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Sorption and Redox Transformation of Arsenite and Arsenate in Two Flooded Soils

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ABSTRACT

The fate of As in soils is regulated mostly by its participation in sorption reactions and redox transformations. Few studies have examined the rate of arsenite and arsenate reduction or the extent to which these redox transformations may be affected by sorption reactions. The objective of this study was to examine changes in solution concentrations of $H_3AsO_3^0$ and $H_2AsO_4^-$ in two soils subjected to prolonged flooding. The soils, which differed in $H_3AsO_3^0$ and $H_2AsO_4^-$ sorption capacities, were flooded by suspending 1 g of soil in 25 mL of a solution containing 0.01 *M* $CaCl_2$ and 1 g D-glucose kg^{-1}. The suspensions were amended with $NaAsO_2$ or $Na_2HAsO_4 \cdot 7H_2O$ and were incubated for 0.5 h to 20 d. Changes in solution chemistry (electrode potential [Eh], pH, and dissolved Fe, Mn, $H_3AsO_3^0$, and $H_2AsO_4^-$) were observed with time. Sorption processes controlled the dissolved concentrations of $H_3AsO_3^0$ and $H_2AsO_4^-$ during initial stages of flooding. When anaerobic conditions were achieved, dissolution of Fe and Mn oxyhydroxides occurred, causing desorption of $H_3AsO_3^0$ and $H_2AsO_4^-$. In $NaAsO_2$-amended suspensions, desorbed $H_3AsO_3^0$ disappeared from solution within 10 d. In $Na_2HaSO_4^-$-amended suspensions, desorbed $H_2AsO_4^-$ also disappeared within 10 d. Concurrent with the disappearance of $H_2AsO_4^-$ was the appearance of $H_3AsO_3^0$, indicating that $H_2AsO_4^-$ was rapidly reduced to $H_3AsO_3^0$. First-order plots of $H_3AsO_3^0$ and $H_2AsO_4^-$ disappearance had a linear relationship. Rates of desorption and disappearance of $H_3AsO_3^0$ and $H_2AsO_4^-$ were slower in the soil with higher adsorption capacity, suggesting that sorption processes may influence redox transformations of As oxyanions.

THE BIOAVAILABILITY, toxicity, and mobility of As in soil-water systems is determined largely by its speciation. Metallic As [As(O)], arsine [As(-III)], and methylated forms of As are thermodynamically stable in reduced systems, whereas $H_2AsO_4^-$ [As(V)] and $H_3AsO_3^0$ [As(III)] predominate in oxidized systems (Ferguson and Gavis, 1972). The oxyanions of As also exhibit various degrees of protonation and valence charge, depending on pH.

The solution concentration of $H_2AsO_4^-$ in soil is controlled primarily by adsorption reactions on oxides and hydroxides of Al (Anderson et al., 1975; Huang, 1975), Fe (Pierce and Moore, 1982; Belzile and Tessier, 1990), and Mn (Oscarson et al., 1983). Arsenite undergoes similar adsorption reactions, although usually of lower magnitude, to those of $H_2AsO_4^-$ (Pierce and Moore, 1982; Oscarson et al., 1983). Adsorption of both oxyanions occurs primarily via a specific adsorption (ligand exchange) mechanism (Parfitt, 1978; Huang, 1980). Nonspecific adsorption (electrostatic attraction) of As also occurs but is limited to pH-dependent charged surfaces at pH values below the zero-point-of-charge for a given adsorbent (Huang, 1980).

Transformation between the various oxidation states and species of As may occur as a result of biotic or abiotic processes. Bacterial oxidation of $H_3AsO_3^0$ to $H_2AsO_4^-$ has been observed in mine waters, arsenical cattle-dipping fluids, and raw sewage (Turner, 1954; Phillips and Taylor, 1976; Wakao et al., 1988). $H_3AsO_3^0$ was readily oxidized to $H_2AsO_4^-$ in aquatic sediments via an abiotic mechanism (Oscarson et al., 1980). It was later shown that this oxidation was catalyzed by Mn dioxides present in the sediments (Oscarson et al., 1983; Moore et al., 1990). Biotic reduction of $H_2AsO_4^-$ has been observed in groundwater (Cherry et al., 1979), aquatic sediments (Aggett and O'Brien, 1985; Andreae, 1979), activated sewage sludge (Myers et al., 1973), and soils (Cheng and Focht, 1979). $H_3AsO_3^0$ and $H_2AsO_4^-$ may also undergo biomethylation to form cacodylic acid [$(CH_3)_2HAsO_2$], which can be reduced to dimethylarsine [$(CH_3)_2HAs$] or trimethylarsine [$(CH_3)_3As$] (Braman, 1975; Woolson, 1977).

