg^{-1})	Phosphate extractable As (mg kg^{-1})
Paba-1	6.600	1.084
Paba-2	6.304	1.300
Paba-3	6.927	0.918
Paba-4	5.749	1.347
Paba-5	6.608	0.981
Paba-6	6.757	1.679
Paba-7	4.469	1.455
Paba-8	9.040	1.049
Paba-9	4.979	1.087
Paba-10	5.450	1.325
Paba-11	3.977	1.174
Paba-12	4.784	1.088
Paba-13	3.162	1.014
Paba-14	3.350	0.800
Paba-15	5.842	1.072
Paba-16	5.943	0.727
Paba-17	2.893	0.557
Paba-18	3.740	0.691
Paba-19	4.450	1.017
Paba-20	3.362	1.018
Paba-21	8.756	1.082
Paba-22	8.353	1.026
Paba-23	8.659	1.353
Paba-24	8.845	1.308
Paba-25	8.591	1.085
Paba-26	9.654	1.089
Paba-27	11.276	1.504
Paba-28	8.542	1.090
Paba-29	7.296	0.435
Paba-30	4.438	0.543
Paba-31	3.843	0.611
Paba-32	8.734	1.816

Paba-33	8.978	1.351
Paba-35	7.822	2.169
Paba-36	7.412	1.896
Paba-37	5.410	1.130
Paba-38	8.629	1.458
Paba-39	9.974	1.084
Paba-40	9.185	0.903
Paba-41	8.112	1.453
Paba-42	3.750	0.784
Paba-43	9.383	1.090
Paba-44	9.723	0.810
Paba-46	4.310	0.843
Paba-47	6.907	0.823
Paba-48	3.350	0.862
Paba-49	7.380	0.772
Paba-50	7.631	1.267
Paba-51	6.399	0.743
Paba-52	5.397	0.835
Paba-54	6.504	0.706
Paba-55	6.580	1.192
Paba-56	6.243	0.972
Paba-57	4.780	0.450
Paba-58	5.441	0.471
Paba-59	4.616	0.726
Paba-60	5.976	0.543
Paba-61	4.246	0.788
Paba-62	6.814	1.085
Paba-63	7.581	0.765
Paba-64	7.753	0.710
Paba-65	8.973	0.989
Paba-66	5.254	0.723
Paba-67	6.796	0.908
Paba-68	5.430	0.726
Paba-69	7.025	1.512
Paba-70	5.821	0.723
Paba-71	5.140	0.908
Paba-72	7.514	1.091
Paba-73	5.626	0.725
Paba-74	4.409	0.720

Paba-75	4.991	1.081
Paba-76	12.426	2.476
Paba-77	12.595	2.560
Paba-78	6.936	1.767
Paba-79	6.992	1.086
Paba-80	6.470	1.222
Paba-81	6.185	1.085
Paba-82	6.004	0.722
Paba-83	10.491	2.501
Paba-84	17.750	4.519
Paba-85	11.408	3.793
Paba-86	6.000	0.697
Paba-87	10.338	2.362
Paba-88	4.755	0.757
Paba-89	5.543	1.089
Paba-90	9.408	1.803
Paba-91	7.246	1.042
Paba-92	7.864	2.124
Paba-93	5.970	0.903
Paba-94	7.823	1.264
Paba-95	3.802	1.155
Paba-96	8.626	1.776
Paba-97	17.446	2.601
Paba-98	7.437	1.486
Paba-99	11.033	1.081
Paba-100	8.076	1.261
Paba-101	8.383	0.703
Paba-102	6.745	1.087
Paba-103	7.150	1.446
Paba-104	8.233	1.360
Paba-105	6.002	0.760
Brahmanbaria-1	2.896	0.605
Brahmanbaria-2	2.985	0.934
Brahmanbaria-3	3.864	1.233
Brahmanbaria-4	5.020	2.490
Brahmanbaria-5	6.348	2.093
Brahmanbaria-6	10.099	2.837
Brahmanbaria-7	7.538	3.548
Brahmanbaria-8	8.553	2.691

