ROLE OF MANGANESE IN THE OXIDATION OF ARSENITE BY FRESHWATER LAKE SEDIMENTS[1]

D. W. Oscarson, P. M. Huang, and W. K. Liaw

Department of Soil Science, University of Saskatchewan
Saskatoon, Saskatchewan S7N 0W0, Canada

Abstract—The importance of various sediment components in the oxidation of As(III) (arsenite) to As(V) (arsenate) by freshwater lake sediments in southern Saskatchewan was examined. Treating the sediments with hydroxylamine hydrochloride or sodium acetate to remove Mn greatly decreased the oxidation of As(III). Furthermore, synthetic Mn(IV) oxide was a very effective oxidant with respect to As(III): 216 μg As(V)/ml was formed in solution when 1000 μg As(III)/ml was added to suspensions of 0.1 g of the oxide. These results indicate that Mn in the sediment was probably the primary electron acceptor in the oxidation of As(III). The conversion of As(III) to As(V) by naturally occurring carbonate and silicate minerals common in sediments was not evident in the system studied. Sediment particles >20 μm in size are the least effective in oxidizing As(III); the oxidizing ability of the 5–20-, 2–5-, and <2-μm particle size fractions varies depending on the sediment. The concentration of As(V) in equilibrated solutions after adding increasing amounts of As(III) (as much as 100 μg/ml) to 1 g of the three sediments ranged from approximately 3.5 to 19 μg/ml. Because As(III) is more toxic and soluble than As(V), Mn-bearing components of both the colloidal and non-colloidal fractions of the sediments may potentially detoxify any As(III) that may enter aquatic environments by converting it to As(V). This is very important in reducing the As contamination and in maintaining the ecological balance in aquatic environments.

Key Words—Arsenic, Lake sediments, Manganese, Oxidation.

INTRODUCTION

The inorganic forms of arsenic, As(III) (arsenite) and As(V) (arsenate), are the predominant arsenic species in aquatic environments under common pH and Eh conditions (Luh *et al.*, 1973; Gohda, 1974). The reduced state, As(III), is much more toxic (Webb, 1966; Penrose, 1974) and more soluble and mobile (Deuel and Swoboda, 1972) than the oxidized state, As(V); consequently, it is of fundamental importance to know the mechanism of transformations of arsenic species in aquatic systems.

Earlier Oscarson *et al.* (1980) reported the abiotic oxidation of As(III) to As(V) by freshwater lake sediments. Here evidence is presented indicating that Mn is the primary sediment component responsible for the oxidation of As(III) to As(V).

MATERIALS AND METHODS

Lake sediments

Sediments from three freshwater lakes (Buffalo Pound, Pasqua, and Katewa Lakes) located in the upper Qu'Appelle River basin in southern Saskatchewan, Canada, were selected for this study. The nature of the lakes and sediments are given elsewhere (Oscarson *et al.*, 1981). Bottom sediments were collected with an Ekman dredge. Several sediment samples from each lake were thoroughly mixed and combined to make a composite sample; the composite samples were used for all experiments. The composite samples were stored in sealed plastic bottles at 4°C.

