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Effect of Redox Potential and pH on Arsenic Speciation and Solubility in a Contaminated Soil

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■ The influence of redox potential and pH on arsenic speciation and solubility was studied in a contaminated soil. Alterations in the oxidation state of arsenic, as influenced by redox potential and pH, greatly affected its solubility in soil. At higher soil redox levels (500–200 mV), arsenic solubility was low and the major part (65–98%) of the arsenic in solution was present as As(V). An alkaline pH, or the reduction of As(V) to As(III), released substantial proportions of arsenic into solution. Under moderately reduced soil conditions (0–100 mV), arsenic solubility was controlled by the dissolution of iron oxyhydroxides. Arsenic was coprecipitated [as As(V)] with iron oxyhydroxides and released upon their solubilization. Upon reduction to −200 mV, the soluble arsenic content increased 13-fold as compared to 500 mV. The observed slow kinetics of the As(V)–As(III) transformation and the high concentrations of Mn present indicate that, under reduced soil conditions, arsenic solubility could be controlled by a $Mn_3(AsO_4)_2$ phase.

Introduction

Because the solubility, mobility, bioavailability, and toxicity of arsenic depends on its oxidation state (*1–5*), studies of As speciation and transformations among species are essential to understanding the As behavior in the environment. Arsenate [As(V)] and arsenite [As(III)] are the primary As forms in soils. Both As(V) and As(III) are subjected to chemically and/or microbiologically mediated oxidation–reduction and methylation reactions in soils and natural waters (*3, 6–8*). Numerous studies have dealt with As sorption on specific minerals and soils. Amorphous iron and aluminum hydroxides (*9, 10*), clay content (*11*), and pH (9–12) are the soil properties reported to be most related to As sorption. Methylated arsenic oxyacids can be produced by a variety of microorganisms, and their presence has been reported in a wide range of natural waters (*8, 13*) and soils and sediments (*7, 14*).

Although of great environmental importance, little detailed information is available about the influence of redox potential on the behavior of As in contaminated soils. Deuel and Swoboda (2) reported an increase of total soluble As under reduced conditions and attributed this increase to the reduction of ferric arsenate compounds. Using an equilibrium thermodynamics approach, Sadiq et al. (*15*) developed solubility isotherms for several metal arsenates. Under oxidized conditions, they predicted that As solubility would be determined by a $Ca_3(AsO_4)_2$, $Mn_3(AsO_4)_2$ or a $Pb_3(AsO_4)_2$ phase. Similar conclusions were reported by Hess and Blanchar (*16*). Under reducing conditions, arsenite minerals are too soluble to persist in soils, but arsenic sulfides were predicted to be stable (*15*). Livesey and Huang (*17*) concluded that soluble arsenate was controlled by adsorption reactions in soils, rather than through the precipitation of arsenate compounds.

The purpose of this paper is to report the effect of soil redox potential and pH on the speciation and solubility of As in a contaminated soil. Results generated identified soil redox–pH conditions that can limit or enhance As translocation and movement in the environment. Interpretations are based on results of laboratory experiments and simple equilibrium thermodynamic calculations.

Experimental Section

Soil. A soil known to be contaminated with As was collected near Kolin, LA. The soil, located in the vicinity of an As dipping vat, had been exposed to As contamination for a period of greater than 20 years. A detailed description of the sampling site was given by Kotuby-Amacher and Gambrell (*18*). Surface (0–20 cm) samples were taken from the soil, belonging to the Acadia–Kolin Association (Aeric Ochraqualf). This association consists of loamy upland soils that have a clayey subsoil. Upon arrival in the laboratory, the soil was air-dried, ground to pass a 1-mm sieve, homogenized by thorough mixing, and stored at room temperature in 4-L polyethylene flasks until use.

The organic matter content and pH of the surface soil were determined to be 1.8% and 5.6, respectively. The surface soil had a total (aqua regia digestion) As content of 555 ± 18 mg kg^{-1} ($n = 5$) dry soil. Quartz constituted more than 90% of the X-ray (Cu Kα radiation) detected mineral fraction of bulk powder samples. Minor concentrations of both potassium feldspars and plagioclase minerals were also detected. The clay fraction contained mostly kaolinite and mixed layered illite–montmorillonite (>85%). Using selective extraction techniques, Kotuby-Amacher and Gambrell (*18*) determined the manganese oxide, and amorphous iron oxide content of the surface soil

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to be in the order of 0.03 and 0.15%, respectively. Correlation analysis revealed that the major part of the As present was associated with the amorphous iron oxide phase (*18*). No crystalline As minerals were detected by the X-ray diffraction technique.