Brahmanbaria-9	3.282	0.969
Brahmanbaria-10	4.440	1.208
Brahmanbaria-11	7.011	2.477
Brahmanbaria-12	3.970	1.763
Brahmanbaria-13	3.248	0.954
Brahmanbaria-14	5.520	1.258
Brahmanbaria-15	9.020	2.091
Brahmanbaria-16	7.722	2.552
Brahmanbaria-17	10.002	2.942
Brahmanbaria-18	2.913	0.538
Brahmanbaria-19	2.170	0.437
Brahmanbaria-20	2.316	0.360
Brahmanbaria-21	1.930	0.305
Brahmanbaria-22	7.640	1.876
Brahmanbaria-23	2.316	0.277
Brahmanbaria-24	1.544	0.360
Brahmanbaria-25	6.950	1.491
Brahmanbaria-26	3.245	0.665
Brahmanbaria-27	2.747	0.692
Brahmanbaria-28	4.253	1.121
Brahmanbaria-29	1.124	0.120
Brahmanbaria-30	1.932	0.885
Brahmanbaria-31	1.544	0.453
Brahmanbaria-32	1.246	0.501
Brahmanbaria-33	2.254	0.394
Brahmanbaria-34	2.571	0.437
Brahmanbaria-35	2.702	0.471
Brahmanbaria-36	6.690	1.988
Brahmanbaria-37	3.763	0.723
Brahmanbaria-38	3.474	0.637
Brahmanbaria-39	3.520	0.924
Brahmanbaria-40	3.084	0.662
Brahmanbaria-41	6.178	1.440
Brahmanbaria-42	7.249	1.147
Brahmanbaria-43	3.631	1.114
Brahmanbaria-44	2.736	0.627
Brahmanbaria-45	3.474	1.124
Brahmanbaria-46	3.282	1.164
Brahmanbaria-47	3.571	0.787

Brahmanbaria-48	3.768	0.908
Brahmanbaria-49	10.038	4.186
Brahmanbaria-50	2.316	0.439
Brahmanbaria-51	2.743	0.821
Brahmanbaria-52	8.243	1.921
Brahmanbaria-53	1.530	0.443
Brahmanbaria-54	1.367	0.152
Brahmanbaria-55	1.499	0.146
Brahmanbaria-56	3.840	1.380
Brahmanbaria-57	1.250	0.241
Brahmanbaria-58	1.158	0.139
Brahmanbaria-59	3.208	0.547
Brahmanbaria-60	4.634	0.554
Brahmanbaria-61	0.772	0.171
Brahmanbaria-62	1.250	0.194
Brahmanbaria-63	2.510	0.775
Brahmanbaria-64	1.760	0.326
Brahmanbaria-65	7.528	2.292
Brahmanbaria-66	10.232	2.902
Brahmanbaria-67	9.657	4.341
Brahmanbaria-68	4.440	1.466
Brahmanbaria-69	3.282	0.968
Brahmanbaria-70	6.690	1.394
Brahmanbaria-71	2.252	0.671
Brahmanbaria-72	3.474	0.923
Brahmanbaria-73	5.830	0.680
Brahmanbaria-74	2.051	0.687
Brahmanbaria-75	2.913	0.944
Brahmanbaria-76	4.248	1.361
Brahmanbaria-77	2.624	0.678
Brahmanbaria-78	6.493	1.351
Brahmanbaria-79	2.510	0.652
Brahmanbaira-80	16.520	6.435
Brahmanbaria-81	8.688	3.055
Brahmanbaria-82	12.720	2.840
Brahmanbaria-83	10.810	2.559
Brahmanbaria-84	23.660	8.496
Brahmanbaria-85	38.500	10.580
Brahmanbaria-86	8.309	2.749

Brahmanbaria-87	15.250	5.346
Brahmanbaria-88	16.550	4.236
Brahmanbaria-89	5.996	1.927
Brahmanbaria-90	9.437	2.642
Brahmanbaria-91	15.051	4.331
Brahmanbaria-92	6.756	1.408
Brahmanbaria-93	28.958	10.103
Brahmanbaria-94	9.408	2.814
Brahmanbaria-95	8.042	2.156
Brahmanbaria-96	26.610	6.201
Brahmanbaria-97	8.258	1.694
Brahmanbaria-98	15.460	3.173
Brahmanbaria-99	4.080	0.867
Brahmanbaria-100	25.130	7.560
Brahmanbaria-101	2.120	1.007
Brahmanbaria-102	3.010	0.817
Brahmanbaria-103	6.760	1.977
Brahmanbaria-104	9.269	2.792
Brahmanbaria-105	9.492	1.719
Brahmanbaria-106	6.420	1.143
Brahmanbaria-107	2.397	0.565
Brahmanbaria-108	3.282	0.725
Brahmanbaria-109	3.995	0.598
Brahmanbaria-110	2.702	0.435
Tala-1	17.389	4.065
Tala-2	17.549	3.841
Tala-3	23.455	5.341
Tala-4	15.752	4.356
Tala-5	18.718	4.579
Tala-6	26.255	5.443
Tala-7	27.882	8.265
Tala-8	30.693	8.235
Tala-9	26.468	7.870
Tala-10	18.329	4.831
Tala-11	26.382	7.709
Tala-12	16.300	6.011
Tala-13	23.483	4.404
Tala-14	16.153	3.078
Tala-15	24.220	7.446