Experimental

Treated sediments. One gram (dry weight basis) of the sediments was treated with hydroxylamine hydrochloride (NH$_2$OH-HCl) (Chao, 1972) and sodium acetate (NaOAc) (Jackson, 1975) to remove Mn. The NH$_2$OH-HCl- and NaOAc-treated sediments were suspended in 70 ml of a solution that contained 10 μg As(III)/ml (prepared from reagent grade NaAsO$_2$ that was standardized colorimetrically using As$_2$O$_3$ as the primary standard) in 125-ml Erlenmeyer flasks. The pH of the As-sediment suspensions was adjusted to 7.5. In another experiment, 1 g of the untreated sediments was suspended in 65 ml of deionized water and flushed with N$_2$ gas for 2 hr before and for 2 hr after the addition of 5 ml of a 140 μg As(III)/ml solution. The flasks containing all the treated sediment-As suspensions were placed on an oscillating shaker in a water bath for 48 hr at 25°C ± 0.2°. (To arrive at a total sediment-As contact time of 48 hr, the flasks containing the N$_2$-flushed sediment-As systems were placed on an oscillating shaker for 46 hr after N$_2$ flushing.) After the reaction period, the Eh (measured with a Pt electrode vs. a AgCl/Ag reference electrode in 4 M KCl) and the pH of the suspensions were determined; the suspensions were then centrifuged at 1000 × g for 30 min followed by ultrafiltration (filters of 0.025-μm pore size manufactured by Schleicher and Schuell, Inc., Keene, New Hampshire,
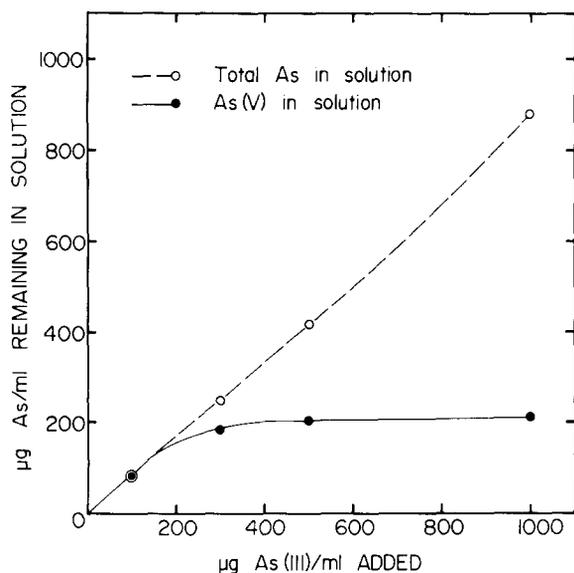
Figure 1.   Amount of As(V) formed and total As concentration remaining in solution at 72 hr after As(III) as $NaAsO_2$ was added to MnO_2.

were used); the filtrate was analyzed for As(III) and As(V) as outlined elsewhere (Oscarson *et al.*, 1980). The oxidizing power of the treated sediments with respect to As(III) was compared with that of an untreated sample of each sediment.

The amounts of Mn, Ca, and Mg in the NH_2OH-HCl and NaOAc extracts were determined by atomic absorption spectrophotometry. The extractable Fe was determined by the orthophenanthroline method (Jackson, 1975), and Al was determined by the aluminon method (Hsu, 1963) with the addition of thioglycolic acid.

Natural minerals. The following clay minerals were obtained from the C.M.S. Source Clays Repository: montmorillonite, Crook County, Wyoming (SWy-1); kaolinite, Washington County, Georgia (KGa-1); illite, Silver Hill, Montana (IMt-1); vermiculite, Llano, Texas (VTx-1); and ferruginous smectite, Grant County, Washington (SWa-1). A sample of each mineral was dispersed by ultrasonification, and the <2-μm particle size fraction was obtained by sedimentation; this fraction was used for all experiments. Microcline (Perth, Ontario), orthoclase (Madagascar), and calcite (Chihuahua, Mexico) were obtained from the Ward's Natural Science Establishment, Rochester, New York. The minerals were ground and passed through a 300-mesh sieve. The <50-μm particle size fraction was used.

One-tenth gram of the various minerals was suspended in 65 ml of deionized water in 125-ml Erlenmeyer flasks. The suspensions were ultrasonified to assure separation and dispersion, and 5 ml of a 140-μg

As(III)/ml solution was added to the suspensions to give a final As(III) concentration of 10 μg/ml. The pH of the As-mineral suspensions was adjusted to 7.5, and the flasks containing the suspensions were placed on an oscillating shaker in a water bath for 48 hr at 25°C $\pm$ 0.2°. After the reaction period, the suspensions were centrifuged and filtered, and the filtrate was analyzed for As(V) as described above.

Particle size. A portion of each sediment was dispersed in deionized water by ultrasonification and separated by sedimentation (Jackson, 1975) into the >20-, 5–20-, 2–5-, and <2-μm particle size fractions. One-tenth gram of the various particle size fractions was suspended in 70 ml of a solution that contained 10 μg As(III)/ml. After a 48-hr reaction period on an oscillating shaker in a water bath at 25°C $\pm$ 0.2°, the suspensions were centrifuged and filtered, and the filtrate was analyzed for As(III) and As(V).