Experiments. In a first experiment, 60-g portions of dry soil were placed in a set of plastic canisters (*19*) and gently compacted with intermittent additions of distilled deionized water followed by incubation under flooded conditions for a desired period of time. The saturated soil created a 6-cm-deep layer in the core. Then, water was introduced from the bottom with the help of a syringe and needle until an overlying floodwater depth of ~2 cm was created. Adding water from the bottom helped to release entrapped air. To ensure reducing conditions the canisters were sealed with the supplied caps. Duplicate canisters were opened after 1, 3, 15, 35, 65, and 105 days of submergence. An Eh–pH depth profile was taken by using a system similar to that described by Patrick and Delaune (*20*). Rather than measuring continuous profiles, we decided to gradually lower the microelectrodes to preselected depths (0.25, 0.5, 1.5, 2.5, 3.5, and 4.5 cm). Preliminary experiments had shown that an equilibration period of 4 h was necessary to obtain constant redox readings. After an Eh–pH depth profile was taken, the overlying water was removed from the cores with a plastic syringe followed by horizontal sectioning at 0.5-, 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-cm core depths. The volume (0.5–0.8 mL) of saturation extracts, recovered from soil sections by centrifugation and filtration, was not sufficient for the determination of all elements of interest. Therefore, each section was immediately transferred to a 40-mL polycarbonate centrifuge tube to which a known volume of oxygen-free deionized distilled water was added. The lids of the centrifuge tubes were equipped with rubber septa, which facilitated the displacement of air with argon. The soil suspensions were shaken for 1 h on a mechanical shaker, centrifuged (20 min at 7000 rpm, Sorvall GSA-400 rotor, Du Pont Co., Wilmington, DE) and filtered through a 0.45-μm micropore filter under an inert argon atmosphere by use of a pressure–vacuum system (*21*). Each supernatant was divided into two aliquots. One was used for the determination of soluble As species and sulfides. Concentrated HNO_3 (200 μL/10 mL of extract) was added to the second aliquot in which selected soluble metals (Ca, Mg, K, Na, Al, Fe, Mn, Cu, Pb, Cd, Ni, and Zn) and total P were determined. After the extraction, the dry weight of the soil in each tube was determined. This allowed the calculation of the soil to water ratio, which varied from 2.70 to 3.40.

In the next series of experiments, soil suspensions were equilibrated under controlled redox and pH conditions. The soil was equilibrated (at 28 ± 2 °C) in laboratory microcosms at various redox–pH conditions by using a modification (*22*) of the pH–redox control system developed by Patrick et al. (*23*). Suspensions were prepared by mixing an amount of soil equivalent to 200 g of dry weight with deionized distilled water so that the final soil/water ratio was 1 to 6. The following redox–pH conditions were used: redox −200, 0, 200, and 500 mV; pH 5, 8, and uncontrolled. In the uncontrolled pH experiments, the microcosms were sampled at 3-day intervals over a 24-day period. The other microcosms were sampled at the end of the 24-day equilibration period. Natural (uncontrolled) pH values at the end of the incubation period were 5.2 for 500 mV, 6.7 for 200 mV, 7.0 for 0 mV, and 7.2 for −200 mV. All experiments were run in duplicate. Sampling proceeded as follows. Two soil suspension aliquots were withdrawn from each microcosm, centrifuged, and filtered through a 0.45-μm micropore filter under an inert argon atmosphere for reduced treatments. One filtered supernatant was used for the determination of As and sulfides, the other was treated as described above and used for cation and metal analysis.

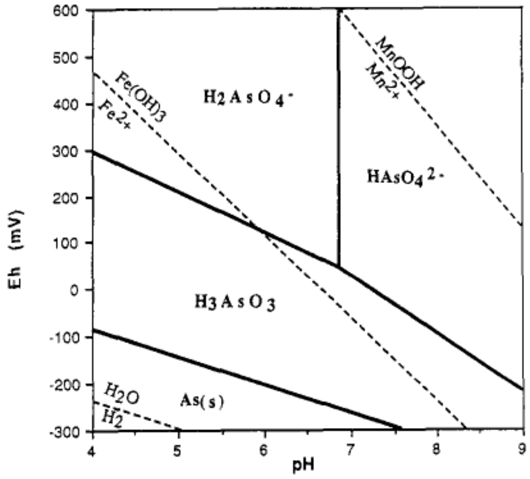

Figure 1. Eh–pH diagram for the system As–H_2O system. Activities of As, Mn, and Fe were all taken to be 10^{-4}.

