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Arsenic’s Interaction with Humic Acid

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Environmental Context
Arsenic is of significant environmental concern in much of the world, because of its contamination of waters, from mining, industry, sewage disposal and agriculture. The environmental mobility of arsenic is controlled primarily by adsorption onto metal oxides, especially iron. Humic substances (natural organic matter), which are ubiquitous in aquatic and soil environments, may interfere with this adsorption and arsenic mobility may be increased. Thus, even if it is assumed that humic substances sorb arsenic less strongly than hydrous iron oxides, they may, nevertheless, influence arsenic sorption and mobility, particularly when the iron oxide content in the environment is low.

Abstract
The environmental mobility of arsenic is primarily controlled by adsorption onto metal oxide surfaces, particularly iron, aluminium and manganese. Humic acid (HA) may interfere with this adsorption, thereby increasing arsenic mobility. This study has characterised the interaction of arsenic with HA in a system consisting of HA with As(III), As(V) and DMAA. Three sets of batch experiments were performed at varying pH (3-12), ionic strength (I = 0 - 0.4), concentration of each arsenic species (0 - 100 mg dm$^{-3}$) and HA concentration (0 - 10 g dm$^{-3}$). Arsenic species were shown to react with humic acid. The interaction is postulated to involve bridging metals and deprotonated functional groups within the HA. The association is dependent on pH, ionic strength and arsenic concentration. The extent of the interaction was greater in the pH range 8 – 10 for As(V) and DMAA, while it extended to pH 12 for As(III). The strong pH dependency is probably due to the aqueous speciation of arsenic. The
logarithmic conditional association constants for the reactions were found to be $1.97 \pm 0.02$, $1.58 \pm 0.07$ and $1.50 \pm 0.10$ for As(V), As(III) and DMAA respectively. These values indicate the formation of weak complexes with humic acid.

**Keywords**
Arsenic, Humic Substances, Speciation, ICP-AES

**Introduction**
Arsenic is a toxic element of significant environmental concern because of its contamination of surface, ground and drinking waters throughout the world\textsuperscript{[1-2]}. Arsenic contamination arises from mining and industrial operations, sewage disposal and agriculture. Major problems have been reported in Bangladesh, Vietnam, China and India\textsuperscript{[2-4]}. The toxic effects on humans result in nervous, vascular and reproductive disorders, gangrea (blackfoot disease) and cancer (skin, bladder and lung)\textsuperscript{[5]}. Arsenic exists in natural environments primarily as the oxyacids of As(V) (arsenates), and of As(III) (arsenites)\textsuperscript{[6]}. The two forms can co-exist because of the relatively slow redox transformation involved\textsuperscript{[7]}. Organic forms are also found, e.g. monomethylarsonic (MMAA) and dimethylarsinic acids (DMAA)\textsuperscript{[6,8-9]}. In general As(III) species are more toxic\textsuperscript{[10]}, soluble and mobile than As(V) species in the environment\textsuperscript{[11]}. 

The mobility of arsenic in natural systems is mainly controlled by adsorption onto metal oxide surfaces\textsuperscript{[12-13]}, involving surface complexation reactions in which the oxygen moiety of the arsenate or arsenite, displaces a hydroxyl group on the metal oxide surface, to generate an inner-sphere complex\textsuperscript{[14-15]}. The oxides of iron, aluminium and manganese are the most important sorbents of arsenic in natural systems\textsuperscript{[16-17]}. Natural organic matter (NOM) is a potentially important factor influencing arsenic biogeochemistry and other heavy metal pollutants\textsuperscript{[18]}. Operationally defined fractions of NOM known as humic and fulvic acids may interfere strongly with arsenic adsorption under some circumstances\textsuperscript{[19-20]} and arsenic mobility may be increased by their presence in soil\textsuperscript{[21]}. The parameters governing these effects are not well understood.
There are few studies dealing with the chemical interaction of arsenic and NOM, considering that NOM is ubiquitous in the environment. Humic acid comprises 50% of NOM\textsuperscript{[22]} and is a unique anionic polyelectrolyte at all pH values. It is known to catalyse both oxidative and reductive reactions among chemical species, in part by the quinine-mediated formation of free radicals\textsuperscript{[23-24]}, and it readily forms both aqueous and surface inner-surface complexes with cationic metals and metal oxides\textsuperscript{[25]}. Aqueous HA metal complexes may in turn associate strongly with other dissolved anions to form mixed complexes, presumably by metal-bridging mechanisms\textsuperscript{[26]}.