Equilibrium As(V) concentrations. The amounts of As(V) in the equilibrated solutions after adding increasing amounts of As(III) to the three sediments were determined by suspending 1 g of the sediments in 70 ml of a solution that contained 10, 15, 20, 25, 35, 50, 75, or 100 μg As(III)/ml. In another experiment, 0.1 g of a synthetic MnO_2 (birnessite) (McKenzie, 1971) was suspended in 70 ml of a solution that contained 100, 300, 500, or 1000 μg As(III)/ml in 125-ml Erlenmeyer flasks; the pH of the MnO_2-As suspensions was adjusted to 7.5. After a 72-hr equilibration period on an oscillating shaker in a water bath at 25°C $\pm$ 0.2°, the sediment- and MnO_2-As suspensions were centrifuged and filtered, and the filtrate was analyzed for As(III) and As(V).

RESULTS AND DISCUSSION

Oscarson *et al.* (1980) hypothesized that Mn was the primary sediment component responsible for the abiotic oxidation of As(III) to As(V) by freshwater lake sediments. To test this hypothesis, the oxidizing power of the sediments with respect to As(III) was determined in the present study after treating the sediments with NH_2OH-HCl (Chao, 1972) and NaOAc (Jackson, 1975). Hydroxylamine hydrochloride was chosen because of its effectiveness in removing Mn from the sediments. Oscarson *et al.* (1981) observed that a NaOAc treatment designed to extract Ca and Mg carbonates from sediments and soils (Jackson, 1975) also removed most of the extractable Mn from the sediments.

The oxidizing power of the NH_2OH-HCl- and NaOAc-treated sediments with respect to As(III) is much less than that of the untreated sediments (Table 1). Significant amounts of Mn and Fe were removed by both extractants (Table 1), and the oxidation of As(III) to As(V) by either Mn(IV) or Fe(III) is a thermodynamically favorable reaction (Oscarson *et al.*, 1980). However, the conversion of As(III) to As(V) by synthetic Fe(III) oxide does not occur within 72 hr at neutral pH

Table 1. Effect of NH₂OH-HCl-, NaOAc-, and N₂-flushing treatments on the oxidation of As(III) by lake sediments.[1]

Treatment	As(III) (μg/ml in solution)	As(V)	As(III)/[As(III) + As(V)]	Final pH	Final Eh (v)	Mn	Fe	Al (μg extracted/g sediment)	Ca	Mg
Buffalo Pound Lake										
None	0	1.60 ± 0.02[2]	0	8.0[3]	0.39[3]					
N₂ flushing	0	1.70 ± 0.27	0	8.2	0.24					
NH₂OH-HCl	4.32 ± 0.32	3.59 ± 0.24	0.55 ± 0.03[4]	7.2	0.25	480 ± 12	3270 ± 40	376 ± 15	29,400 ± 900	3690 ± 40
NaOAc	6.97 ± 0.63	1.54 ± 0.36	0.82 ± 0.05	7.5	0.39	350 ± 10	3370 ± 170	136 ± 10	23,000 ± 900	3360 ± 370
Pasqua Lake										
None	0	1.04 ± 0.01	0	7.6	0.49					
N₂ flushing	0	1.14 ± 0.07	0	7.8	0.24					
NH₂OH-HCl	2.99 ± 0.28	3.25 ± 0.08	0.48 ± 0.03	7.2	0.28	660 ± 15	1880 ± 120	210 ± 18	43,900 ± 1900	5190 ± 80
NaOAc	5.48 ± 0.62	0.58 ± 0.15	0.90 ± 0.03	7.5	0.41	534 ± 25	3460 ± 300	146 ± 18	38,200 ± 400	5690 ± 120
Katepwa Lake										
None	0	0.28 ± 0.03	0	7.6	0.44					
N₂ flushing	0	0.80 ± 0.15	0	7.9	0.19					
NH₂OH-HCl	5.55 ± 0.40	1.68 ± 0.02	0.77 ± 0.01	7.5	0.27	1090 ± 20	2730 ± 20	178 ± 10	92,700 ± 1100	5050 ± 30
NaOAc	6.68 ± 0.08	1.26 ± 0.04	0.84 ± 0.01	7.5	0.39	1280 ± 40	5310 ± 50	117 ± 13	76,300 ± 300	7100 ± 420