Analysis. The water extracts were analyzed for As species with a pH-selective hydride generation/separation technique followed by atomic absorption spectrophotometry detection (*24*). The arsines from inorganic As(III) were selectively generated and purged for analysis from a solution buffered at pH 6.5 with Tris [tris(hydroxymethyl)aminomethane] buffer. The solution was then further acidified with concentrated HCl (to a final concentration of 3 M HCl) and analyzed for As(V). Although our analytical technique was optimized for the determination of methylarsonic acid and dimethylarsenic acid in the presence of large concentrations of inorganic As species, we were not able to detect any organic arsenicals present. The performance of the analyzing step involving hydride generation, cryogenic condensation, and volatilization was assessed by analysis of EPA reference standards for total inorganic As [As(III) + As(V)] and yielded values of 25 and 241 μg L^{-1} compared with the true values of 26.7 and 235 μg L^{-1}. Absorbance was found linear over the range 2–120 ng of As and had a sensitivity of 0.0083 absorbance units/ng of As. Six measurements of absorbance at the 50-ng level gave a relative standard deviation of 2.3%. All As species in the extracts were analyzed within 5 h after sampling.

Metals, major cations, and total P in solution were analyzed with a Jarrel Ash ICP. The performance of the ICP was checked with EPA reference samples. Sulfide was measured by an ion-specific Ag/S electrode in an anoxic buffer solution (sulfide electrode operating instructions; Lazar Research Laboratories, Los Angeles, CA), and titration alkalinity determinations (*25*) were used to estimate the concentrations of soluble carbonate species.

Possible mineral saturation was evaluated through the use of the equilibrium computer model (PC version 1.23) GEOCHEM (*26*). Statistical analysis were preformed with PC-SAS (*27*).

Results and Discussion

Arsenic Speciation, Transformations, and Solubility as Affected by Soil Redox Potential. The predicted effect of redox potential (Eh) and pH on the oxidation state of As is summarized in Figure 1, which was constructed by use of critically evaluated thermodynamic data (*28*, *29*). It can be seen that H_3AsO_3, $H_2AsO_4^-$,

$HAsO_4^{2-}$, or As(s) will be the thermodynamically dominant As species present in a soil, depending on its Eh and pH. It is important to remember that this Eh–pH diagram is really a "predominance-area" diagram because the outlined fields are those areas where the designated species make up more than 50% of the total concentration. To make the diagram more useful, the redox couples $Fe(OH)_3/Fe(II)$ and MnOOH/Mn(II) were also included. Since both manganese and iron oxides and hydroxides exist in various degrees of crystallinity (amorphous, meta-stable poorly crystalline, and crystalline), the actual stability fields for these compounds may differ from computed boundaries from soil to soil. In using the term Eh, it is also important to distinguish between the quantity that is calculated form the activities of a specific redox pair (as in Figure 1) and the quantity measured with a platinum electrode. In the reported experiments Eh was used in the latter sense and it is to be understood that the measured "equilibrium" Eh represents a mixed redox potential, i.e., the composite of different ongoing redox processes. In order to make the measured Eh values amendable to quantitative interpretation, we also measured the As(III)/As(V), soluble Mn [Mn(II)], soluble Fe [Fe(II)], and the S (–II) redox species. As will be illustrated, the measured Eh corresponded to buffering with respect to particular redox pairs.

In the first experiment, a time series evaluation between Eh, pH, soluble redox elements, and As species in soil cores was made. Changes in vertical distribution of Eh, As(III), As(III+V), Mn, and Fe upon flooding are presented in Figure 2. During the equilibration under submerged conditions, the pH increased from 5.6 to 7.1 (Figure 2A–D). Little variation in pH (±0.2) was found throughout a particular profile. Flooding periods longer than 35 days did not significantly alter the vertical distribution of Eh and redox elements studied. Flooding (reducing conditions) of the soil did not have an influence on soluble Al, Ca, Mg, Na, and K concentrations. However, as early as 3 days after flooding, there was a considerable increase in soluble Mn throughout the soil core (Figure 2, parts A vs B). As more reducing conditions (Eh $<$ 150 mV) developed, dissolved Mn increased to a near constant value of approximately 35 mg kg^{-1} soil. No Fe was solubilized after 3 days of flooding (Figure 2B). When, between the 15th and 35th day of submergence, redox levels dropped below 100 mV, soluble Fe concentrations reached a maximum (Figure 2, parts C vs D) and stayed unchanged for the rest of the equilibration period.