Tala-16	24.211	7.953
Tala-17	4.838	0.779
Tala-18	5.542	1.511
Tala-19	9.641	2.586
Tala-20	31.616	8.626
Tala-21	26.317	4.877
Tala-22	16.701	4.907
Tala-23	33.197	6.913
Tala-24	19.146	2.948
Tala-25	22.601	6.653
Tala-26	24.197	3.827
Tala-27	25.750	5.664
Tala-28	19.803	3.773
Tala-29	19.652	5.172
Tala-30	19.380	2.874
Tala-31	18.722	4.069
Tala-32	17.016	3.261
Tala-33	11.840	3.443
Tala-34	18.118	3.588
Tala-35	22.010	0.996
Tala-36	11.988	1.778
Tala-37	17.300	2.005
Tala-38	13.627	2.566
Tala-39	5.854	1.772
Tala-40	9.250	1.827
Tala-41	11.716	2.521
Tala-42	17.223	4.351
Tala-43	15.492	4.948
Tala-44	20.870	4.845
Tala-45	26.853	7.177
Tala-46	51.786	14.804
Tala-47	9.650	1.337
Tala-48	17.969	4.365
Tala-49	5.679	1.030
Tala-50	16.799	3.726
Tala-51	13.950	4.870
Tala-52	23.130	9.104
Tala-53	23.910	6.473
Tala-54	14.564	4.294

Tala-55	10.143	5.273
Tala-56	9.255	1.248
Tala-57	6.582	1.543
Tala-58	6.796	1.709
Tala-59	4.302	0.939
Tala-60	7.754	1.428
Tala-61	19.497	4.122
Tala-62	24.420	6.569
Tala-63	11.950	3.033
Tala-64	14.930	1.002
Tala-65	13.635	3.828
Tala-66	15.265	3.277
Tala-67	16.993	3.649
Tala-68	12.474	2.899
Tala-69	26.938	4.973
Tala-70	6.360	1.894
Tala-71	22.825	2.889
Tala-72	19.470	4.034
Tala-73	12.867	3.125
Tala-74	10.614	2.109
Tala-75	23.422	6.524
Tala-76	13.749	3.587
Tala-77	27.236	7.797
Tala-78	22.592	6.655
Tala-79	16.567	1.001
Tala-80	33.885	7.703
Tala-81	11.983	2.756
Tala-82	14.561	4.521
Tala-83	19.108	4.383
Tala-84	25.668	4.555
Tala-85	29.109	9.251
Tala-86	17.003	5.006
Tala-87	13.619	3.658
Tala-88	20.991	6.971
Tala-89	17.371	5.324
Tala-90	17.378	6.238
Tala-91	18.333	4.324
Tala-92	20.203	5.991
Tala-93	14.962	3.845

Tala-94	28.710	5.989
Tala-95	18.606	4.164
Tala-96	17.797	3.120
Tala-97	24.211	4.946
Tala-98	13.416	3.320
Tala-99	9.722	2.637
Tala-100	23.810	3.166
Tala-101	11.459	2.892
Tala-102	7.730	1.514
Tala-103	20.120	0.998
Tala-104	10.266	1.664
Tala-105	8.520	1.786
Senbag-1	5.000	0.840
Senbag-2	4.290	0.998
Senbag-3	3.805	0.783
Senbag-4	3.025	0.660
Senbag-5	3.975	0.821
Senbag-6	3.367	0.899
Senbag-7	2.329	0.506
Senbag-8	4.749	0.755
Senbag-9	4.822	1.476
Senbag-10	4.673	2.142
Senbag-11	5.443	0.650
Senbag-12	3.490	0.628
Senbag-13	5.322	1.180
Senbag-14	6.530	1.436
Senbag-15	3.884	0.468
Senbag-16	3.252	0.416
Senbag-17	3.800	0.314
Senbag-18	3.612	0.782
Senbag-19	4.060	0.710
Senbag-20	5.833	1.237
Senbag-21	6.100	0.612
Senbag-22	4.200	0.936
Senbag-23	9.334	0.786
Senbag-24	3.310	0.818
Senbag-25	5.520	0.912
Senbag-26	5.705	0.811
Senbag-27	4.823	0.391

