

Influence of humic and low molecular weight organic acids on arsenic mobility in contaminated soils

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Abstract

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A comparative study on the effect of humic acid and some low molecular weight organic acids, (phthalic, oxalic, and citric) on the mobilization of arsenic has been studied by adding different concentrations of the organic acids to the natural level of an arsenic contaminated soil.

All the organic acids studied were found to enhance the release of arsenic from soil. However, the magnitude of enhancement was not found to be the same. The low molecular weight organic acids were more effective in mobilizing arsenic as compared to humic acid in the pH values studied (3, 5, and 7). In the case of the low molecular weight organic acids investigated the soluble arsenic concentration has been found to increase substantially as the quantity of the organic acids added to the soil increased and a decrease in the solubility of arsenic was observed with increasing pH. With humic acid unlike in the case of the low molecular weight organic acids the solubility of arsenic has been found to increase with an increase in pH.

INTRODUCTION

Arsenic, which is toxic to man and other living organisms, presents potentially serious environmental problems throughout the world. It is a commonly occurring toxic metal in natural ecosystems (McKeague J.A *et al* 1986, Tan K.H 1986). It can cause toxic effects to plants or may accumulate in plants and thereby enter the animal and human food chain.

Soil Organic Matter (SOM) is one of the oldest research subjects in soil science. Despite the huge bulk of scientific knowledge that has accumulated in the meantime, the concept of SOM are still quite fuzzy. A major reason is the intricate structure of feedback effects which makes it extremely difficult to clearly separate different factors and mechanisms. Correlations between concentrations of dissolved metals and of either dissolved organic matter (DOM) or organic acids in infiltrating waters suggest that DOM, or some component of DOM, facilitates metal solubilization and translocation in soil. Transformations of biogenic compounds, through partial degradation and polymerization, result in the formation of structurally ill-defined mixture of humic substances, a term used to include both humic and fulvic acids (Hering J.G 1995). Both fulvic and low molecular weight humic acids are generally considered to be important chemical weathering agents (Fox T.R and Comerford N.B 1990, Manley E.P and Evans L.J 1986, Robert M and Berthelin J 1986, Ugolini F.C and

Spaltenstein H 1992). The ability of humic and fulvic acids to form stable complexes with metal ions is based on their high content of electron-donor functional groups, in particular -COOH and phenolic -OH but also -OCH₃, -NH₂, =N-, -SH and -C=O (Schulin R *et al* 1995). Fulvic acids are fairly strong acids (about half of the carboxyl groups are dissociated at pH = 3.5), and humic acids are dissociated to the extent of 50% only at pH = 6 (Schulin R *et al* 1995).

It is also well known that plants directly influence the soil chemical environment through the generation of weathering agents. The basic processes whereby plants directly influence the soil chemical environment is through the generation of weathering agents, biocycling of cations, and the production of biogenic minerals (Banks M.K. *et al* 1994, Kelly E.F. *et al* 1998). The identifiable compounds produced directly by plants encompass a range of acids including: oxalic, citric, malic, succinic, gallic, aspartic and salicylic. Some of these are derived directly from higher plant substance but in many cases the derivation is not necessarily clear (Pohlman A.A. and McColl J.G. 1988). Although low molecular weight organic acids are only minor constituents of soil DOM, these compounds have been identified both in soil solutions and in leachates of forest litter and soils. Concentrations of low molecular weight organic acids up to 1.2 mM have been measured in leachates of forest litter and soil, corresponding to up to 5% of the DOM in leachates (Fox T.R. and Comerford N.B. 1990). Oxalate concentrations as high as 1 mM have been measured in soil solutions (Hendershot W.H. and Duquette M. 1976). In some soils concentrations of low molecular weight organic acids are high enough that salts of the acids are precipitated.

Concerning the influence of humic substances on weathering kinetics, while most studies reported a significant enhancement of mineral dissolution in the presence of humic or fulvic acids (Huang W.H. and Keller W.D. 1972, Tan K.H. 1980, Tan K.H. 1986) controversial ideas which suggest that humic substances had either no effect or an inhibitory effect on the dissolution of minerals have also been reported (Chin P.-K.F. and Mills G.L. 1991, Ochs M. *et al* 1993). This suggests that there is a real lack of clarity regarding the influence of humic acids on mineral dissolution rates. In the present study, we investigated the effect of humic acid and other low molecular weight organic ligands (citrate, oxalate and phthalate) on the dissolution kinetics of arsenic in a soil collected from the oxidizing zone of an arsenic rich soil in an attempt to answer the question whether these organic ligands enhance or inhibit the weathering of arsenic from soil or from arsenic bearing minerals.