Some arsenic was reduced and released into solution before the solubilization of the ferric hydroxide layer. Differences in depth profiles presented in Figure 2A and B clearly illustrate this. While soluble Fe concentrations remained unchanged, dissolved As concentrations increased by a factor of 2, and As(III) became the major species present. Solubilization of As was occurring simultaneously with the reduction of As(V) to As(III) (Figure 2B).

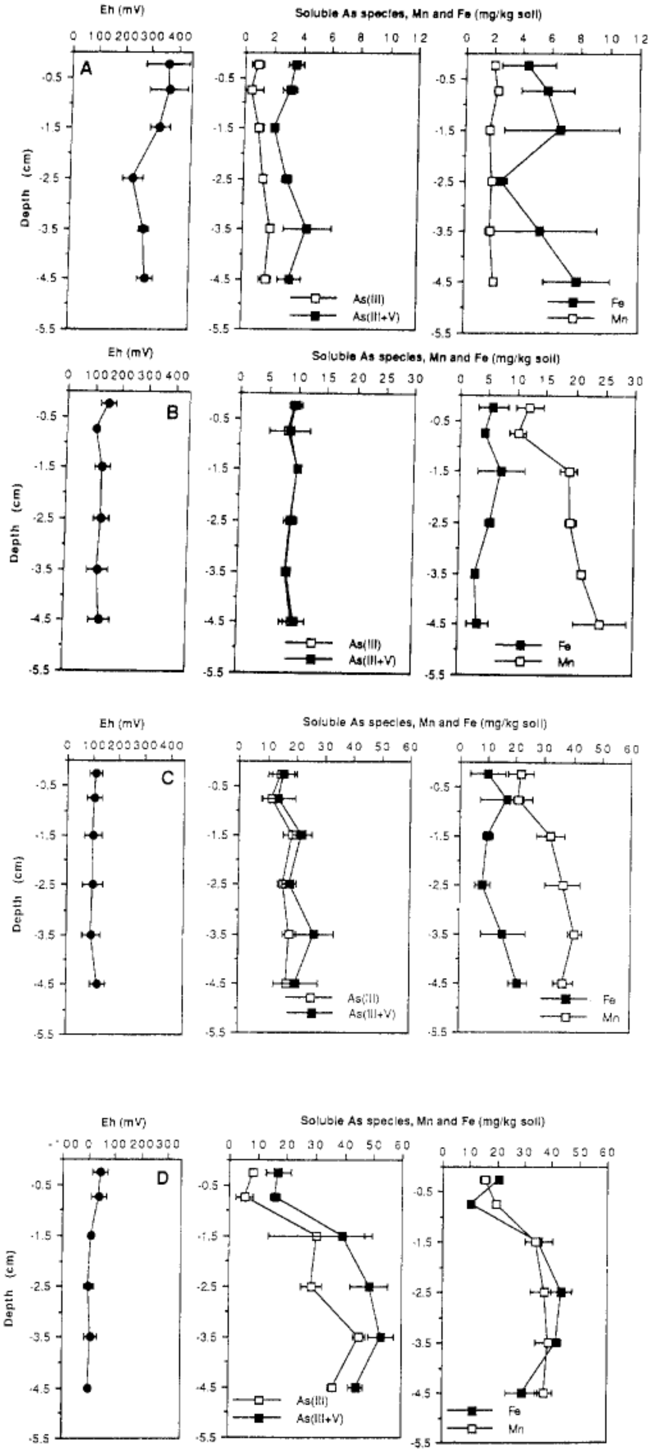

Figure 2. Vertical distribution of Eh, soluble As species, Mn, and Fe. (A) after 1 day of flooding (pH = 5.7 ± 0.1). (B) after 3 days of flooding (pH = 6.4 ± 0.2). (C) after 15 days of flooding (pH = 7 ± 0.2). (D) after 35 days of flooding (pH = 7 ± 0.3). Note changes in scale.