Few studies have examined the rate of $H_3AsO_3^0$ and $H_2AsO_4^-$ reduction or the extent to which these redox transformations may be affected by sorption reactions. The objective of this study was to examine the changes in solution concentrations of $H_3AsO_3^0$ and $H_2AsO_4^-$ in two soils subjected to prolonged flooding.

MATERIALS AND METHODS

The surface mineral horizons of the Santa (coarse-silty, mixed, frigid Typic Fragiochrept) and Huckleberry (medial

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Table 1. Selected chemical properties of Santa and Huckleberry silt loam soils.

Soil	pH†	Organic C‡	Extractable¶ Al	Fe	Mn	Si
		$g\ kg^{-1}$				
Santa	6.1	20.0	1.0	2.8	0.3	0.2
Huckleberry	6.5	18.0	10.5	4.3	0.2	4.1

† Saturated water paste.
‡ Combustion method (CHN Analyzer, LECO Corp., St. Joseph, MI).
¶ Acid ammonium oxalate (Jackson et al., 1986).

over loamy-skeletal, mixed Entic Cryandept) silt loam soils were used in this study (Table 1). Soils were flooded by suspending 1 g of soil in 25 mL of a solution containing 0.01 *M* $CaCl_2$ and 1 g D-glucose kg^{-1} contained in 50-mL polypropylene centrifuge tubes. The suspensions were amended with microliter volumes of $NaAsO_2$ or $Na_2HAsO_4 \cdot 7H_2O$ to yield the desired initial As concentrations. An earlier study (McGeehan et al., 1992) showed that initial concentrations of 10 mg L^{-1} H_3AsO_3–As or H_2AsO_4–As were necessary to maintain at least 1 mg soluble As L^{-1} in the Santa suspensions. Initial concentrations of 10 mg H_3AsO_3–As L^{-1} and 70 mg H_2AsO_4–As L^{-1} were required for the Huckleberry suspensions. The suspensions were tightly capped and incubated at 295 ± 1 K with daily shaking. Incubation periods ranged from 0.5 h to 20 d. Following incubation, suspension pH was recorded using a glass combination pH electrode. A direct electrode potential (Eh) was determined using a combination Pt electrode with a Ag/AgCl reference electrode (Corning Glass Works, Corning, NY). The Pt electrode was placed in direct contact with the flooded soil, and the potential was recorded (in millivolts) after a stable reading was obtained (usually <30 s). The true Eh was calculated by adding 202 mV to the measured potential to correct for the potential of the reference electrode (Cox and O'Reilly, 1986). Because the electrode was not calibrated, the electrode reliability was checked weekly by comparing the electrode potential of a solution containing 0.1 *M* potassium ferrocyanide [$K_4Fe(CN)_6 \cdot 3H_2O$] and 0.05 *M* potassium ferricyanide [$K_3Fe(CN)_6$] to that of a solution containing 0.01 *M* $K_4Fe(CN)_6 \cdot 3H_2O$, 0.05 *M* $K_3Fe(CN)_6$, and 0.36 *M* $KF \cdot 2H_2O$ (Orion, 1983). The headspace of each sample was purged with O_2-free N_2 gas during Eh measurements. The redox parameter, pe, was calculated using the following equation:

$$pe = Eh(mV)/59.2$$

and the pe + pH parameter (Lindsay, 1979) was used to define the overall redox status. The suspensions were centrifuged at 3410 × *g* for 15 min, and the supernatant solutions passed through a 0.45-μm filter (Gelman Supor-450, Gelman Science, Ann Arbor, MI). An aliquot of the filtered solution was acidified to pH 2 with concentrated HCl and analyzed for Fe and Mn by flame atomic absorption spectroscopy. Nonacidified samples were analyzed simultaneously for $H_3AsO_3^0$ and $H_2AsO_4^-$ by suppressed ion chromatography (McGeehan and Naylor, 1992). All experiments were conducted in triplicate. In some cases, the mean dissolved $H_3AsO_3^0$ and $H_2AsO_4^-$ concentrations were compared using Fisher's least significant difference procedure (Steel and Torrie, 1980).