Senbag-28	3.375	0.561
Senbag-29	6.902	0.756
Senbag-30	6.153	1.670
Senbag-31	5.323	1.006
Senbag-32	5.012	0.868
Senbag-33	4.313	0.944
Senbag-34	3.974	0.477
Senbag-35	5.595	1.196
Senbag-36	3.796	0.575
Senbag-37	4.900	0.691
Senbag-38	3.462	0.422
Senbag-39	7.085	0.923
Senbag-40	2.680	0.338
Senbag-41	2.080	0.367
Faridpur-1	20.266	6.020
Faridpur-2	27.351	9.075
Faridpur-3	14.555	3.802
Faridpur-4	10.757	2.102
Faridpur-5	38.401	12.503
Faridpur-6	25.995	7.485
Faridpur-7	28.730	9.102
Faridpur-8	20.934	5.346
Faridpur-9	16.553	5.450
Faridpur-10	8.654	1.945
Faridpur-11	28.229	9.969
Faridpur-12	9.583	1.689
Faridpur-13	25.100	1.003
Faridpur-14	11.760	2.339
Faridpur-15	14.786	3.536
Faridpur-16	21.251	7.594
Faridpur-17	14.322	2.606
Faridpur-18	22.675	5.926
Faridpur-19	33.966	10.119
Faridpur-20	38.172	13.090
Faridpur-21	60.883	20.770
Faridpur-22	14.803	3.582
Faridpur-23	13.787	3.262
Faridpur-24	27.355	7.353
Faridpur-25	66.003	20.431

Faridpur-26	35.299	6.466
Faridpur-27	36.947	8.201
Faridpur-28	19.468	10.577
Faridpur-29	4.981	1.651
Faridpur-30	7.833	2.532
Faridpur-31	12.818	3.425
Faridpur-32	17.912	5.985
Faridpur-33	14.774	3.388
Faridpur-34	14.252	3.020
Faridpur-35	27.330	5.174
Faridpur-36	22.339	5.178
Faridpur-37	22.513	5.238
Faridpur-38	11.150	1.788
Faridpur-39	21.550	7.269
Faridpur-40	19.990	6.050
Faridpur-41	13.824	2.522
Faripdur-42	15.167	4.404
Faridpur-43	18.603	4.288
Faridpur-44	18.711	5.024
Faridpur-45	16.966	3.190
Faridpur-46	13.631	3.540
Faridpur-47	10.552	2.009
Faridpur-48	17.751	4.599
Faridpur-49	12.630	1.001
Faridpur-50	18.148	4.624
Faridpur-51	17.478	5.042
Faridpur-52	9.070	1.930
Faridpur-53	7.696	1.463
Faridpur-54	15.089	3.407
Faridpur-55	16.066	4.009
Faridpur-56	18.966	5.636
Faridpur-57	11.803	2.745
Faridpur-58	11.121	2.163
Faridpur-59	16.997	4.979
Faridpur-60	27.850	9.461
Faridpur-61	6.685	1.922
Faridpur-62	26.392	6.949
Faridpur-63	20.903	6.785
Faridpur-64	11.983	3.062

Faridpur-65	12.686	2.164
Faridpur-66	9.060	3.240
Faridpur-67	13.864	2.953
Faripdur-68	27.928	6.895
Faridpur-69	13.402	6.901
Faridpur-70	26.788	8.291
Faridpur-71	34.780	0.995
Faridpur-72	8.340	1.003
Faridpur-73	14.137	2.475
Faridpur-74	14.560	3.486
Faridpur-75	12.291	2.087
Faridpur-76	17.718	4.640
Faridpur-77	14.697	3.638
Faridpur-78	9.984	1.966
Faridpur-79	6.450	1.003
Faridpur-80	10.161	1.682
Faridpur-81	15.590	3.161
Faridpur-82	12.717	2.150
Faridpur-83	15.867	2.882
Faridpur-84	10.725	2.195
Faridpur-85	15.444	2.802
Faridpur-86	11.581	1.842
Faridpur-87	14.863	2.671
Faridpur-88	10.586	1.909
Faridpur-89	13.723	2.535
Faridpur-90	13.262	2.821
Faridpur-91	23.161	3.568
Faridpur-92	17.289	4.522
Faridpur-93	25.735	6.388
Faridpur-94	18.869	3.943
Faridpur-95	13.843	2.711
Faridpur-96	20.445	5.360
Faridpur-97	15.981	3.564
Faridpur-98	16.711	5.087
Faridpur-99	10.427	2.110
Faridpur-100	16.738	5.457

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Su Jin Yean received her B.S. in environmental engineering from Chungnam National University in the Republic of Korea, in February 2001. After graduation, she worked as a teaching assistant at Chungnam National University in environmental physics to undergraduates before she enrolled at Texas A&M University. She received her M.S. in Soil Science from Texas A&M University in College Station, Texas, in August 2004. In August 2004, she will start her Ph. D studies in civil and environmental engineering at Rice University in Houston, Texas. During her experiences at Texas A&M, she taught undergraduate “Introduction to Soil Science” during fall 2003 and spring 2004 and presented her thesis research poster at ASA-CSSA-SSSA annual meetings in Denver, CO, 2003.

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