

EFFECTS OF ACIDIFICATION AND NATURAL ORGANIC MATERIALS ON THE MOBILITY OF ARSENIC IN THE ENVIRONMENT

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ABSTRACT. Effects of acidification on adsorption and potential mobility of various As forms have been studied in batch-type distribution experiments. The adsorption of As on alumina decreased in the order As(V) > MMAA = DMAA > As(III) at pH below 6 and As(V) > As(III) > MMAA = DMAA at pH above 6. The adsorption reached a maximum around pH 5 for As(V), pH 7 for As(III) and pH 4 for MMAA and DMAA. The presence of a fulvic acid at concentration levels of 10 mg L⁻¹ or higher generally reduced the As adsorption in the pH range 5 to 7. In light of both laboratory and field observations environmental acidification would increase the leaching of As from soils or sediments to surface and groundwaters under reducing conditions, but could also reduce the mobility due to enhanced adsorption under oxidizing conditions.

1. Introduction

Environmental acidification may affect As mobility in aquatic systems in a number of ways. The redox equilibrium between As(V) and As(III) is highly pH-dependent (Ferguson and Gavis, 1972). Thus, pH as well as the redox potential would have a large impact on speciation and mobility (Frost and Griffin, 1977; Gupta and Chen, 1978; Pierce and Moore, 1982). Biotransformational processes may lead to both methylation (to e.g. monomethylarsonic acid, MMAA, and dimethylarsinic acid, DMAA) and demethylation of As in surface waters and sediments (Wong *et al.*, 1977; Brannon *et al.*, 1980; Baker *et al.*, 1983). Acidification can affect these processes which in turn change the distribution of organic as well as inorganic species and thereby the mobility. An increased solubility of e.g. iron hydroxides at low pH could lead to a release of iron-bound As from soils and sediments to waters (Khourey *et al.* 1983).

The adsorption of As onto geologic materials is generally highly pH-dependent. For As(III) there is a maximum in adsorption by oxides and hydroxides around pH 7 to 8. At lower pH the adsorption is reduced (Pierce and Moore, 1982; Schlicher and Ghosh, 1985; Singh *et al.*, 1988; Xu *et al.*, 1990a). For As(V), however, the adsorption is high at low pH and decreases drastically with increasing pH (Anderson *et al.*, 1976; Frost and Griffin, 1977; Gupta and Chen, 1978; Pierce and Moore, 1982; Xu *et al.*, 1988). Adsorption data in the literature can, however, not easily be compared due to differences in experimental procedures and conditions. Most of previous adsorption experiments were performed using inorganic As(V), and in a few cases As(III), at high total concentrations (10⁻³ to 10⁻⁵ M), and effects of natural organic materials were not considered.

The purpose of this paper is to provide information on the adsorption of As(V), As(III), MMAA and DMAA onto some geologic materials under the influence of pH and natural organic

materials at low As concentrations. The results are discussed with the emphasis on the potential impact of environmental acidification on the mobility of As as well as the leaching from soils and sediments to surface and groundwaters.

2. Materials and Methods

2.1. ADSORPTION SYSTEMS

Three different geologic materials were chosen as adsorbents: alumina (α -Al₂O₃; from Aldrich-Chemie), hematite (α -Fe₂O₃; from Ward's) and quartz (SiO₂; from Merck), . They were crushed and sieved. The size fraction 0.063 to 0.125 mm was selected, washed by Milli-Q water (deionized water from a Milli-Q purification system) several times, and gently dried at 105 °C.

A solution of 0.1 M NaCl was used as aqueous phase. The initial pH was adjusted to a preselected level with HCl or NaOH.

The stock solution of As(III) was prepared by dissolving NaAsO₂ in Milli-Q water. The As(V) stock solution was prepared from As₂O₅. The isotope ⁷⁴As (in the form of H₃AsO₄; from Amersham) was used as an As(V) radio-tracer. Labelled As(III) was prepared by heating H₃AsO₄ in the presence of HSO₃⁻. The organic forms MMAA and DMAA (labelled with ⁷⁴As) were synthesized as described by Stary *et al.* (1982).