The constructed phase diagram (Figure 1) adequately depicts the sequence of redox reactions encountered in our soil. Quantitative inferences could not always be made with respect to critical redox levels at which particular redox pairs are unstable. Manganese became mobilized when the measured Eh dropped from 300 to ~150 mV, while according to the equilibrium thermodynamic considerations, the reduction of MnOOH to Mn^{2+} should occur at approximately 600 mV (pH 7.0). On the other hand, at redox levels below 100 mV (pH 6.4) As(III) became the predominant As species in solution, this in agreement with the computed phase diagram for the As–H_2O system. Furthermore, the observed mobilization of Fe at an Eh of ~50 mV (pH 7.0) is in reasonable agreement with the calculated $Fe(OH)_3/Fe^{2+}$ stability boundary.

Data for equilibrations at 35 days show a sharp and correlative increase ($P < 0.01$) of total soluble As and Fe. When expressed on a molar basis, the dissolution of As occurred at Fe to As ratios varying from 0.8 to 1.7. Although it is very difficult to distinguish between adsorption and coprecipitation reactions without direct examination of the solid surfaces involved (*30, 31*), consideration of the molar Fe/As ratios released upon reduction suggests that As was coprecipitated with the iron oxyhydroxides. It appears that As(V) was released upon solubilization of the hydroxides and slowly reduced to As(III).

Generally, observed increase in soluble As upon reduction have been attributed to the solubilization of ferric arsenate and other forms of iron combined with arsenic (*2, 32–34*). From our experiment, however, it can be seen that the reduction and release of As may occur before the dissolution of iron oxyhydroxides. Apparently, the dissolution of the ferric hydroxide layer led to a further increase in As concentrations. Up to 10% of the total As present in the soil became soluble. Although thermodynamically unfavorable, a considerable amount of As(V) was observed under reduced conditions after solubilization of the ferric hydroxide layer (Figure 2C,D). Our study indicates that As(V) served as an effective electron acceptor in microbial mineralization of organic matter and thereby became reduced to the more mobile and toxic As(III) species. A possible explanation for the slow and incomplete As(V) reduction is the competition of Fe(III) as a terminal electron acceptor in microbial respiration. It has been shown that manganese(IV) oxides are effective oxidants with respect to As(III) (*35, 36*); however, the abiotic oxidation of As(III) was not of major importance in our soil. Although there were enough manganese(IV) oxides in the soil to oxidize all of the As(III) to As(V), As(III) remained the predominant soluble As species (Figure 2B–D).

Possible arsenic mineral saturation was evaluated by comparing ion activity products of $(Al^{3+})(AsO_4^{3-})$, $(Ca^{2+})^3(AsO_4^{3-})^2$, $(Mg^{2+})^3(AsO_4^{3-})^2$, $(Mn^{2+})^3(AsO_4^{3-})^2$, and $(Fe^{3+})(AsO_4^{3-})$ with their most recent tabulated solubility products (*16, 29*). Other metal arsenates (Cu, Ni, Pb) were ignored because the soluble concentrations of the corresponding metals were very low (<0.2 mg kg^{-1} soil). Under oxidized conditions, soil extracts were undersaturated with respect to aluminum, calcium, magnesium, manganese, and iron arsenate minerals. Although the experimental data clearly indicated that As solubility was mainly controlled by an iron phase, the Fe(III) activity in solution was not sufficient for precipitation of $FeAsO_4$. Furthermore it has been predicted (*16, 29*) that an $FeAsO_4$ mineral formed in soil incongruently will dissolve to iron hydroxide and soluble arsenate, according to the following equation:

$$FeAsO_4{\cdot}2H_2O + H_2O = H_2AsO_4^- + Fe(OH)_3 + H^+ \qquad (1)$$

The release of high concentrations of Mn upon reduction and the slow kinetics of arsenate–arsenite transformations made the precipitation of a $Mn_3(AsO_4)_2$ phase under reduced conditions a likely event, as was indicated by GEOCHEM (*26*). The following reactions, based on thermodynamic data (*15, 28*), illustrate this:

$$\begin{array}{lrr}
 & \log K & \\
3[MnOOH + 3H^+ + e^- = Mn^{2+} + 2H_2O] & 3\times 25.27 & (2) \\
3Mn^{2+} + 2HAsO_4^{2-} = Mn_3(AsO_4)_2 + 2H^+ & 8.51 & (3) \\
\hline
3MnOOH + 2HAsO_4^{2-} + 7H^+ + 3e^- = & 84.32 & (4) \\
\quad Mn_3(AsO_4)_2 + 6H_2O & &
\end{array}$$