[1] Initial As(III) concentration was 10 μg/ml.
[2] $\bar{x} \pm$ SD, n = 3.
[3] The precision of the pH and Eh measurement is ±0.1 and ±0.01 v, respectively.
[4] The error of the ratio was calculated by the conventional expression for the exact differentiation of a function of two variables; the computation is as follows:

$$\left|\frac{As(V)}{[As(III) + As(V)]^2}\right| \left\|\,\left|\Delta As(III)\right|\,\right\| + \left|\frac{-As(III)}{[As(III) + As(V)]^2}\right| \left\|\,\left|\Delta As(V)\right|\,\right\|$$

where As(III) and As(V) are the concentrations of the respective As species in solution in μ/ml and ΔAs(III) and ΔAs(V) are the standard deviations of the above values.

values (unpublished data); therefore Fe is deemed to be of minor significance in the oxidation of As(III) in this system. On the other hand, synthetic Mn(IV) oxide was a very effective oxidant with respect to As(III): 216 μg As(V)/ml was formed in solution when 1000 μg As(III)/ml was added to a suspension of 0.1 g of MnO_2 (Figure 1). The formation of As(V) through the oxidation of As(III) by MnO_2 leveled off with increasing additions of As(III) (Figure 1); apparently the Mn(IV) at or near the surface of the oxide and accessible to As(III) was reduced creating a barrier that prevented the reduction of structural Mn(IV) present in the inner part of the oxide. The results indicate that ~19% of the Mn(IV) present in the 0.1-g sample of MnO_2 was reduced to Mn(II) when 1000 μg of As(III)/ml was added to the oxide. These data (Table 1, Figure 1) indicate that manganese is a main sediment component responsible for the oxidation of As(III).

The NH_2OH-HCl- and NaOAc-treated sediment-As systems had a lower Eh than the untreated sediment-As system (Table 1); a result that might partially explain the decreased oxidation of As(III) by the NH_2OH-HCl- and NaOAc-treated sediments. The lower the redox potential of the system, the more energy was required to effect the transfer of electrons from As(III) to the sediment because the electron activity was greater. However, when the sediment-As suspensions were flushed with N_2 gas, the Eh of the system was lower than that of the NH_2OH-HCl and NaOAc-treated sediment-As systems; As(III) was not detected in solution after 48 hr in the N_2-flushed systems (Table 1). Moreover, comparing the Eh of the untreated and N_2-flushed sediment-As systems, the oxidation of As(III) was apparently not significantly affected over the range of Eh values studied here. Consequently, the Eh of the NH_2OH-HCl- and NaOAc-treated sediment-As systems cannot account for the decrease in oxidation of As(III) relative to the untreated and N_2-flushed sediment-As systems.

The NaOAc-treated sediment was less effective in oxidizing As(III) than was the NH_2OH-HCl-treated sediment (Table 1). This relation cannot be readily explained. The amount of Mn removed by the two extractants was not greatly different (Table 1). Furthermore, the Eh of the two systems cannot be an explanation because the NH_2OH-HCl-treated sediment-As system had a lower Eh and this would have tended to retard the oxidation reaction. It is possible, however, that the two extractants may have removed different Mn phases. Surprisingly, NH_2OH-HCl removed more calcium carbonate from the sediments than did NaOAc (Table 1); carbonates can coat other sediment components and thereby retard reaction rates (Jenne, 1977). Therefore, it is possible that the active Mn still remaining in the sediments was more accessible to As(III) in the NH_2OH-HCl-treated than in the

NaOAc-treated sediment because the carbonate content was less.

The total As sorbed by the NH_2OH-HCl- and NaOAc-treated sediments was also significantly less than that sorbed by the untreated and N_2-flushed sediments (Table 1). This difference is attributed to the partial removal of Fe and Al oxides from the sediments by the extractants; these oxides are known to be strong sorbents of As (Huang, 1975; Huang and Liaw, 1979; Huang, 1980).

Many naturally occurring minerals are known to catalyze oxidation reactions (Theng, 1974). To test the possibility that minerals common in sediments and soils may catalyze the oxidation of As(III) to As(V), the following minerals were examined: montmorillonite, kaolinite, illite, vermiculite, ferruginous smectite, microcline, orthoclase, and calcite. No As(V) was detected in solution in any of the above mineral systems within 48 hr after adding a solution of As(III) to the mineral suspensions. Therefore, it is concluded that the various silicates and carbonates commonly present in the sediment do not play an important role in the conversion of As(III) to As(V).