The natural organic material used was a FA extracted from a surface water (molecular weight around 1800, acid capacity of 4.8 meq g⁻¹ for carboxylic groups and 1.3 meq g⁻¹ for phenolic groups (Ephraim *et al.*, 1989).

All chemicals used were analytic grade and all solutions were prepared with Milli-Q water.

2.2. DISTRIBUTION MEASUREMENTS

The adsorption of As onto geologic materials was studied in batch experiments using a radiotracer technique (Xu *et al.*, 1988, 1990). The distribution of various chemical forms (As(V), As(III), MMAA or DMAA) between a solid well-defined geologic phase and an aqueous phase was measured as a function of pH, As-concentrations and the presence of a fulvic acid (FA). The samples were prepared in a ratio of 25 g L⁻¹ by adding 19.0 mL of the aqueous phase into a 50-mL polycarbonate centrifuge tube containing 0.500 g of the solid sorbent. After pH-adjustment the samples were pre-equilibrated for 2 d. Appropriate amounts of As(V), As(III), MMAA or DMAA stock solutions (with ⁷⁴As) were added to give a total preselected As concentration. In some of the systems a FA solution was added. Readjustment of pH was made to give the desired pH values. The aqueous volume was finally adjusted to 20.0 mL, and the samples were placed in a shaking table at room temperature (23 ± 1 °C). Preliminary experiments indicated that adsorption pseudo equilibrium was reached within 3 d for As(V), MMAA and DMAA and within 12 hr for As(III). After equilibrium (3 d or 12 hr, respectively), the aqueous phase was separated from the solid by centrifugation (5500 rpm for 15 min). An aliquot of the supernatant was taken for analysis of ⁷⁴As (scintillation counting) and the final pH of the solution was measured.

3. Results

3.1. EFFECTS OF pH

The adsorption of As(V) (10^{-6} M) onto three different solids is plotted against final pH in Figure 1 (expressed as decimal logarithm of the distribution coefficient, K_d , $\text{dm}^3 \text{kg}^{-1}$). The amount of As(V) adsorbed by alumina increased with pH to a maximum value at pH around 5 and then decreased with increasing pH. A similar adsorption pattern was also observed for hematite with a maximum at pH around 6. The adsorption on quartz was invariably low in the pH range studied.

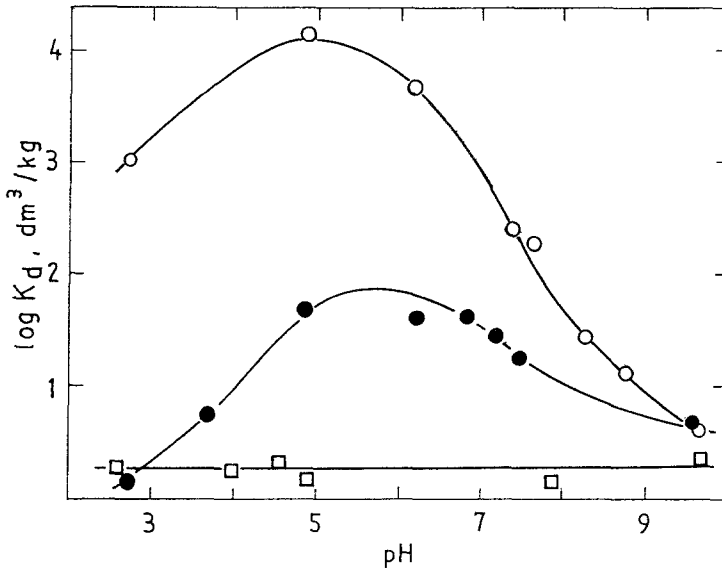


Figure 1. Adsorption of As(V) as a function of pH ($[\text{As}] = 10^{-6}$ M; adsorbent/solution = 25 g L^{-1}):
 ○ alumina, ● hematite, □ quartz.

Figure 2 shows the adsorption of As(V), As(III), MMAA and DMAA on alumina at various pH. As observed for As(V), the adsorption of As(III), MMAA and DMAA was also pH-dependent with adsorption maxima at pH around 7 for As(III) and at pH 4 for both MMAA and DMAA. The adsorption was significantly higher for As(V) than for any of the other forms in the pH range 3 to 8, while the adsorption of As(III) and MMAA/DMAA was of similar level.