After rearranging eq 4, assuming activities of solid phases and H_2O equal to 1, and substituting values of 7 and 0.5, respectively, for pH and pe (Eh = 30 mV), we obtain log $a_{(HAsO_4^{2-})} = -16.91$. From this expression it can be seen that, upon reduction, MnOOH becomes unstable and very small amounts of soluble As(V) are sufficient to obtain supersaturation with respect to a manganese arsenate phase. The formation of $Mn_3(AsO_4)_2$ could set an upper limit for dissolved arsenate concentrations under reducing conditions.

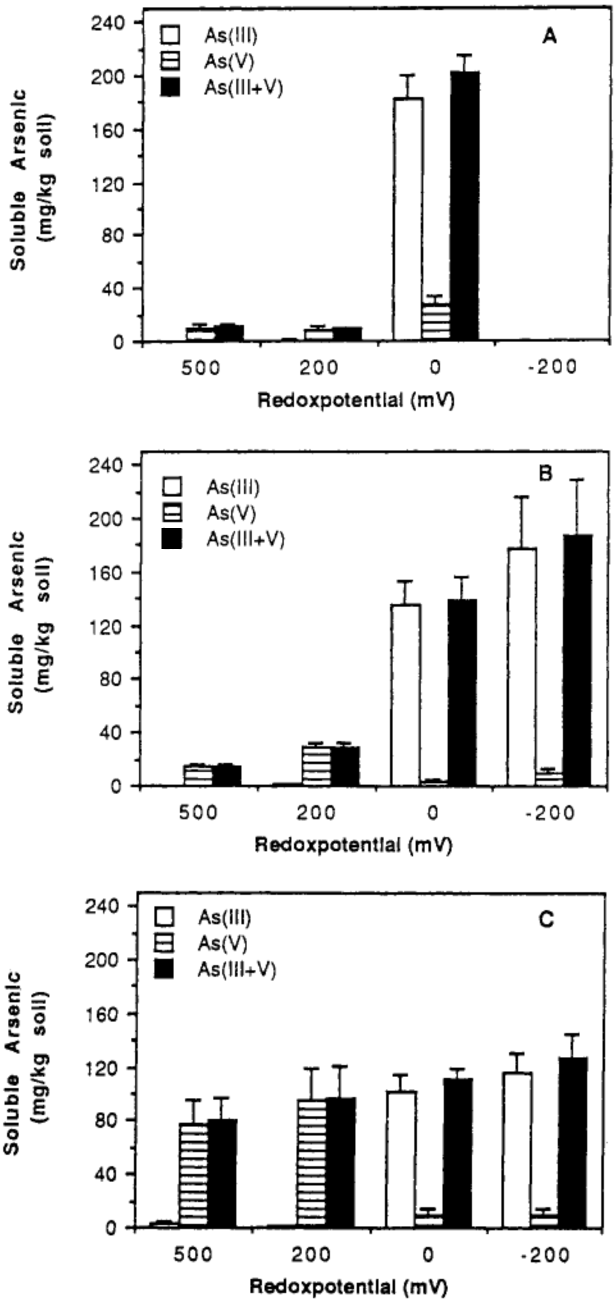

Figure 3. Distribution of soluble arsenic species after a 24-day equilibration period under controlled redox and pH conditions. (A) at pH 5.0. (B) at natural pH (5.2 for 500 mV, 6.7 for 200 mV, 7.0 for 0 mV, and 7.2 for −200 mV). (C) at pH 8.0.

Sulfide concentration stayed well below the detection limit (0.05 ppm) of our analytical technique and its influence on As solubility in the soil can therefore be neglected.

Redox–pH Chemistry of Arsenic. The redox–pH chemistry of As was studied by equilibrating soil suspensions under controlled E_h–pH conditions. Parts A–C of Figure 3 show the species distribution of As at three suspension pH levels (5.0, natural, and 8.0) in combination with four different redox levels (−200, 0, 200, and 500 mV). After ~10 days of equilibration, the preselected redox and pH were reached and maintained during a 2-week period. Upon acidification of the soil to pH 5, strongly reduced conditions (−200 mV) could not be achieved, and results are therefore not available.