Numerous studies have been conducted on arsenic sorption on oxy-hydroxides of iron and aluminium\textsuperscript{[27-31]}, lake and stream sediments\textsuperscript{[32]}, clays\textsuperscript{[19,33]} and soils\textsuperscript{[34-37]}, but only one of these has considered the interactions with humic acid\textsuperscript{[26]}. Similarly, many laboratory studies have focused on cation binding to humic acid and have yielded a considerable body of data\textsuperscript{[38]}. Thus, even if it is assumed that humic acid adsorbs less arsenic than hydrous iron oxides, it may, nevertheless, influence arsenic sorption and mobility, especially when the iron oxide content in the environment is low. Understanding the interactions of arsenic with humic acid in clean laboratory systems, will help in the understanding of its behaviour in complex systems in the environment. Therefore, the objectives of this study were to characterise arsenic speciation in a system consisting of soluble HA and arsenic, and to investigate the extent of its interaction with HA.

2. Experimental
The experimental procedure consisted of purifying Aldrich humic acid, and then studying arsenic species (As(V), As(III) and DMAA) interaction with HA using batch experiments under varying conditions of pH, ionic strength and HA and arsenic concentration.

2.1 Materials
The HA was purified by precipitation using the method described by Warwick \textit{et al.}\textsuperscript{[39]}. The analytical data are shown in King \textit{et al.}\textsuperscript{[40]}. Arsenic inorganic salts were supplied by Across Organics, UK as the pentoxide (As$_2$O$_5$) and trioxide salt (As$_2$O$_3$) with a purity of 99.99 %. The dimethylarsinic acid salt was supplied by Fluka Chemika, UK under the commercial name of cacodylic acid with a purity of 99 %. All
other reagents used in this work were high purity reagent grades supplied by Fisher Scientific, UK

2.2 Stock solutions
A 2000 mg dm$^{-3}$ humic acid stock solution was prepared by dissolving 2 g of HA in 1 dm$^3$ of milliQ water, at pH 9.0 ± 0.1. The non-dissolved HA fraction was removed by centrifugation at 3000 r.p.m. for 15 minutes using a Beckman UK, L8-55M ultracentrifuge. The final concentration of HA was expressed in terms of the proton exchange capacity (PEC), which was determined by titration$^{[41]}$ as 5.3 x 10$^{-3}$ mol g$^{-1}$. Stock solutions containing 10 000 mg dm$^{-3}$ of As(V), As(III) and DMAA were prepared by dissolving the appropriate amounts of As$_2$O$_5$, As$_2$O$_3$ and (CH$_3$)$_2$AsOOH in milliQ water following standard procedures$^{[42-43]}$.

2.3 Arsenic species sorption on HA
Three sets of batch experiments were performed to study the interaction of As(III), As(V) and DMAA with humic acid. The experiments were repeated at varying pH (3-12), ionic strength (I = 0-0.4), concentration of each arsenic species (0-100 mg dm$^{-3}$) and HA concentration (0-10 g dm$^{-3}$). Batch experiments were performed using 20 ml polypropylene acid acid-washed vials. For pH adjustments, addition of small volumes of concentrated nitric acid or sodium hydroxide solutions were used. For ionic strength adjustments, potassium nitrate solution was used. Samples were put into an end-over-end mixer immersed in a water bath at 25°C. Following equilibration (24 h for As(V) and As (III); 30 d for DMAA) the samples were centrifuged at 7000 r.p.m. for 1 h using polysulphone membrane filter tubes (1000 MWCO PALL Life Science, UK). Typically > 99% of the HA was removed from solution even at pH 12. This was checked by measuring the amounts of HA in the filtrate by UV spectrophotometry. Control samples were prepared by simply omitting the HA for each set of batch experiments. Finally the filtrates (control and samples) were acidified (HCl : HNO$_3$, 2:1) and analysed for arsenic content using ICP-AES at a wavelength of 189.042 nm. A Thermo Jarrell Ash Atomic 16 model was used$^{[42-43]}$.

2.3 Isotherms
The interaction of arsenic species with HA may be described by sorption isotherms which show the relationship between the activity, or equilibrium concentration of the adsorbate, and the quantity of the adsorbent on the surface at constant temperature.