MATERIALS AND METHODS

The soil sample was collected from the till layer (upper 20 cm) of a grazing land in southern part of Austria. The soil was air-dried, coarse stones and gravel were removed by hand picking from the air-dry soil. The gravel and stone free soil was then homogenized by using a self-made rotating mixer. A portion of the homogenized air-dry soil was allowed to pass through a 2-mm mesh prior to mixing with the required amounts of the organic acids.

Four levels (0, 10, 20, or 30 g kg⁻¹ of the air-dry soil on mass basis) of each of the organic acids: humic acid (10-15% ash content, Fluka, 53680), Citric acid (Fluka, p.a. 27490), Phthalic acid (Merck, p.a. 9611), oxalic acid (Merck, p.a. 8510267), were thoroughly mixed with 4.0 g of soil in a 50 mL centrifuge tube. Milli-Q water (20 mL) was added to each of the

soil-organic acid mixtures and shaken for about 10 minutes. The pH of the treatments were adjusted to 3, 5, or 7 and allowed to equilibrate for 1 h. A second pH adjustment was conducted for the observed change from the originally adjusted values after a 1 h of equilibration time. Each treatment was replicated three times. Varying amounts of solid calcium hydroxide (Merck, p.a. 2047) and 0.4 M nitric acid (Merck, p.a. k24666456) were used for pH adjustment. The heterogeneous soil-organic acid mixtures were shaken on an end-over-end shaker at room temperature for three days to equilibrate the mixture completely. The resulting solution was then centrifuged on a Jouan B3 11 centrifuge at 3000 rpm for 30 minutes. The overlying clear solution was decanted and filtered through an S&S black ribbon filter paper. The filtrate was analyzed for its arsenic content by using a Graphite Furnace Atomic Absorption Spectrometer.

Sample analysis

The concentrations of some selected elements in the soil were determined by ICP-MS (VG Elemental, Winsford, UK) after mineralizing the soil in a microwave digestion system (MLS-1200 MEGA, Mls GmbH operating at a microwave frequency of 2450 MHz). The cation exchange capacity (CEC) of the soil was determined by extraction with 0.1 M barium chloride (Fluka, p.a. 11760) solution (18) and subsequently measuring the concentrations of Na, K, Mg, Ca, Al, Fe, and Mn on a UNICAM-929 Flame-AAS. The original pH of the soil collected from the field was measured in a 1:12.5 (soil: 0.01 M calcium chloride solution ratio) (Hendershot W H *et al* 1993). The soil suspension was allowed to stand overnight prior to pH determination by a pH meter. The dry ashing method (Karam A 1993) was used for the determination of soil organic matter content. The organic matter was removed by combustion of the soil sample at medium temperature (375 to 600 °C) in a temperature regulated muffle furnace and the percent organic matter content was obtained by subtracting the percent mineral content from the total mass.

RESULTS

In the soil water, which was collected without the addition of organic acids, the concentration of arsenic was found to increase very slightly with an increase in pH. The trend in the increment of arsenic concentration has been found to be similar to that obtained with the addition of humic acid.

Humic acid has been found to enhance the mobilization of arsenic in the soil in all the pH values studied. For a given amount of humic acid added, the concentration of dissolved arsenic increased with pH. At a fixed pH soluble arsenic has also been found to increase with increasing humic acid concentration (Fig. 1a). However, as compared to the other low molecular weight organic acids studied, the effect of humic acid on the dissolution of arsenic was not dramatic.

The low molecular organic acids studied were observed to enhance arsenic mobility but, with a different trend of dissolution characteristics than humic acid as the pH was raised. Citric and phthalic acids revealed a more or less similar trend in that, both of them solubilized arsenic remarkably at pH 3 and a decreased dissolution was observed as the pH increased for a given concentration of citric or phthalic acid added (Figs 1 b & c). Maximum dissolution of arsenic

with the addition of oxalic acid was obtained at pH 5 relative to the other pH values studied and the effect of dissolution was less pronounced at pH 7 as the concentration of oxalate added increased (Fig. 1d)

The equilibration time required for all the organic acids as a function of shaking time has been investigated. All the low molecular weight organic acids were found to reach equilibrium within 36 h of shaking time while humic acid required a minimum of 72 h of shaking time to obtain a constant concentration of arsenic (Fig. 2).