RESULTS AND DISCUSSION

The pe + pH redox parameter declined rapidly during the first 2 d of the flooding period, eventually reaching a plateau near 2 (Fig. 1). The decline in pe + pH reflected concurrent decreases in Eh, which reached a minimum steady-state value near −200 mV, and in pH, which declined from 6.3 to 4.8 in the Santa suspensions and from 6.5 to 4.8 in the Huckleberry suspensions. A relatively rapid decline in pH (≈0.5 units during the first 2 h) resulted from the release of salt-replaceable acidity in the 0.01 *M* $CaCl_2$ suspensions. The more gradual acidification, from pH 6.0 to 4.8, observed during the entire flooding period is attributed to CO_2 release from microbial respiration. The trend in pe + pH was similar in both soils and was not influenced by added As species.

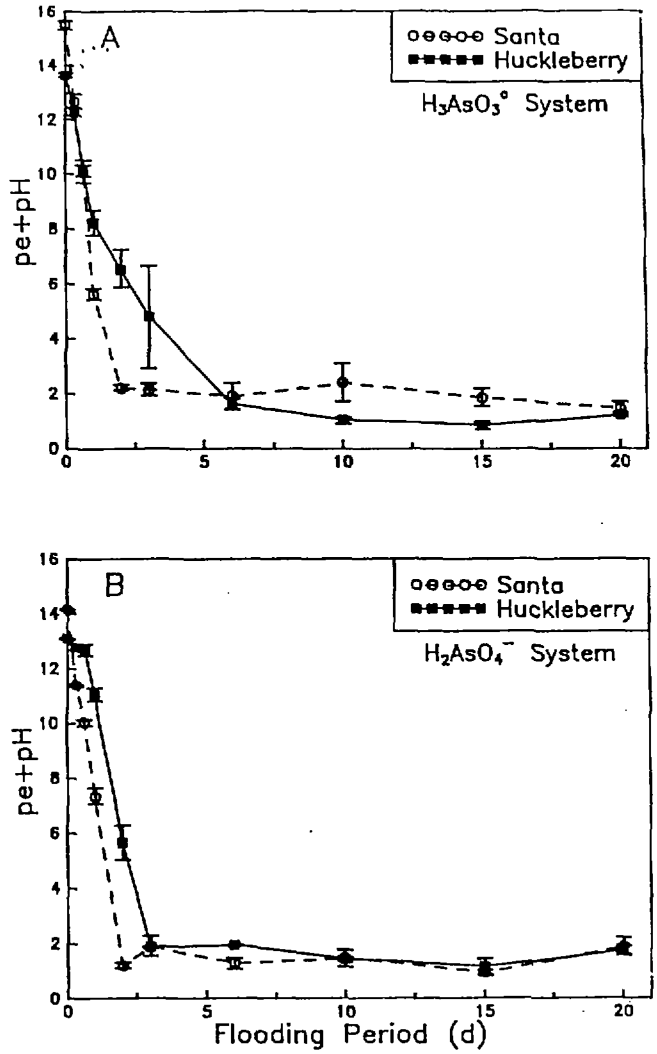

Fig. 1. Changes in the pe + pH redox parameter in response to soil flooding in (A) $NaAsO_2$- and (B) Na_2HAsO_4-amended suspensions of Santa and Huckleberry soils. Vertical bars represent one standard error.

The dissolved Fe concentrations at 0.5 h averaged 0.13 mg Fe L^{-1} for the Santa and 0.23 mg Fe L^{-1} for the Huckleberry suspensions (Fig. 2). Average Mn values at 0.5 h of flooding were 1.1 mg Mn L^{-1} in the Santa suspension and 0.9 mg Mn L^{-1} in the Huckleberry suspension (Fig. 3). Solution concentrations of both Fe and Mn increased slowly during the first 24 h but began to increase rapidly within 48 to 96 h. This change in