The degree of adsorption was calculated using the following equation,

\[
\Gamma (\text{mmoles/kg}) = \frac{([\text{As}]_i - [\text{As}]_f) \cdot V_t}{M}
\]

Where:
- \( M \) = mass of humic acid (kg)
- \([\text{As}]_i\) = initial concentration of arsenic species in the control (mmol dm\(^{-3}\))
- \([\text{As}]_f\) = equilibrium concentration of free Arsenic species (mmol dm\(^{-3}\))
- \( V_t\) = total volume of solution (dm\(^{-3}\))

2.4 Conditional association constants

An alternative to using isotherms is to calculate the conditional association constants for arsenic interactions with HA. The association reaction may be represented as:

\[
\text{As} + \text{HA} \rightleftharpoons \text{As-HA}
\]

(i.e. the reaction is assumed to be a one arsenic species to one binding site complex).

Based on this view of the reaction, conditional association constants (\( K_{\text{cond}} \)) can be derived at each pH using:

\[
K_{\text{cond}} = \frac{[\text{As-HA}]}{[\text{As}][\text{HA}]}
\]

Humic substances are a complex mixture of organic molecules and it is not possible to describe their complexation reactions in the same way as for the case of single ligand reactions. Thus the concept of stoichiometry is unclear and it is not really meaningful to report stoichiometries on a mole:mole basis, since many humic materials consist of a mixture of large polyelectrolytic molecules for which a simple integral value would not be expected\(^{44}\).
3 Results and discussion

3.1 Effect of pH on arsenic species interaction with humic acid

In order to determine which arsenic species is involved in the complexation at the various different pH values used, the distribution of arsenic species in solution as a function of pH has been calculated from known stability constants by many authors, and is repeated here using the speciation programme JCHESS\textsuperscript{[45]}. For As(III) (Fig. 1), the neutral species As(OH)$_3$ and HAsO$_2$ predominate up to about pH 9. The singly charged anionic species H$_2$AsO$_4^-$ and AsO$_3^-$ become significant between 9 and 11, and above pH 11 the speciation is dominated by the doubly-charged anionic species AsO$_2$OH$^2^-$. For As(V) (Fig. 2), the speciation is dominated by four different species in turn as the pH rises. Below pH 2 the neutral species H$_3$AsO$_4$ predominates; from 2 to 6.5 the singly charged anionic species H$_2$AsO$_4^-$ becomes the most significant; from pH 6.5 to 11 the speciation is dominated by the doubly-charged anionic HAsO$_4^{2-}$; and in very alkaline solutions above pH 11 AsO$_4^{3-}$ is the most common species. DMAA has been shown to produce (CH$_3$)$_2$AsO$_2^-$ as the main solution species at pH 8 – 9\textsuperscript{[34, 46-47]}.  

The sorption of arsenic species ($10^{-4}$ mol dm$^{-3}$) on humic acid ($10^{-3}$ mol dm$^{-3}$) was plotted against the final pH of the solution (Fig. 3). As(V) and DMAA, also an arsenic(V) species, recorded a maximum sorption between pH 8 and 9; while As(III) species showed continued increases in sorption up to pH 12.

The low sorption of arsenic at low pH (<5), has been explained by Thanabalasingam and Pickering\textsuperscript{[26]} to be due to the stronger protonation equilibria of both arsenic species and humic acid compared to sorption equilibria. However, as the pH increases, the humic acid becomes more soluble leaving associated counter ions in the form of humate salt or complexes, which may dissociate at high pH to yields hydrous oxides (e.g. Fe, Al) which adsorb As species\textsuperscript{[26]}. This may be responsible for the observation in this study of increased sorption from pH 8 for all arsenic species, whereas, Thanabalasingam and Pickering (1986), obtained maximum sorption for As (V) at pH 5.5. The difference in results may be due to improved separation techniques, where a 1000 MWCO (molecular weight cut off) ultracentrifuge filter device was used instead of the 0.45 µm membrane used by the previous authors.
Despite the pre-treatment for the removal of metal ions, the HA may still have contained small quantities of bridging metals, so it is possible that the arsenic species could have formed complexes with these bridging metals rather than the organic functional groups on the humic acid. However, these arsenic complexes remain weak in comparison to humic acid complexes with cations.

3.2 Effect of ionic strength on arsenic species interaction with humic acid

The effect of ionic strength on the amount of arsenic species bound to humic acid is shown in Fig 4. The ionic strength of the As–HA solutions were varied by using potassium nitrate (0 to 0.5 mol dm$^{-3}$). For all arsenic species, the amount bound to HA decreases with increasing ionic strength.