DISCUSSION

In alkaline and calcareous soils the dominant form of arsenic under oxic conditions is $\text{Ca}_3(\text{AsO}_4)_2$ while at lower pH values AlAsO_4 and FeAsO_4 are the prevalent arsenate species. In the soil water which was collected without the addition of the organic acids arsenic concentration has been found to increase with an increase in pH presumably by bringing about a change from aluminium and iron arsenates to calcium arsenate which is more soluble. Such enhancement of arsenic mobility has been observed when the pH of a soil was raised by liming (Furrer G. and Stumm W 1986)

A number of factors could be responsible for the observed increase in arsenic solubility with an increase in pH. At lower pH values more functional groups on a humic molecule will be protonated and be unavailable for the formation of coordinative bonds with the metal centers; thus, decreased humate-promoted dissolution of arsenic is observed. As the pH was raised most of the humic acid molecules get dissociated and acquire more coordination sites for the formation of bi- or polydentate coordination complexes. The bidentate complexes will notably promote the dissolution process than the polydentate complexes. The detachment of metal centers could be hampered in the case of polydentate complexes because the simultaneous breaking of several metal-O⁻ bonds would be required for a detachment, making the process more unlikely with an increasing number of complexed surface metal centers. On the other hand humic acid consists of very huge molecules with a number of different types of functional groups. When isolated segments of the humate molecules form complexes with the metal centers to which arsenic is bound, the overall effect on the solubility of arsenic should be the resultant of the stabilities of the variety of complexes formed.

In the literature (Huang W.H and Keller W.D 1972) it is reported that with strongly complexing acids a relatively high concentration of Al and Fe was found to dissolve due to the formation of stable water-soluble Al or Fe complexes or chelates in the solution. Thus, in our study, the relatively higher dissolution of arsenic with citric acid (strongly complexing, hydroxy tricarboxylic aliphatic acid) may reveal the fact that the mobilization of arsenic from the soil undergoes mainly by the complexation of the organic ligands with the metal center to which arsenic is bound and there by releasing arsenic into solution. In addition to this, As(III) and As(V) are known to be readily adsorbed onto amorphous hydrous iron oxides which are soluble at low temperature. The relatively higher solubility of e.g. iron hydroxides at low pH values could lead to a release of iron-bound As from soils to waters (Ross S.M 1994, Schulin R *et al* 1995, Tan K.H 1986). This fact could be a supplementary factor for the higher dissolution of arsenic at lower pH values in the case of citric and phthalic acids. In organic

acid systems, the dissolution behaviour depends on the complexing properties and the stability of the complexes which the acids form at different pH and Eh conditions (Ochs M *et al* 1993). Oxalic acid has been found to dissolve arsenic from the soil, better at pH 5 than at pH 3 and 7. This may indicate that in the soil, oxalate forms stable complexes at pH 5 as compared to the other pH values.

Conclusion

Humic acid and all the investigated low molecular weight organic acids appreciably increase arsenic mobility in soil. The effect of a particular organic acid on arsenic mobility depends on its capacity to form stable complexes with the central atoms to which arsenic is bound under the existing ionic strength and pH condition. Iron and aluminum compounds of arsenic (arsenates) are usually insoluble at the normal soil pH range. However, the solubility of these substances is enhanced by complex formation of Fe and Al with soil organic acids.

Humic acid is comprised of a multiligand mixture. The observed contrasting influence of the low molecular weight organic acids and humic acid on the dissolution of arsenic at an increasing pH suggests that, in this regard, a single low molecular weight organic acid ligand could not be an appropriate model for the more structurally complex geopolymers such as humic acids.

Shaking time

The shaking time required for equilibration was about 36 h for the low molecular weight organic acids studied while humic acid required a minimum of 72 h of shaking time to acquire a constant value of arsenic concentration (Fig.2). The prolonged shaking time required for humic acid may indicate that the humate-promoted solubilization process of arsenic passes through certain intricate reaction steps. The longer shaking time might have facilitated the possible chemical and physical interaction between iron or aluminium arsenate species and humate molecules, finally leading to the cleavage of parts from the humate molecule and formation of isolated segments which stabilize arsenate in solution.

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Table 1. Some properties of the soil

Property	Value
PH	4.6
Effective CEC	4.2 cmol kg ⁻¹
Organic matter	9.5 %

Table 2 Concentrations of some selected elements in the soil digest

Element	Concentration. mg kg ⁻¹	Element	Concentration mg kg ⁻¹
Na	8298±1100	As	2000±390
Al	7777±580	Pb	1082±200
Ca	4620±40	Mn	800±12
Mg	4303±75	Ba	590±198
K	3401±480	Ni	222±7
Fe	2350±70	Cr	200±10