Both redox status and pH affected the speciation and solubility of As. At redox potentials of 200 and 500 mV, As(V) was the major dissolved As species, constituting

Table I. Concentration of Soluble As Species, Mn, and Fe as a Function of Soil Redox–pH Conditions

day	pH	Eh, mV	concn, mg kg^{-1} soil			
			As(III)	As(V)	Mn	Fe
0	5.6	340	1.4	5.6	1.9	17.5
3	6.7	100	46.8	3.1	20.8	15.3
6	6.8	20	76.5	6.6	21.2	72.0
0	5.8	440	0.9	7.9	2.4	27.3
3	6.6	80	34.3	1.2	17.4	29.5
6	7.0	−100	69.4	3.4	16.2	75.8

>95% of the total soluble As. Upon reduction (0 and −200 mV), As(III) became the major dissolved As species, although concentrations of As(V) up to 14 mg kg^{-1} dry soil remained, and As solubility generally increased. Up to 40% of the total As present in the soil became soluble. While the first experiment gave an idea of As transformations under natural conditions, the stirred suspension experiment indicated maximum transformations rates.

Similar mechanisms controlling As solubility were observed in both experiments. Table I contains data obtained during two of the controlled Eh experiments. The increase in As solubility before the solubilization of the iron oxyhydroxides was characterized by a reversal in As speciation. Although Mn was reduced after 3 days of incubation, As(III) remained the dominant soluble As species, suggesting that the abiotic oxidation of As(III) to As(V) by Mn(IV) compounds was not important in our soil. A sharp increase of soluble As concentrations coincided with the solubilization of iron oxyhydroxides and the released As(V) was slowly reduced.

Interesting information was obtained from the alkaline (pH 8) equilibrations (Figure 3C). Under oxidized conditions, soluble As concentrations were as much as 3 times higher than in the equilibrations at lower pH. Almost all As was present as As(V). This can be explained by the pH-dependent adsorption characteristics of As(V) onto the oxide surfaces (*9*, *30*). The decreasing positive surface charge of the oxides with increasing pH facilitated the desorption of arsenate. Under reducing conditions, As(III) became the major dissolved species with total soluble As being less than in the more acidic equilibrations. The reason for this is somewhat unclear. An incomplete or slower solubilization of iron oxyhydroxides under alkaline conditions could be responsible for the lower As concentrations observed. At pH 8, dissolved Fe concentrations did not significantly increase upon reduction. Furthermore, the presence of soluble organics under alkaline conditions (pH 8.0) and the formation of iron oxyhydroxides–organic matter complexes could have retarded Fe reduction (*37*) and the release of As into solution.

In summary, redox potential and pH were shown to control the speciation and solubility of As in a contaminated soil. Both parameters are, therefore, important in assessing the fate of As-containing compounds in soil. Qualitatively, As speciation changed according to thermodynamic predictions. At higher redox levels, As(V) was the predominant As species and As solubility was low. Alkaline conditions and/or reduction of As(V) to As(III) led to a mobilization of As. Under moderately reduced conditions (0–100 mV), As solubility was controlled by the dissolution of iron oxyhydroxides. Data indicate that As was coprecipitated [as As(V)] with the oxyhydroxides and released upon their solubilization. Due to the slow kinetics of the As(V)–As(III) transformation, a considerable amount of the thermodynamically unstable As(V) species was observed under reducing conditions. This slow transformation rate and the release of high concentrations of Mn upon reduction make the precipitation of a $Mn_3(AsO_4)_2$ phase possible. When disposal of As-containing wastes is planned, consideration should be given to maintaining high redox and nonalkaline conditions necessary for minimum As solubility and mobilization.

Registry No. As, 7440-38-2; Mn, 7439-96-5; Fe, 7439-89-6.

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Aqueous-Phase Oxidation of Polychlorinated Biphenyls by Hydroxyl Radicals

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■ Hydroxyl radicals ($OH^{\bullet}$'s), generated with Fenton's reagent, rapidly oxidized polychlorinated biphenyls (PCBs) in aqueous solutions. The observed product distributions indicated that the reaction proceeds via addition of a hydroxyl group to one of the nonhalogenated sites. The unreactive nature of the halogenated sites accounts for the lower reaction rates observed for the more highly chlorinated congeners. Within homologue groups, chlorine substitution in the meta or para positions results in lower reaction rates due to steric hindrance occurring when hydroxyl radical attacks at the site ortho to the aromatic ring. Estimates of environmental half-lives, based upon kinetic measurements, reported steady-state $OH^{\bullet}$ concentrations, or estimates of radical production rates, suggest that aqueous-phase oxidation by $OH^{\bullet}$'s may be an important PCB loss mechanism in cloudwater and surface waters under certain conditions.