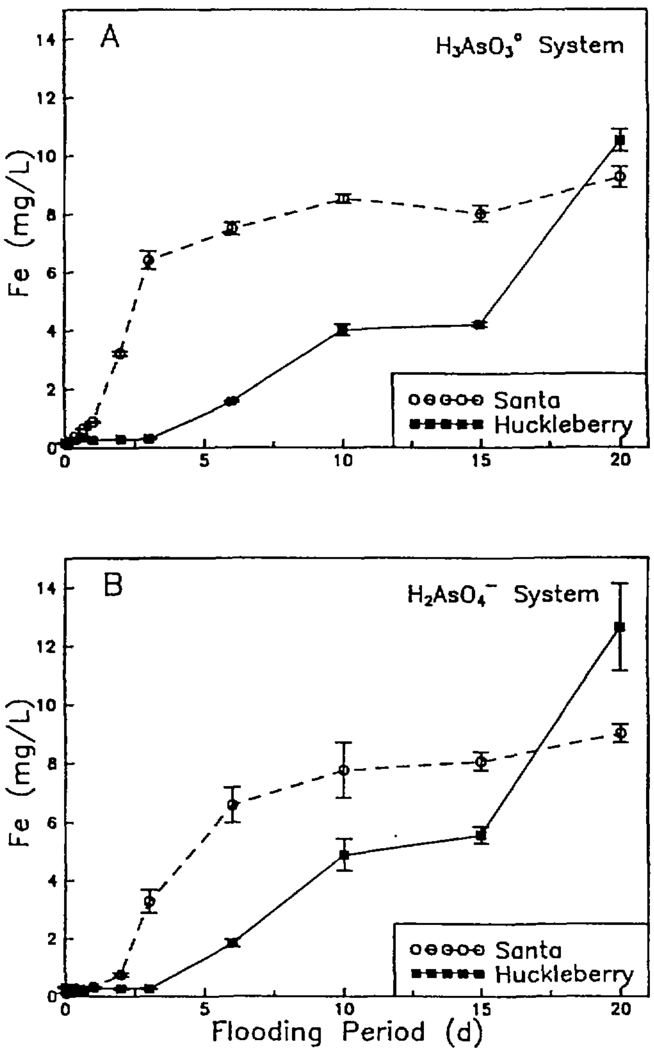

Fig. 2. Changes in dissolved Fe concentration in response to soil flooding in (A) $NaAsO_2$- and (B) Na_2HAsO_4-amended suspensions of Santa and Huckleberry soils. Vertical bars represent one standard error.

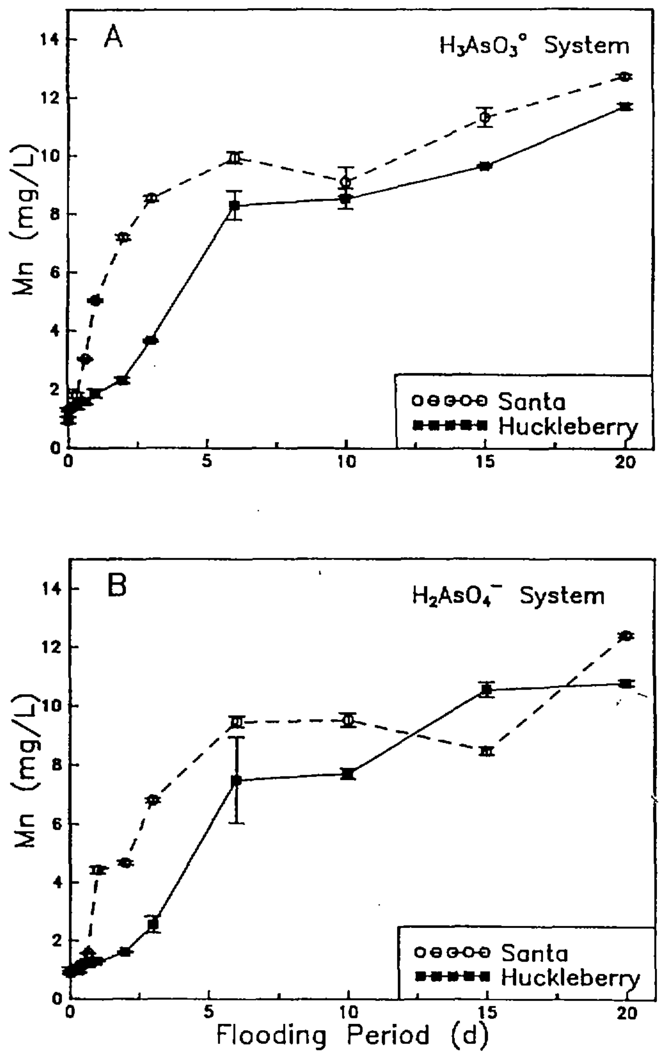

Fig. 3. Changes in dissolved Mn concentration in response to soil flooding in (A) $NaAsO_2$- and (B) Na_2HAsO_4-amended suspensions of Santa and Huckleberry soils. Vertical bars represent one standard error.

dissolution rate corresponded to attainment of anaerobic conditions (Eh < 0 mV) in the soil suspensions. The rate change for Mn occurred approximately 24 h earlier than for Fe, reflecting the higher reduction potential of the Mn(IV)/Mn(II) redox couple (Hunsberger, 1974). Both Fe and Mn concentrations increased throughout the flooding period, reaching values of ≈ 10 mg Fe L^{-1} and 12 mg Mn L^{-1} in each suspension at 20 d. The added $NaAsO_2$ and Na_2HAsO_4 did not influence Fe or Mn solubility.