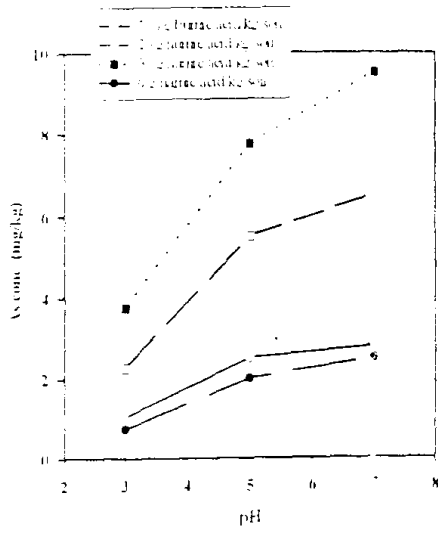


Fig. 1a

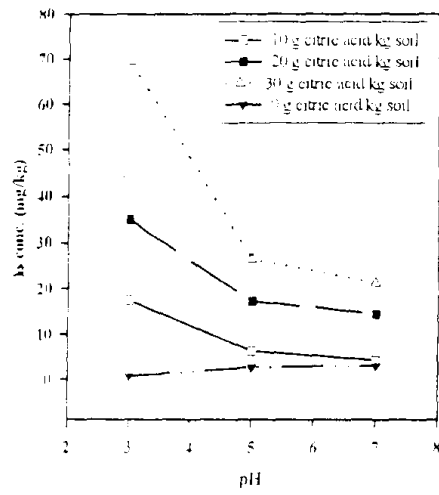


Fig. 1b

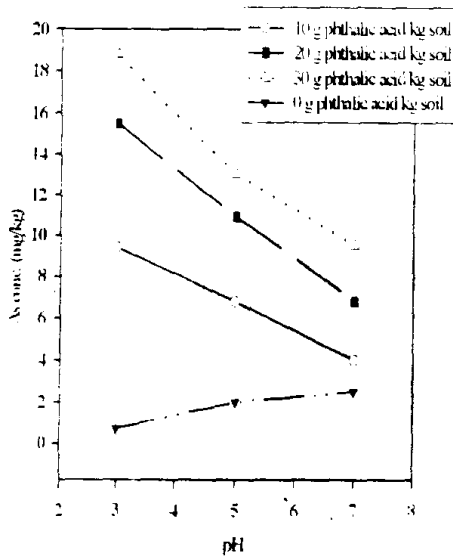


Fig. 1c

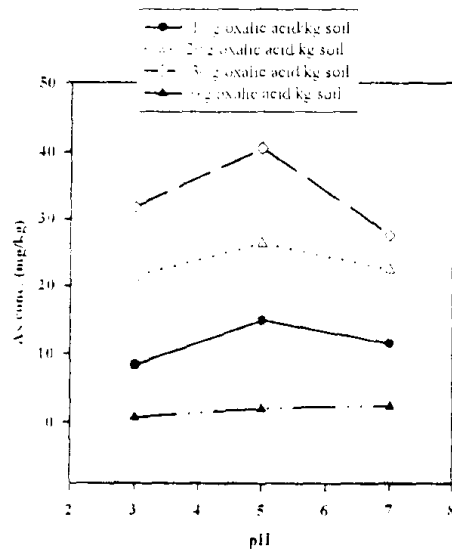


Fig. 1d

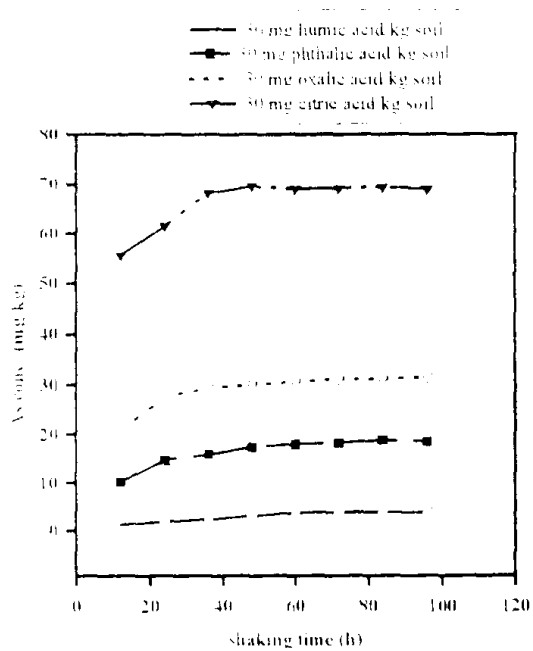


Fig. 2

Fig. 1. The influence of a) humic b) citric c) phthalic and d) oxalic acids on the dissolution of arsenic in soil as a function of pH

Fig. 2. The influence of shaking time on equilibration.