In earlier studies, microorganisms present in the sediments were deemed to be of minor importance in the oxidation of As(III) (Oscarson *et al.*, 1980), and unpublished data from this laboratory show that Fe(III) oxide does not oxidize As(III) within 72 hr at neutral pH. The present study shows that calcite and various silicates common in sediments do not oxidize detectable amounts of As(III). In addition, the conversion of As(III) to As(V) by organic material, here CH_2O, is not a thermodynamically favorable reaction as indicated by the negative log K(W) value of the following reaction:

$$HAsO_2 + CH_2O + 2H_2O \rightleftharpoons H_3AsO_4 + CH_3OH,$$
$$\log K(W) = -10.9.$$
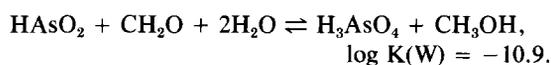
The relevant half reactions for the organic material and As were taken from Stumm and Morgan (1970) and Latimer (1952), respectively; log K(W) is the equilibrium constant for the redox reaction at pH 7 and 25°C (Stumm and Morgan, 1970). In light of the above discussion and the data presented in Table 1 and Figure 1, it is concluded that Mn, which is present as discrete oxides and/or as oxide coatings on other sediment components (Jenne, 1968), is probably the primary electron acceptor in the oxidation of As(III) to As(V) by the freshwater lake sediments.

The >20-μm particle size fraction of all sediments is least effective in oxidizing As(III) (Table 2). The relative oxidizing power of the 5–20-, 2–5-, and <2-μm size fractions varied depending on the sediment. The results indicate that all particle size fractions of the sediments, especially the <20-μm fraction, can oxidize As(III), a capability that can be attributed to the presence of ac-
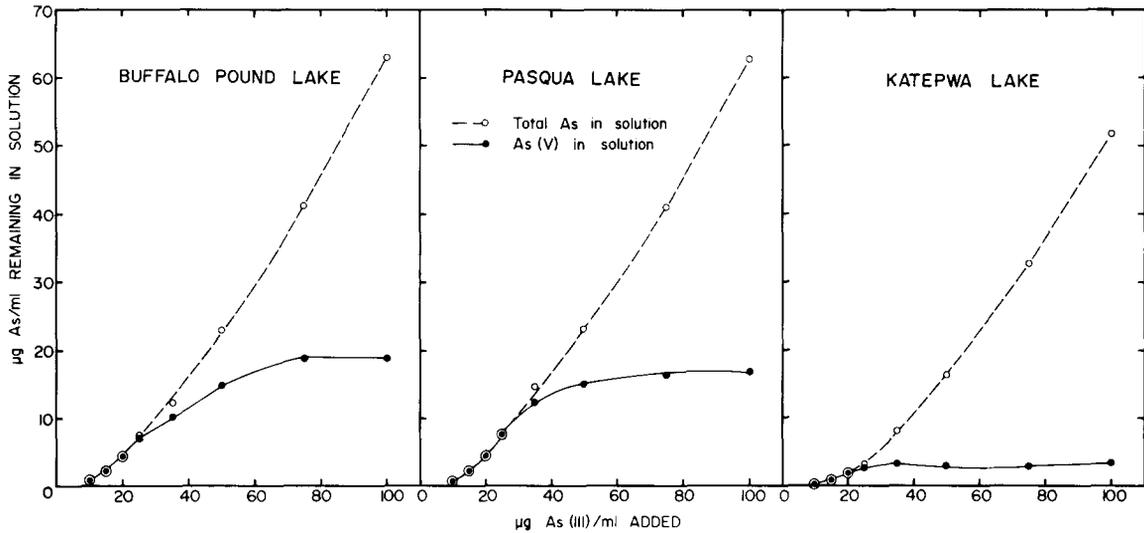
Figure 2. Amount of As(V) formed and total As concentration remaining in solution at 72 hr after As(III) as $NaAsO_2$ was added to the lake sediments.

tive Mn which occurs in a series of particle size fractions of the sediments (Oscarson et al., 1981).