Dissolved Arsenic in Arsenite-Amended Suspensions

Dissolved $H_3AsO_3^0$ declined during the first 8 h of flooding from 10 to 4.3 mg As L^{-1} in the Santa suspensions and to 1.2 mg As L^{-1} in the Huckleberry suspensions (Fig. 4). A previous study of As sorption rates showed that $H_3AsO_3^0$ reached a sorption plateau within 8 h with consequent steady-state dissolved concentrations of 6.3 mg As L^{-1} in the Santa and 3.2 mg As L^{-1} in the Huckleberry suspensions (McGeehan et al., 1992). Despite the somewhat lower solution concentration of $H_3AsO_3^0$ observed in this study, it is likely that sorption was controlling dissolved concentration of $H_3AsO_3^0$ in both suspensions during the first 8 h of flooding.

Dissolved $H_3AsO_3^0$ declined further in the Santa suspension through the second day of flooding but increased in all replicates by the third day. Statistical comparison of dissolved $H_3AsO_3^0$ concentrations from the second day (the minimum concentration resulting from sorption) and the third day (the maximum concentration following desorption) showed this increase to be significant (P = 0.011). A second maximum was also observed in the Huckleberry suspension, although it was not observed until the sixth day of flooding. Comparison of dissolved $H_3AsO_3^0$ concentrations in the Huckleberry suspensions from 0.66 d (the minimum concentration resulting from sorption) and 6 d (the maximum concentration following desorption) showed this increase to be significant (P = 0.003). Dissolved $H_2AsO_4^-$ was not detected in any of the

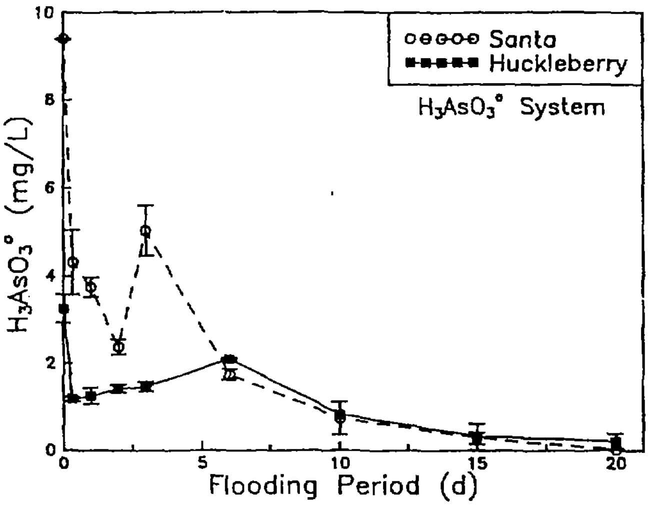

Fig. 4. Changes in dissolved $H_3AsO_3^0$ concentration in response to soil flooding in $NaAsO_2$-amended suspensions of Santa and Huckleberry soils. Initial $NaAsO_2$ concentration was 10 mg As L^{-1} for each soil. Vertical bars represent one standard error.

$NaAsO_2$-amended suspensions. The increase in $H_3AsO_3^0$ solubility coincided with rapid increases in dissolved Fe and Mn in both soils (Fig. 2 and 3). Thus, while sorption appears to have controlled $H_3AsO_3^0$ solubility in the initially oxidized suspensions, desorption of $H_3AsO_3^0$ occurred after reducing conditions were achieved. Furthermore, these data suggest that $H_3AsO_3^0$ desorption results from reductive dissolution of Fe and Mn oxyhydroxides (this mechanism will be discussed in more detail below). Following desorption, dissolved $H_3AsO_3^0$ declined to a concentration near zero within 10 d.