3.2. EFFECTS OF ARSENIC CONCENTRATION

Adsorption isotherms of As(V) and As(III) on alumina at pH 7.6 are given in Figure 3. For both As(V) and As(III) the isotherms are linear at low As concentration (below 10^{-6} M). This indicates

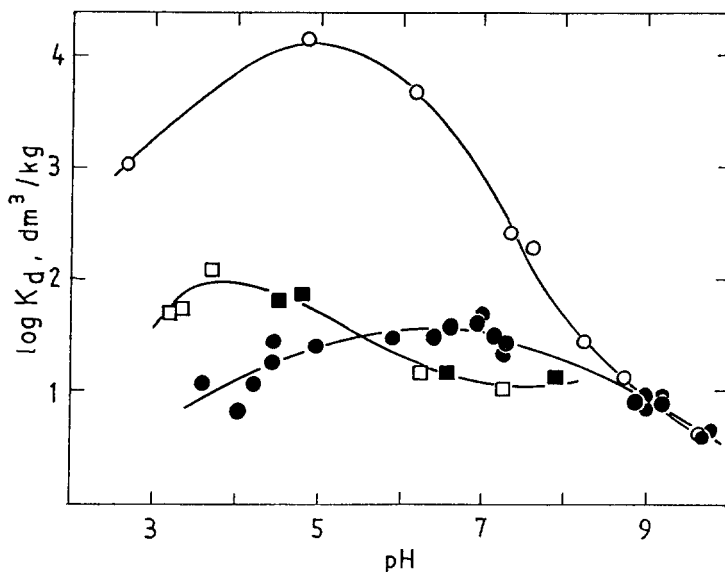


Figure 2. Adsorption of As(V), As(III), MMAA and DMAA on alumina as a function of pH ([As(V)], [As(III)] = 10^{-6} M, [MMAA], [DMAA] = 10^{-8} M; adsorbent/solution = 25 g L^{-1}): \circ As(V), \bullet As(III), \square MMAA, \blacksquare DMAA.

that a significant loading of the alumina phase appears already at total As concentrations above 10^{-6} M. A higher adsorption capacity for As(V) compared to As(III) is clearly shown by Figure 3.

3.3. EFFECTS OF FULVIC ACID

The effects of FA on the adsorption of As(V) and As(III) on alumina are illustrated in Figure 4. Generally, the presence of FA decreased the As adsorption in the pH range 4 to 8. The decrease of the adsorption of As(V) was minor at FA concentration of 10 mg L^{-1} or lower and large as the concentration increased to 25 mg L^{-1} . A slight reduction of the adsorption of As(III) was observed at 10 mg L^{-1} FA. Further increasing FA levels did not markedly change the adsorption. In the strong acidic (pH 3) and basic conditions (pH 9), the effects of FA were minor.

4. Discussion

4.1. ADSORPTION PROCESSES

The adsorption of all the studied As forms is strongly affected by pH. This can be attributed to the fact that the distribution of As species and the development of surface charge on the solids are also pH-dependent. Assuming the stability constants in Table I, the distribution of As species in the aqueous media is given in Figure 5.