The amount of As(V) in the equilibrated solutions after adding increasing amounts of As(III) to 1 g of the sediments ranged from approximately 3.5 (Katepwa Lake) to 19 $\mu g/ml$ (Buffalo Pound Lake) (Figure 2). The concentration of As(V) in solution was lowest in the Katepwa Lake sediment-As system (Figure 2); this means that the Katepwa Lake sediment has a lower capacity to oxidize As(III) to As(V) and/or a greater sorption capacity for As. The extractable Mn content in the Katepwa Lake sediment was significantly greater than that in the Buffalo Pound Lake and Pasqua Lake sediments (Table 1), but the Katepwa Lake sediment also had significantly more extractable Ca and Mg carbonates (Table 1) and, as discussed above, carbonates can coat other sediment components and thereby retard reaction rates. It is possible, therefore, that the active Mn in the Katepwa Lake sediment was "deactivated" to a greater extent by a coating of carbonates than was the active Mn in the Buffalo Pound Lake and Pasqua

Lake sediments. Consequently, the oxidation of As(III) appeared to be less. On the other hand, comparing the total As remaining in solution for the three untreated sediment systems (Table 1, Figure 2), it is evident that the Katepwa Lake sediment had the greatest sorption capacity for As. Both processes—oxidation and sorption—are, therefore, probably important in explaining the results in Figure 2.

A closed system was used in this study; hence, with increasing additions of As(III), the accessible and active Mn was apparently consumed, and the production of As(V) leveled off (Figure 2). In a natural, open system, Mn is able to function catalytically, and the oxidizing capacity of the sediments for As(III) would be unlimited. The oxidation of Mn(II) by O_2 is very slow at pHs less than 8.5 (Stumm and Morgan, 1970); however, the oxidation of Mn(II) may be catalyzed at the surfaces of various sediment components or mediated by microorganisms (Hem, 1963; Stumm and Morgan, 1970).

Because As(III) is much more toxic than As(V), the

Table 2. The effect of particle size fractions of the lake sediments on the oxidation of As(III).

Particle size (μm)	Buffalo Pound Lake			Pasqua Lake			Katepwa Lake		
	As(III)[1]	As(V)	As(III)/	As(III)	As(V)	As(III)/	As(III)	As(V)	As(III)/
	(μg/ml in solution)		[As(III) + As(V)]	(μg/ml in solution)		[As(III) + As(V)]	(μg/ml in solution)		[As(III) + As(V)]
>20	9.01 ± 0.02[2]	0.18 ± 0.01	0.98 ± 0.00[3]	9.50 ± 0.10	0.04 ± 0.01	1.00 ± 0.00	9.50 ± 0.13	0.06 ± 0.01	0.99 ± 0.00
5–20	8.25 ± 0.02	0.84 ± 0.04	0.91 ± 0.00	6.85 ± 0.04	1.38 ± 0.03	0.83 ± 0.00	4.67 ± 0.10	1.36 ± 0.09	0.77 ± 0.02
2–5	7.01 ± 0.04	1.54 ± 0.08	0.82 ± 0.01	0	6.34 ± 0.03	0	4.21 ± 0.04	2.33 ± 0.01	0.64 ± 0.00
<2	1.74 ± 0.08	5.57 ± 0.10	0.24 ± 0.01	0.91 ± 0.06	6.03 ± 0.09	0.13 ± 0.01	7.54 ± 0.03	1.00 ± 0.01	0.88 ± 0.00

[1] The initial As(III) concentration was 10 $\mu g/ml$.

[2] $\bar{x}$ ± SD, n = 3.

[3] The error of the ratio was calculated by the method stated in Table 1; a value of ±0.00 indicates the error is <0.005.

Mn in both the colloidal and noncolloidal fractions of the sediments may potentially detoxify As(III) that may enter aquatic systems by converting it to As(V). This is very important in terms of human and animal health and in maintaining the ecological balance in aquatic environments.

ACKNOWLEDGMENTS

REFERENCES

Chao, T. T. (1972) Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride: *Soil Sci. Soc. Amer. Proc.* **36,** 764–768.

Deuel, L. E. and Swoboda, A. R. (1972) Arsenic solubility in a reduced environment: *Soil Sci. Soc. Amer. Proc.* **36,** 276–278.

Gohda, S. (1974) The content and the oxidation state of arsenic and antimony in coastal water of Japan: *J. Oceanogr. Soc. Jap.* **30,** 163–167.