Introduction

Polychlorinated biphenyls (PCBs) are a group of chlorinated aromatic compounds that have been used in dielectric fluids, plasticizers, and cutting oils (*1*). Concerns about the potential deleterious effects of these compounds on aquatic and terrestrial ecosystems prompted the United States to ban their production subsequent to 1979 (*2*). Despite a reduction in total emissions, PCBs persist in the environment. To assess the efficacy of the ban and to predict future PCB levels it is necessary to quantify both the amount of PCBs entering the environment and the rate at which they are removed through various pathways. Residence times for individual PCB congeners in the atmosphere and in lakes have recently been investigated in some detail. Calculations indicate residence times of 2–4 months in the atmosphere (*3*). Residence times in lakes vary as a function of such factors as depth, size, hydraulic residence times, productivity, and sedimentation rates. Recent estimates for Lakes Michigan and Superior seem to indicate residence times on the order of 2–10 years (*4*, *5*). Although physical removal mechanisms appear to be of primary importance, both in the atmosphere and in lakes, the extent of chemical and microbial degradation remains to be determined.

Biodegradation studies have shown that reductive dehalogenation and metabolic oxidation occur under both aerobic (*1*, *6*) and anaerobic conditions (*7–9*). Although biodegradation is possible, significant concentrations may be required to induce enzymatic activity. Furthermore, organisms capable of metabolizing PCBs have only been observed in a few specific environments, such as anaerobic river sediments (*7–9*). Biodegradation is probably not an important loss mechanism for PCBs, except in certain highly contaminated environments.

Direct photodegradation of PCBs by ultraviolet light also occurs to some extent, and recent evidence suggests that atmospheric half-lives for PCBs due to this pathway may be on the order of weeks (*10*). One of the important direct photolysis reactions results in production of less chlorinated PCB congeners through reductive dehalogenation, and total PCB concentrations may only decrease slowly through this process. Without detailed information on the importance of the various photolysis pathways it is difficult to determine the effect of these reactions on the atmospheric lifetimes of PCBs. Reactions of PCBs with common environmental oxidants such as hydroperoxy radicals ($HO_2^{\bullet}$) and ozone (O_3) have not been reported and are probably not very important because only very strong oxidant species can react with PCBs.

One potentially important degradation mechanism for PCBs is oxidation by hydroxyl radicals ($OH^{\bullet}$'s). Hydroxyl radicals are among the strongest environmental oxidants known (*11*) and their reaction with biphenyl and monochlorobiphenyl has been observed in both the gas (*12*) and liquid (*13*) phases. Hydroxyl radicals are ubiquitous in the environment and are present in low concentrations under normal conditions in surface water (*14*, *15*) and in the atmosphere (*16*, *17*). It is believed that $OH^{\bullet}$'s are responsible for the degradation of many environmental contaminants such as NO_2 (*16*) and PAHs (*16*, *17*) and for the formation of natural organic polymers (*18*). Provided that $OH^{\bullet}$ fluxes in the environmental media are sufficient, they could provide an important removal pathway for PCBs.

Atkinson (*19*) and Leifer (*20*) estimated atmospheric decay rates for gas-phase PCBs using average steady-state values for atmospheric $OH^{\bullet}$ concentrations, an extension of the Hammett coefficient linear free energy relationship, and measured rate constants for biphenyl and chlorobiphenyl. Atmospheric half-life estimates for all of the different congeners derived by Atkinson ranged from 3 to 120 days, which is approximately equal to the atmospheric residence times estimated for PCBs (*3*). This reaction is especially important from a global standpoint because a significant portion of the world's PCB burden is transported through the atmosphere in the gaseous phase. It should be noted that results from these calculations are somewhat uncertain because actual rate constant measurements are only available for biphenyl and monochlorobiphenyl and the Hammett coefficient relationship may not be very accurate for the more highly chlorinated congeners.

Understanding the reactions of PCBs with $OH^{\bullet}$'s is crucial to predicting the future persistence of PCBs and

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