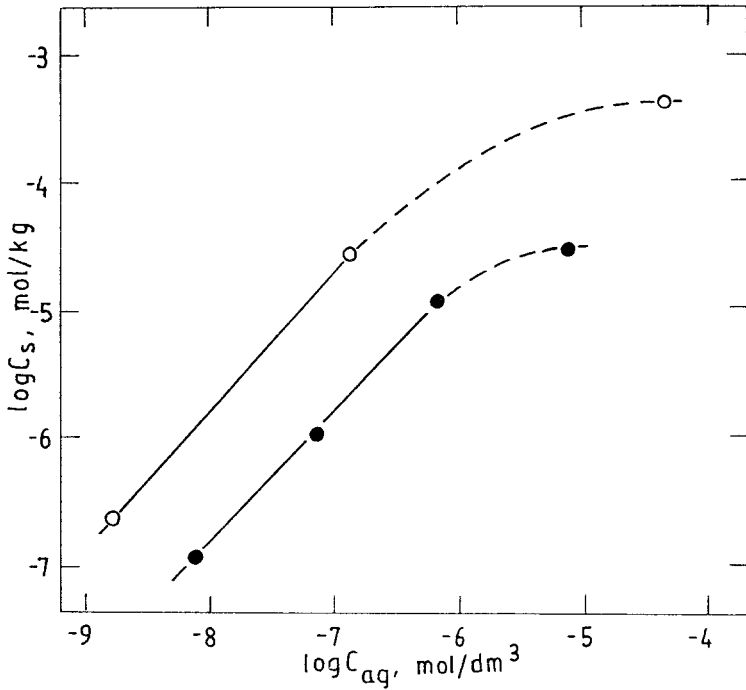


Figure 3. Adsorption isotherms for As(V) and As(III) on alumina (pH 7.6; adsorbent/solution = 25 g L⁻¹):
 ○ As(V), ● As(III).

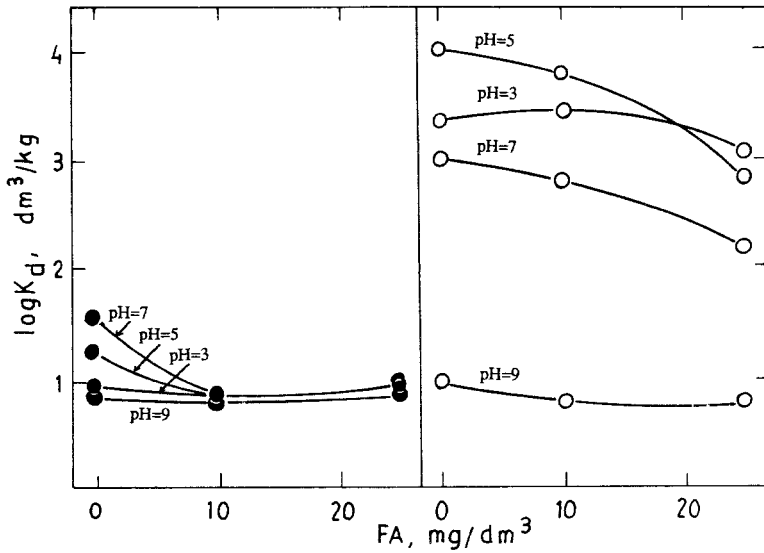


Figure 4. Adsorption of As(V) and As(III) on alumina as a function of FA and pH ([As] = 10⁻⁶ M; adsorbent/solution = 25 g L⁻¹): ○ As(V), ● As(III).

TABLE I. Acid dissociation constants of As species

Arsenic species	pK ₁	pK ₂	pK ₃
H ₃ AsO ₄ ^a	2.2	6.9	11.5
H ₃ AsO ₃ ^b	9.2	12.1	12.7
CH ₃ AsO(OH) ₂ ^a	3.6	8.2	
(CH ₃) ₂ AsO(OH) ^a	6.2		

^a From Baes and Mesmer (1976).

^b From Sadiq *et al.* (1983).

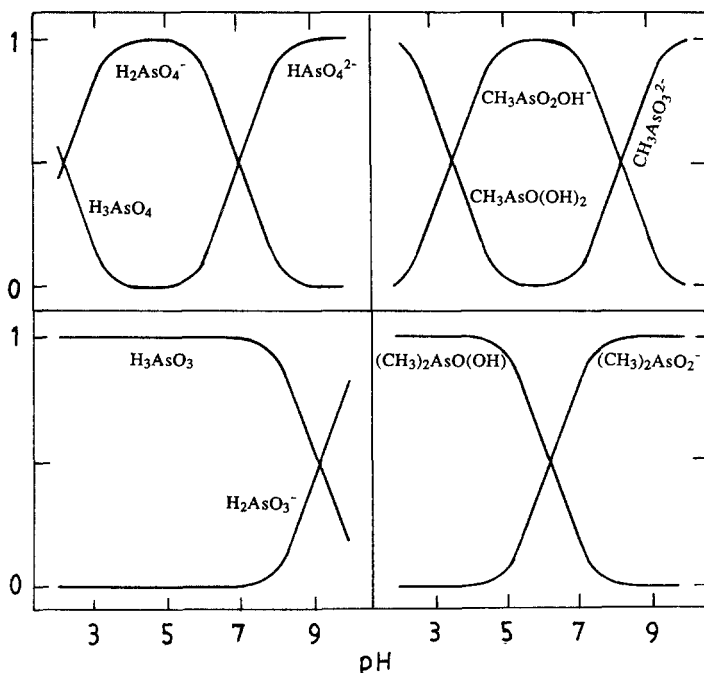


Figure 5. Distribution of As-species as a function of pH (c.f. Table I).