Dissolved Arsenic in Arsenate-Amended Suspensions

Dissolved $H_2AsO_4^-$ followed a trend similar to that of $H_3AsO_3^0$ during the first 8 h of flooding (Fig. 5). Dissolved $H_2AsO_4^-$ declined from 10 mg As L^{-1} to 5.3 mg As L^{-1} in the Santa suspensions and from 70 mg As L^{-1} to 12.4 mg As L^{-1} in the Huckleberry suspensions. Results from our sorption rate study (McGeehan et al., 1992) showed that $H_2AsO_4^-$ reached a sorption plateau within 8 h with consequent steady-state dissolved concentrations of 4.1 mg As L^{-1} in the Santa and 14.8 mg As L^{-1} in the Huckleberry suspensions. Following this initial decline, a second dissolved $H_2AsO_4^-$ maximum was observed at 16 h in the Santa suspensions ($P = 0.234$) and 24 h in the Huckleberry suspensions ($P = 0.201$). Although the $H_2AsO_4^-$ maxima were not significant at the 95% confidence level in either soil (caused in part by the large variability among treatment replicates), the correspondence of these maxima to increases in dissolved Fe and Mn suggests that desorption of $H_2AsO_4^-$, like $H_3AsO_3^0$, may be controlled by the dissolution of Fe and Mn oxyhydroxides.

Dissolved $H_2AsO_4^-$ decreased logarithmically, reaching a value near zero by the 10th day in the Santa suspensions and the 15th day in the Huckleberry suspensions (Fig. 5). Concurrent with the disappearance of dissolved $H_2AsO_4^-$ was the appearance of dissolved

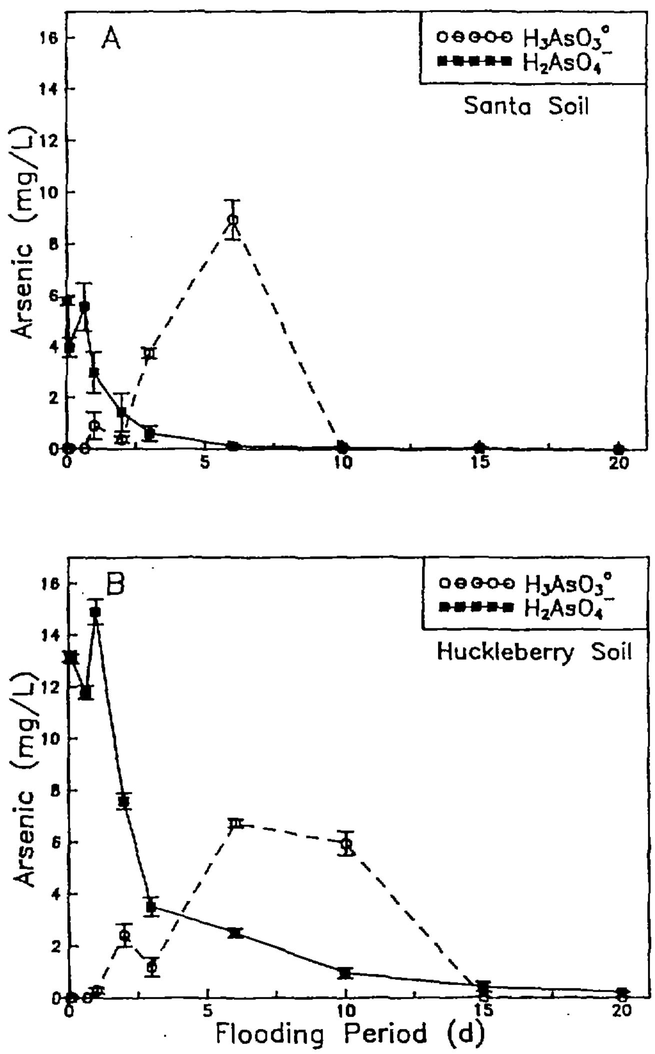

Fig. 5. Changes in dissolved $H_3AsO_3^0$ and $H_2AsO_4^-$ concentration in response to soil flooding in Na_2HAsO_4-amended suspensions of (A) Santa and (B) Huckleberry soils. Initial Na_2HAsO_4 concentration was 10 mg As L^{-1} for Santa soil and 70 mg As L^{-1} for Huckleberry soil. Vertical bars represent one standard error.

$H_3AsO_3^0$, providing strong evidence that $H_2AsO_4^-$ was rapidly reduced to $H_3AsO_3^0$. Once formed, dissolved $H_3AsO_3^0$ also decreased to nondetectable concentrations by 5 d in the Santa and by 10 d in the Huckleberry suspensions.