The effect of ionic strength on arsenic sorption may be attributed to changes in the surface chemical properties of the humic molecules$^{[36]}$. Increasing ionic strength increases the net negative charge on the humic molecules, therefore, for anions which may be binding through simple coulombic forces, increasing the ionic strength should decrease sorption above the Point of Zero Charge$^{[48-49]}$. For HA the surface is entirely negative for the pH range studied, but at high pH and low ionic strength, the molecules of HA are known to uncoil, providing more binding sites$^{[50]}$, which agrees with the finding of these studies.

3.3 Effect of increasing arsenic species concentrations

Experiments were carried out to investigate the effect of varying concentrations of arsenic species on the amount of arsenic bound to humic acid. These experiments were conducted at pH 5 and 9, and at ionic strengths 0.05 and 0.005 mol dm$^{-3}$ using KNO$_3$.

Fig. 5 gives the results at pH 5 and 0.05 mol dm$^{-3}$ ionic strength. About 10 % of the total As(V) sorbed to the HA, along with about 5 % of As(III) and DMAA. Maximum sorption of 16 ± 4.5 mmol kg$^{-1}$ for As (III) and 13 ± 3.5 mmol kg$^{-1}$ for DMAA was reached at 0.03 mmol dm$^{-3}$ As(III) and 0.028 mmol dm$^{-3}$ DMAA respectively. The saturation point for As(V) had not been reached for the concentration range studied. Fig. 6. shows the result at pH 9 and 0.05 mol dm$^{-3}$ ionic
strength. A similar trend was observed, but with increased interaction for all the species. 30% of As(V) interacted while 15% of As(III) and DMAA associated with the humic acid.

Fig. 7 shows the results for pH 9 ionic strengths of 0.005 and 0.05 mol dm$^{-3}$. High pH and low ionic strength favoured the association of arsenic species with humic acid, as reflected in increases in the amount bound, (As(V) 540 ± 30 mmol kg$^{-1}$, 240 ± 2 mmol kg$^{-1}$ for As(III) and DMAA 170 ± 21 mmol kg$^{-1}$). For As(V) there was a 50% increase in sorption with a decrease in ionic strength from 0.05 to 0.005 mol dm$^{-3}$ while a 15% increase was observed for DMAA.

For all arsenic species, greater sorption occurred with increased concentration. There was a higher As(V) sorption capacity than for the other arsenic species. At pH 5, the sorption isotherms for As(V) showed double layer formation of the complex which was not seen with As(III). This indicated that there was a different mechanism of sorption taking place. Similarly, at pH 5, the dominant As(V) species is H$_2$AsO$_4^-$ which is the main species attracted to surfaces of mineral oxides. For As(III), the main species being As(OH)$_3$ which interacts minimally with oxides at low pH$^{[34]}$.

DMAA is deprotonated at high pH and showed low sorption throughout. The increased sorption at high pH and low ionic strength may be simply due to electrostatic attraction between metal contaminants in HA and the organic acids.

The distribution ratios ($R_d$), determined using Freundlich isotherms are shown in table 1. The order of magnitude for $R_d$ values is As(V) > DMAA(V) > As(III).

<table>
<thead>
<tr>
<th>pH</th>
<th>IS (mol dm$^{-3}$)</th>
<th>As(V)</th>
<th>As(III)</th>
<th>DMAA(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.05</td>
<td>347.62</td>
<td>65.99</td>
<td>102.25</td>
</tr>
<tr>
<td>9</td>
<td>0.005</td>
<td>768.42</td>
<td>-</td>
<td>175.63</td>
</tr>
<tr>
<td>12</td>
<td>0.005</td>
<td>-</td>
<td>240.99</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1- Distribution ratios (dm$^3$ kg$^{-1}$) for arsenic species
Higher $R_d$ values indicate that much of the adsorbate is taken up by the adsorbent and, therefore, the results again show that As(V) species is more sorbed to humic acid than either As(III) or DMAA(V).

3.4 Effect of increasing humic acid concentration

The complexation of As(V) with humic acid was investigated at different HA concentrations, because it was seen to interact more than the other species. The results are presented in Fig. 8, which shows a decrease in sorption of As (V) (per kg HA) in solution with an increase in humic acid concentration. The trend observed can be explained in terms of the solubility of HA. Humic acid exists in the solution, and in the solid phase at high concentrations. As the total HA concentration increases, the amount of solid phase increases, resulting in a decrease in As(V) sorbed (per g HA) in the aqueous phase.