Obviously, H₂AsO₄⁻ and HAsO₄²⁻ are the main As(V) species in the systems studied. When pH < p*H*_{ZPC}, the surfaces are positively charged, and the adsorption of anions is favorable due to coulombic attraction. When pH > p*H*_{ZPC}, the surfaces are negatively charged and the anion adsorption is limited. Since p*H*_{ZPC} is around 6.5 to 7 for the varieties of alumina and hematite of the present study (Xu *et al.*, 1988), the surface is negatively charged at pH above this level. This could explain why the adsorption of As(V) on alumina and hematite drastically decreases at pH 6 and 7, respectively. For quartz, p*H*_{ZPC} is around 2. Hence, there is always a negative charge on the surface in the pH range studied, and the adsorption of anions is suppressed.

However, the decrease of As(V) adsorption on alumina and hematite at pH below 4 is unexpected. Based on the solubility products of Al(OH)₃(s) (log*K*_s = -35) and Fe(OH)₃(s)

($\log K_S = -38.3$), Al^{3+} and Fe^{3+} could be released under acidic conditions. The maximum concentrations of Al^{3+} and Fe^{3+} are however, not high enough to form solid $AlAsO_4(s)$ and $FeAsO_4(s)$ (Xu *et al.*, 1988). One possible interaction of Al^{3+} and Fe^{3+} with As anions is the formation of positively charged $Al^{3+}-H_2AsO_4^-$ or $Fe^{3+}-H_2AsO_4^-$ complexes. If these complexes are formed, there could be a pronounced reduction of the adsorption of As(V) at pH below pH_{ZPC} . Also the shift of the $H_3AsO_4/H_2AsO_4^-$ ratio at pH below 3 would have a similar effect.

In contrast to As(V), the neutral H_3AsO_3 is the dominant As(III) species at pH below 9. A maximum adsorption is observed at pH value close to pH_{ZPC} of alumina. The adsorption of As(III) decreases when the surface is positively charged in strongly acidic media as well as negatively charged in basic media.

The organic forms MMAA and DMAA are also deprotonated at high pH. Thus, a low adsorption of MMAA and DMAA at pH above pH_{ZPC} is related to the electrostatic repulsion. However, the observed maximum adsorption of MMAA and DMAA around pH 4 can not be explained solely by electrostatic interactions but suggests other sorption mechanism.

The fulvic acid is mainly present as an anion in the systems studied. Thus, FA can compete with As for the positively charged sites on the solid surface. The negative effect of FA on As(V) adsorption is stronger at 10 than at 25 mg L⁻¹ FA. On the other hand, the decrease of As(III) adsorption by FA is similar at these two concentration levels. This may imply a difference in the adsorption mechanisms between As(V) and As(III). For As(III), some specific adsorption may be the major mechanism, while for As(V), in addition to specific adsorption, electrostatic attraction may play an important role.

4.2. MOBILITY

The substantial difference in adsorption behavior between As(V), As(III), MMAA and DMAA suggests that the speciation largely determines the mobility of As in natural water systems. The distribution of inorganic As species is controlled by a combination of redox potential (Eh) and pH, as illustrated in Figure 6 (based on data by Ferguson and Gavis, 1972; Wagemann, 1978; Sadiq *et al.* 1983). Microbiological activity would also play an important role for the formation of organic species.

Thus, the As(III)/As(V) ratio, related to the redox potential and strongly affected by pH, is perhaps the most important factor influencing the overall leachability and mobility of As in water/soil systems. Blakey (1984) reported that under anaerobic conditions, the conversion of As(V) to As(III) in leachates from domestic waste was more than 80% at pH 5 and 7, and only 10% at pH 9 within 25 weeks. Significant volatilization of As due to microbiological activity was observed in the neutral leachate. Coprecipitation of As(V) with ferric hydroxide was only observed at pH 7 and 9.