Kinetics and Mechanisms Controlling Arsenite and Arsenate Disappearance

The kinetics of $H_3AsO_3^0$ and $H_2AsO_4^-$ reduction are poorly characterized. A first-order rate equation for the reduction of each arsenic species takes the form

$$\frac{-d[\text{As species}]}{dt} = k[\text{As species}]$$

which, on integration, yields

$$\ln[\text{As species}] = -kt + c$$

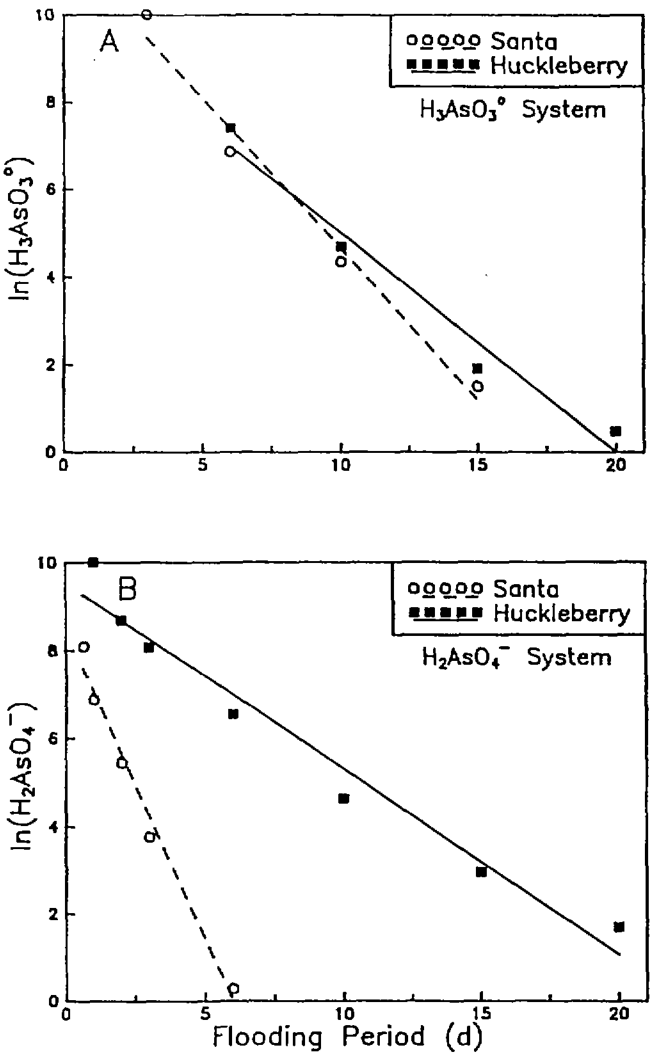

Fig. 6. First-order plots for the disappearance of (A) $H_3AsO_3^0$ and (B) $H_2AsO_4^-$ in Santa and Huckleberry soils.

where [As species] represents the dissolved concentration of $H_3AsO_3^0$ or $H_2AsO_4^-$ present at time t, k is the rate constant, and c is the integration constant. The kinetics of $H_3AsO_3^0$ and $H_2AsO_4^-$ disappearance were evaluated for the time period between the second dissolved As maximum (following desorption) and the point at which $H_3AsO_3^0$ or $H_2AsO_4^-$ was no longer detectable. These time periods ranged from 3 to 15 d for $H_3AsO_3^0$ disappearance in the $NaAsO_2$-amended Santa and from 6 to 20 d in the Huckleberry suspensions. The kinetics of $H_2AsO_4^-$ disappearance were evaluated from 0.66 to 6 d in the Na_2HAsO_4-amended Santa suspension and from 1 to 20 d in the Huckleberry suspension. Linear first-order plots were obtained for the disappearance of $H_3AsO_3^0$ and $H_2AsO_4^-$ from both soil suspensions (Fig. 6), and coefficients of determination (r^2) exceeded 0.95 in all cases.

Potential fates of As in the $NaAsO_2$- and Na_2HAsO_4-amended suspensions include sorption, reduction, and conversion to volatile organic forms. McBride and Wolfe (1971) suggested that the ultimate fate of $H_2AsO_4^-$ in anaerobic environments is conversion to $(CH_3)_2HAs$. Later investigations showed that both $(CH_3)_2HAs$ and $(CH_3)_3As$ were produced in soil treated with $NaAsO_2$ (Braman, 1975) and Na_2HAsO_4 (Woolson, 1977). Thus, while the disappearance of $H_2AsO_4^-$ clearly involved reduction to $H_3AsO_3^0$, the mechanism controlling the disappearance of $H_3AsO_3^0$ cannot be discerned from our data, although its loss as a volatile alkylarsine is very likely.