Hem, J. D. (1963) Deposition and solution of manganese oxides: *U.S. Geol. Surv. Water-Supply Pap.* **1667-B,** B1–B42.

Hsu, P. H. (1963) Effect of initial pH, phosphate, and silicate on the determination of aluminum with aluminon: *Soil Sci.* **96,** 230–238.

Huang, P. M. (1975) Retention of arsenic by hydroxy-aluminum on surfaces of micaceous mineral colloids: *Soil Sci. Soc. Amer. Proc.* **39,** 271–274.

Huang, P. M. (1980) Adsorption processes in soil: in *Handbook of Environmental Chemistry,* O. Hutzinger, ed., Springer-Verlag, Amsterdam, 47–59.

Huang, P. M. and Liaw, W. K. (1979) Adsorption of arsenite by lake sediments: *Int. Rev. Gesamten Hydrobiol.* **64,** 263–271.

Jackson, M. L. (1975) *Soil Chemical Analysis—Advanced Course:* 2nd ed., published by the author, University of Wisconsin, Madison, Wisconsin, 895 pp.

Jenne, E. A. (1968) Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides: *Amer. Chem. Soc., Adv. Chem. Ser.* **73,** 337–387.

Jenne, E. A. (1977) Trace element sorption by sediments and soils—sites and processes: in *Molybdenum in the Environment,* W. Chappell and K. Peterson, eds., Marcel Dekker, New York, 425–553.

Latimer, W. M. (1952) *Oxidation Potentials:* 2nd ed., Prentice-Hall, Englewood Cliffs, New Jersey, 392 pp.

Luh, M. D., Baker, R. A., and Henley, D. E. (1973) Arsenic analysis and toxicity—a review: *Sci. Total Environ.* **2,** 1–12.

McKenzie, R. M. (1971) The synthesis of birnessite, cryptomelane, and some other oxides and hydroxides of manganese: *Mineral. Mag.* **38,** 493–502.

Oscarson, D. W., Huang, P. M., and Liaw, W. K. (1980) The oxidation of arsenite by aquatic sediments: *J. Environ. Qual.* **9,** 700–703.

Oscarson, D. W., Rogers, J. S., Huang, P. M., and Liaw, W. K. (1981) The nature of selected prairie lake and stream sediments: *Int. Rev. Gesamten Hydrobiol.* **66,** 95–107.

Penrose, W. R. (1974) Arsenic in the marine and aquatic environments: analysis, occurrence and significance: *CRC Crit. Rev. Environ. Cont.* **4,** 465–482.

Stumm, W. and Morgan, J. J. (1970) *Aquatic Chemistry:* Wiley-Interscience, New York, 583 pp.

Theng, B. K. G. (1974) *The Chemistry of Clay-Organic Reactions:* Adam Hilger Ltd., London, 343 pp.

Webb, J. L. (1966) *Enzyme and Metabolic Inhibitors:* Vol. 3, Ch. 6, Academic Press, New York, 595–790.

Резюме—Исследовалось значение различных компонентов осадка при окислении As(III) (мышьяковистокислой соли) в As(V) (мышьяковокислую соль) при помощи осадков из свежей озерной воды в нижном Саскачеване. Воздействие гидроксиламинового гидрохлорида или натриевого ацетата на осадки, чтобы удалить Mn, значительно уменьшает окисление As(III). Кроме этого, синтетические окиси Mn(IV) были очень эффективными окислителями по отношению к As(III): 216 μг As(V)/мл было образовано в растворе при добавке 1000 μг As(V)/мл в суспензиях 0,1 г окиси. Эти результаты указывают, что Mn в осадке был, вероятно, акцептором первичных электронов при окислении As(III). Переход As(III) в As(V) при помощи натурально выступающих карбонатовых и кремниевых минералов, часто находящихся в осадках, не был очевиден в изучаемой системе. Частицы осадка размером >20 μм были наименее эффективны при окислении As(III); окислительная способность частиц размером 5–20, 2–5, и 2 μм изменялась в зависимости от осадка. Концентрация As(V) в равновесных растворах после добавки увеличивающегося количества As(III) (до 100 μг/мл) к одному грамму трёх осадков находилась в диапазоне приблизительно от 3,5 до 19 μг/мл. Так как As(III) более токсический и растворяемый, чем As(V), Mn содержащие компоненты коллоидальных и неколлоидальных фракций осадков могут потенциально обезвредить любой As(III), который может поступать в водную среду, путём превращения её в As(V). Это очень важно при уменьшении загрязнения As и при сохранении экологического баланса водной среды. [E.C.]