The mobility of As in reducing sulfidic sediments was studied by Moore *et al.* (1988). The concentration of As in the pore water was low in the oxidizing zone and increased with decreasing Eh. At very low Eh, however, the As concentrations suddenly decreased. Based on the Eh-pH diagram (Figure 6), As(V) would prevail at pH 7 to 8 in the oxidizing zone. Since As(V) could be more efficiently adsorbed by metal hydroxides than As(III) at pH below 8, the concentration of As in the pore water would be low. Under anoxic conditions, As(III) becomes dominant. The poor adsorption of As(III) on the sediments results in higher As concentrations in the aqueous phase. Also, the dissolution of iron hydroxide with decreasing pH could increase the release of As into the pore water. At very low Eh, arsenic sulfides could precipitate, which could explain the sudden decrease of As in solution in such systems.

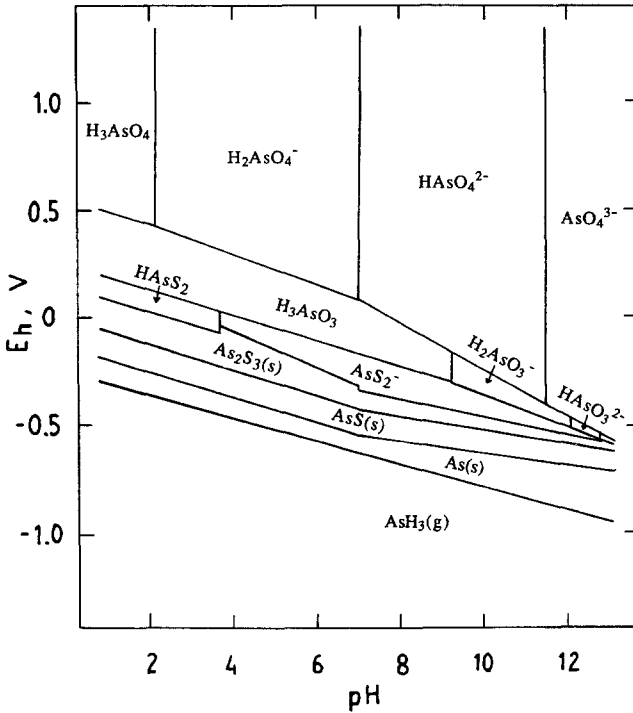


Figure 6. Eh/pH- diagram for As ($[As] = 10^{-6}$ M, $[S] = 10^{-3}$ M, 25 °C, 1 atm).

Apparently, a high concentration of As in the pore water under mildly reducing conditions is generally related to the domination of As(III). Likewise, it was reported that As(III) was the mobile form of As from sediments to waters in Lake Ohakuri (Aggett and O'Brien, 1985; Aggett and Kriegman, 1988).

The speciation of As in groundwater has recently been studied (Xu *et al.*, 1990b). The total As concentrations from 66 groundwater wells was positively related to pH (from 6.2 to 7.7). The ratio of As(III)/As(V) was around 1.0 in 5 wells with relatively high As levels (from 0.2 to 3 μ M). The concentration of ferrous iron was high (40 to 50 μ M) in two wells with extremely high concentrations of As (up to 3 μ M), which indicated reducing conditions in the wells. No As(III) could be detected in the wells with lower As concentrations (below 0.1 μ M). Neither MMAA nor DMAA was found in all these samples. Thus, high concentrations of As in the groundwater was related to As(III), and the increase of As concentrations with pH probably indicates a reduction of the adsorption of As(V) by geologic phases.

5. Conclusions

The adsorption of As on the selected geological phases is related to the chemical speciation which is highly dependent on pH as well as Eh and microbiological activity. High adsorption of As(V) at low pH is related to electrostatic interactions between the As(V) anions and the solid surface. The adsorption of As(V) is generally higher than that of As(III) and the organic forms. The presence of humics could further reduce the adsorption.