3.5 Conditional Association Constants

The variation in the conditional association constants with pH, and ionic strength, are shown in Figs. 9 and 10. Each point is a mean of 6 replicates. In all cases the association generally increased with pH and decreased with ionic strength. As(V) and DMAA(V) reached broad maxima at moderate alkalinites, whilst As(III) continued to increase up to the highest pH investigated. Across the pH range (except at 12), the As(V) complexes were stronger bound than the As(III) and DMAA(V) complexes.

In the literature the most meaningful approach to expressing stoichiometry for metal humic interactions is probably the site-binding approach, where the complexes are assumed to have a 1:1 stoichiometry in terms of moles of binding sites per mole of metal. This approach accommodates the polyelectrolytic nature of the humic substances and eliminates the necessity of knowing the number of ligand donor groups attached to each metal ion[51]. Therefore this approach is used in As-HA interaction where a 1:1 stoichiometry is assumed.

The other consideration was that because of side reactions, and because the net charge on humic material changes with solution composition, the ratio of bound to free metal activities varies with Ionic strength and pH, as well as with ligand concentration. The measurement of free and bound metal can, therefore, give only a conditional stability
constant, in this case, an association constant i.e. any constant calculated from measured values of free and bound metal is only valid for the conditions of the experiment. Clearly if predictions and comparisons are to be made it is essential that a model be developed from which intrinsic constants, i.e. true constants, can be obtained. Several models have been developed mainly for metal-humic acid interaction in the literature\textsuperscript{52-53} but none has been developed for anion-humic acid interaction. The conditional association constants for the reactions were found to be log K = 1.97 ± 0.02 for As(V), log K = 1.58 ± 0.07 for As(III) and log K = 1.50 ± 0.10 for DMAA.

4. Conclusion
Arsenic species were shown to react with humic acid. The logarithmic conditional association constants for the reactions were found to be 1.97 ± 0.02 for As(V), 1.58 ± 0.07 for As(III) and 1.50 ± 0.10 for DMAA for similar conditions found in natural waters. These low values indicate the formation of weak complexes with humic acid in solution phase which will not reduce the mobility of arsenic in aqueous systems. The extent of arsenic species associating with humic acid is greater in the pH range of 8 – 10 for As(V) and DMAA while it extends to pH 12 for As(III). Arsenic - humic acid interaction is postulated to involve bridging metals and organic functional groups deprotonated at high pH within the humic molecule. The association is highly dependent on pH, ionic strength and concentration of arsenic. The strong pH dependency is most likely due to the distribution and speciation of arsenic in solution and also on the solubility of humic acid.

References


Fig 1. Speciation of arsenic(III).
Fig 2. Speciation of arsenic(V).

Fig. 3. Sorption isotherms of arsenic species on HA. Background electrolyte: 0.05 mol dm$^{-3}$ KNO$_3$; HA concentration 1500 mg dm$^{-3}$; arsenic species concentration 10$^{-4}$ mol dm$^{-3}$. 
Fig. 4. Effect of increasing ionic strength on sorption of arsenic species onto humic acid. HA concentration 1500 mg dm$^{-3}$; arsenic species concentration $10^{-4}$ mol dm$^{-3}$; pH 9.

Fig. 5. Effect of increasing concentration of arsenic species on sorption of arsenic species onto humic acid. HA concentration 1500 mg dm$^{-3}$; Background electrolyte: 0.05 mol dm$^{-3}$ KNO$_3$; pH 5.
Fig. 6. Effect of increasing concentration of arsenic species on sorption of arsenic species onto humic acid. HA concentration 1500 mg dm$^{-3}$; Background electrolyte: 0.05 mol dm$^{-3}$ KNO$_3$; pH 9

Fig. 7. Comparison of As (V) and DMAA sorption onto humic acid at two ionic strengths of 0.05 and 0.005 mol dm$^{-3}$ KNO$_3$. HA concentration 1500 mg dm$^{-3}$; pH 9
Fig. 8. Effect of increasing humic acid concentration on As (V) sorption. Concentration of As (V) $10^{-4}$ mol dm$^{-3}$; Background electrolyte 0.05 mol dm$^{-3}$ KNO$_3$; pH 5.

Fig. 9. Variation of conditional association constants of arsenic species sorption onto humic acid with pH. HA concentration 1500 mg dm$^{-3}$; Background electrolyte: 0.05 mol dm$^{-3}$ KNO$_3$;
Fig. 10 Variation of conditional association constants of arsenic species sorption onto humic acid with ionic strength. HA concentration 1500 mg dm$^{-3}$; pH 9.