Resümee—Die Bedeutung der verschiedenen sedimentären Komponenten bei der Oxidation von As(III), Arsenit, zu As(V), Arsenat, durch Süβwassersedimente wurde im südlichen Saskatchewan untersucht. Die Behandlung der Sedimente mit Hydroxylaminhydrochlorid oder Natriumacetat—um Mangan weitgehend zu entfernen—führte zu einer Abnahme der Oxidation von As(III). Darüberhinaus war synthetisches Mn(IV)-Oxid ein sehr wirksames Oxidationsmittel im Hinblick auf As(III): 216 μg As(V)/ml bildete sich in der Lösung bei einer Zugabe von 1000 μg As(III)/ml zu Suspensionen von 0,1 g Oxid. Diese Ergebnisse deuten darauf hin, daβ Mangan in den Sedimenten wahrscheinlich der wichtigste Elektronenakzeptor bei der Oxidation von As(III) war. Die Umwandlung von As(III) in As(V) durch natürlich auftretende Karbonate und Silikatminerale, die gewöhnlich in Sedimenten auftreten, wurde in den untersuchten System nicht beobachtet. Die Kornfraktionen gröβer als 20 μm spielen bei der Oxidation von As(III) die kleinste Rolle. Die Oxidationskraft der Fraktionen 5–20, 2–5, und <2 μm variiert je nach Sediment. Die Konzentration von As(V) in den Gleichgewichtslösungen, die sich einstellten, wenn zunehmende Mengen As(III) (bis zu 100 μg/ml) zu jeweils 1 g der 3 Sedimente hinzugefügt wurde, reichte von etwa 3,5 bis 19 μg/ml. Da As(III) giftiger und leichter löslich als As(V) ist, können Mangan-haltige Komponenten der kolloidalen und nichtkolloidalen Fraktionen der Sedimente als mögliches Entgiftungsmittel für As(III) gelten, das in aquatisches Milieu gelangt, indem sie es in As(V) umwandeln. Dies ist von groβer Bedeutung für die Verringerung der As-Kontamination und für die Erhaltung des ökologischen Gleichgewichtes im aquatischen Milieu. [U.W.]

Résumé—L'importance de composants sédimentaires variés dans l'oxidation d'As(III) (arsenite) à As(V) (arsenate) par des sédiments de lac d'eau douce dans le Saskatchewan du sud a été examinée. Le traitement des sédiments à l'hydrochloride hydroxylamine ou à l'acétate de sodium pour retirer Mn a fortement décru l'oxidation d'As(III). De plus, l'oxide Mn(IV) synthétique s'est montré un oxidant très éfficace en ce qui concerne As(III): 216 μg As(V)/ml a été formé en solution après que 1000 μg As(III)/ml avait été ajouté à des suspensions de 0,1 g de l'oxide. Ces résultats indiquent que Mn dans le sédiment était probablement l'accepteur d'électrons primaire dans l'oxidation d'As(III). La conversion d'As(III) à As(V) par des minéraux carbonates et silicés courants dans les sédiments n'était pas évidente dans le système étudié. Les particules sédimentaires de taille >20 μm sont les moins éfficaces pour oxyder As(III); l'abilité d'oxydation des fractions de particules de taille 5–20, 2–5-, et <2-μm varie selon le sédiment. La concentration d'As(V) dans des solutions équilibrées, après avoir ajouté des quantités croissantes d'As(III) (jusqu' à 100 μg/ml) à 1 g des trois sédiments s'étageait d'approximativement 3,5 à 19 μg/ml. Des composants portant Mn des fractions colloïdales et noncolloïdales des sédiments peuvent partiellement détoxifier tout As(III) qui pénètre les environements aquatiques en le convertissant en As(V), parcequ'As(III) est plus toxique et plus soluble qu'As(V). Ceci est très important pour la réduction de la contamination par As et pour le maintient de l'équilibre écologique dans les environements aquatiques. [D.J.]