A continuing acid deposition could consume the buffer capacities in the intermediate and high pH-range and finally result in a sudden decrease of pH in soil and groundwaters. A reduced pH in combination with reducing conditions will enhance the As(III)/As(V) ratio, which in turn increases the leaching of As from geologic phases to the waters. A decrease of pH (between 6 to 7 down to 4) under oxidizing conditions could reduce As concentrations however, due to an increasing adsorption of As(V) by e.g. soil component. Reduced biological activity due to acidification would affect the formation of organic As forms.

Thus, acidification would no doubt have a significant effect on As-mobility in the environment, but in a complex way. Under *reducing* conditions the predominance of As(III) over As(V) and the release of As from iron hydroxide phases would lead to enhanced mobility and aqueous concentrations with decreasing pH. Under *oxidizing* conditions, however, a slight reduction of pH would reduce the mobility due to enhanced adsorption, and perhaps precipitation/coprecipitation with iron. However, a large pH reduction (to 4 or lower) would enhance the mobility even under oxidizing conditions. Humic substance would affect the overall mobility at concentration levels of 10 mg L⁻¹ or above.

Acknowledgments

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References

- Aggett, J. and Kriegman, M.R.: 1988, *Water Res.* **22**, 407.
- Aggett, J. and O'Brien, G.A.: 1985, *Environ. Sci. Technol.* **19**, 231.
- Anderson, M.A., Ferguson, J.F., and Gavis, J.: 1976, *J. Colloid Interface Sci.* **54**, 391.
- Baker, M.D., Wong, P.T.S., Chau, Y.K., Mayfield, C.I. and Inniss, W.E.: 1983, *Can. J. Fish Aquat. Sci.* **40**, 1254.
- Baes, C.F., Jr. and Mesmer, R.E.: 1976, *The Hydrolysis of Cations*, John Wiley and Sons, New York, p. 366.
- Blakey, N.C.: 1984, *J. WPCF* **56**, 69.
- Brannon, J.M., Plumb, R.H., Jr. and Smith, I., Jr.: 1980, 'Long-term release of heavy metals from sediments from sediments'. *Contaminants and Sediments, Vol. 2, Analysis, Chemistry, Biology* (R.A. Baker, Ed.), Ann Arbor Science, Ann Arbor, p. 221.
- Ephraim, J.H., Boren, H., Arsenie, I., Pettersson, C. and Allard, B.: 1989, *Sci. Total Environ.* **81/82**, 615.
- Ferguson, J.F. and Gavis, J.: 1972, *Water Res.* **6**, 1259.
- Frost, R.R. and Griffin, R.A.: 1977, *Soil Sci. Soc. America* **41**, 53.
- Gupta, S.K. and Chen, K.Y.: 1978, *Water Poll. Control Fed. J.* **50**, 493.

- Khourey, C.J., Matisoff, G., Strain, W.H. and Varnes, A.W.: 1983, *Trace Subst. Environ. Health* **17**, 174.
- Moore, J.N., Ficklin, W.H. and Johns, C.: 1988, *Environ. Sci. Technol.* **22**, 432.
- Pierce, M.L. and Moore, C.B.: 1982, *Water Res.* **16**, 1247.
- Sadiq, M., Zaidi, T.H. and Mian, A.A.: 1983, *Water Air Soil Poll.* **20**, 369.
- Schlicher, R. and Ghosh, M.M.: 1985, *AIChE Symposium Series* **81**, 152.
- Singh, D.B., Prasad, G., Rupainwar, D.C. and Singh, V.N.: 1988, *Water Air Soil Poll.* **42**, 373.
- Sary, J., Zeman, A. and Kratzer, K.: 1982, *Radiochem. Radioanal. Letters* **52**, 263.
- Wagemann, R.: 1978, *Water Res.* **12**, 139.
- Wong, P.T.S., Chau, Y.K., Luxon, L. and Bengert, G.A.: 1977, *Trace Subst. Environ. Health* **11**, 100.
- Xu, H., Allard, B. and Grimvall, A.: 1988, *Water Air Soil Poll.* **40**, 293.
- Xu, H., Allard, B. and Grimvall, A.: 1990a, 'Influence of pH and organic substance on the adsorption of As(III) on alumina'. Submitted to *Sci. Total Environ.* .
- Xu, H., Allard, B., Grimvall, A. and Boren, H.: 1990b, 'Arsenic concentration and speciation in groundwaters - a case study'. Submitted to *Vatten*.