Table 2. Sorption capacities, apparent rate constants, and half-lives for the disappearance of $H_3AsO_3^0$ and $H_2AsO_4^-$ in Santa and Huckleberry soils.

Soil	Sorption capacity†		Apparent rate constant		$t_{1/2}$	
	$H_3AsO_3^0$	$H_2AsO_4^-$	$H_3AsO_3^0$	$H_2AsO_4^-$	$H_3AsO_3^0$	$H_2AsO_4^-$
	mg kg^{-1}		d^{-1}		d	
Santa	95	148	0.24	0.73	2.9	0.9
Huckleberry	158	250	0.17	0.32	4.1	2.2

† Determined using initial concentrations of 10 mg L^{-1} as H_3AsO_3–As or H_2AsO_4–As (McGeehan et al., 1992).

This study shows that the reduction of $H_2AsO_4^-$ to $H_3AsO_3^0$ can take place in a matter of days in an anaerobic soil. This time frame is consistent with reports for $H_2AsO_4^-$ reduction in lacustrine sediments (Aggett and O'Brien, 1985), groundwater (Cherry et al., 1979), and activated sewage sludge (Myers et al., 1973) and is more rapid than the suggested time frame of several months reported for ocean sediments (Andreae, 1979).

Rates of redox reactions involving arsenic species are sensitive to both adsorbent concentration, U, and adsorption capacity, Γ. Holm et al. (1979) found that increases in both U and the product $U\Gamma$ resulted in decreases in reduction rates of $H_2AsO_4^-$. In our study, apparent rate constants were lower and half-lives longer for $H_3AsO_3^0$ and $H_2AsO_4^-$ in the higher sorption-capacity Huckleberry soil (Table 2). In a true first-order reaction, the rate constant for a given soil will vary only with changes in substrate concentration. Many kinetic techniques, including the batch technique employed in this study, are limited to measuring mass transport phenomena rather than true chemical kinetics (Sparks, 1989). The fact that adsorbent characteristics appear to be influencing the rate constants suggests that transport-controlled kinetics were operative and, hence, apparent rate constants are reported in Table 2. The lower rate constants observed for the high-adsorption-capacity Huckleberry suspensions are attributed to slower As desorption, which controlled the concentration of dissolved As available for reduction or volatilization.

The changes in solution chemistry observed in this study during soil flooding suggest that desorption of $H_2AsO_4^-$ preceded its reduction. Several studies of As cycling in aquatic sediments and soils suggest that arsenate solubility is controlled by the stability of Fe(III) oxyhydroxides (Aggett and O'Brien, 1985; Belzile and Tessier, 1990; Masscheleyn et al., 1991a,b) and Mn oxides (Moore et al., 1988). The preponderance of evidence currently available indicates that Fe(III) oxyhydroxides are of primary importance in regulating the concentration of As available for reduction, while Mn plays a minor role. Whereas Fe oxides exhibit a positive surface charge in the pH range of most soils and, hence, preferentially adsorb anions, Mn oxides are negatively charged in the same pH range and would be less likely to adsorb anionic $H_2AsO_4^-$ (Oscarson et al., 1980). Because $H_3AsO_3^0$ is neutral in the pH range of our study, adsorption by Mn oxides is possible (Oscarson et al., 1980). In a flooded soil, however, Mn(IV) will be reduced and the Mn solid phase dissolved before Fe(III) begins to be reduced. Any release of As during Mn reduction probably will be followed by the immediate readsorption by Fe(III) oxyhydroxides (Cullen and Reimer, 1989). Thus, despite the presence of reducible Mn in the Santa and Huckleberry soils, the Fe(III) phase probably controls the concentration of As available for reduction under low redox conditions.

The results of this study show that a variety of factors must be considered when attempting to predict the fate of As in a flooded soil system. The decrease in pe + pH observed in flooded soils favors dissolution of Fe oxyhydroxides and desorption of $H_3AsO_3^0$ and $H_2AsO_4^-$, which in turn, controls the soluble As available for redox transformations. Each of these processes – oxyhydroxide dissolution, As desorption, and As reduction – took place more slowly in the soil with the higher sorption capacity. Although these results are indicative of the processes occurring in only two As-amended soils, the interactions described suggest that control of dissolved As levels by sorption processes may be an important factor in the redox transformations of $H_3AsO_3^0$ and $H_2AsO_4^-$.

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