

# Modelling the chemical influences on bioavailability of geogenic arsenic in soils

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## Abstract

Arsenic contaminated soils are a major problem worldwide and understanding how soil affects the fate of arsenic is important in determining the risk to humans who use the land. Most studies have investigated the influence of individual soil physico-chemical variables on arsenic mobility, but they are not readily extrapolated to predict the fate of arsenic in more complex soil systems. In this study the chemical controls on arsenic mobilisation were investigated using a geogenic arsenic rich soil from an allotment site in Northern England. Investigations of the distribution of arsenic suggested that the dominant factor (>70%) influencing arsenic mobility in the soils was the presence of iron oxide and hydroxide minerals. Bioavailability of arsenic in the soils was highest in the top 30 cm of the soil. Multiple regression analysis of the dataset suggested that the presence of phosphate ions increased the bioavailability of arsenic. Moreover, calcium ions increased arsenic sorption to the soil surface thereby reducing bioavailability. These findings have important implications for current land-use where applications of phosphate fertilisers may mobilise arsenic and increase its bioavailability.

## Key Words

Brownfield, sequential extraction procedure, ICP-MS, principle component analysis.

## Introduction

Arsenic contamination of soils is a worldwide problem. Research has been undertaken to study the human health risks associated with anthropogenic arsenic while geogenic arsenic (i.e. from natural sources) has been largely overlooked. To meet the demands for the ever increasing global population, and the need to development land for housing and agriculture, contaminated land that has previously been seen as unfit for human inhabitation (e.g. contaminated land) is being utilised. However, such land uses may increase the risk to humans from exposure to toxic elements such as arsenic. Remediation of arsenic contaminated land is currently not feasible and so risk assessments must be undertaken to determine potential land use for contaminated sites before development can take place. Risk assessments have previously been based on the total metal loading of the soil with a concentration of 20 mg/kg soil generally considered the maximum safe limit for residential soils (UK EPA 2004). However, recent research suggests total arsenic is not necessarily a reliable measure of risk from contaminated soils and other factors such as speciation (Ge *et al.* 2000), bioaccessability (Palumbo-Roe *et al.* 2005) and the fractional distribution of arsenic in soils (McLaren *et al.* 1998) may represent a more accurate measure of potential risk.

Arsenic distribution in soils is variable (both spatially and temporally) and is dependent on the soil's physical, chemical and biological properties. In order to predict risk from exposure to contaminated soils it is important to model the effects of these different properties on the cycling of arsenic. Soil parameters including pH and redox potential (Masscheleyn *et al.* 1991), organic matter (Gustafsson *et al.* 2003), calcium and phosphate ion concentration (Davenport and Peryea 1991) and iron and aluminium oxides/hydroxides (Cances *et al.* 2005) have all been found to affect the biogeochemical cycle of arsenic.

Often these studies investigated the effects of soil properties in isolation and may not represent the behaviour of arsenic in complex media such as soils. Soil is a heterogeneous matrix and it is important to model the soil as a whole system in order to fully understand the risks posed to humans and the environment from arsenic contaminated land. The aim of this project was to identify the chemical parameters that influence the adsorption and desorption of arsenic from a geogenic arsenic rich soil.

## Methods

### *Study site and sampling regime*

The location selected for this study was Buckingham Avenue allotment site in Scunthorpe (53°36'N,

0°39'E), North Lincolnshire, UK (see Figure 1). The soil on the site was formed on Jurassic Ironstone which has been found to be naturally rich in arsenic (Palumbo-Roe *et al.* 2005). One area of the site that was chosen for sampling has been under "natural" vegetation for over 15 years, with no recorded anthropogenic activity. Soil sampling was carried out at this site in January 2006, and consisted of a series of topsoil samples taken at 5 m increments along a 25 m transect. In addition a soil pit (dimensions: (w) 1 m x (l) 2 m x (d) 0.7 m) was dug in the centre of one of the allotment plots, and samples taken from the soil profile at 5 cm increments to a depth of 70 cm. These samples were taken to determine spatial variability both across the site and with depth in the soil.

#### *Sequential Extraction Procedure*

Fractionation of arsenic in the soil samples was carried out using a modified sequential extraction procedure (SEP) (Wenzel *et al.* 2001), with the final step in the procedure changed to a nitric acid digestion method taken from Castlehouse *et al.* (2003). The SEP identified five operationally defined phases for arsenic sorption in soils (i) non-specifically sorbed; (ii) specifically sorbed (exchangeable); (iii) sorbed to amorphous iron oxyhydroxides; (iv) sorbed to crystalline iron oxyhydroxides; and (v) residual. The concentration of arsenic in the fractions was analysed by ICP-MS. Speciation of arsenic in the non-specifically sorbed phase was carried out by HPLC-ICP-MS.

#### *Chemical characterisation*

Total metals in the soils were extracted by nitric acid digestion and analysed by ICP-MS (Castlehouse *et al.* 2003). Soil waters were extracted using a 1:10 soil solution ratio and the 0.45µm filtered extracts analysed for soluble cations and anions by ion chromatography and total inorganic and total organic carbon using a carbon analyser. Other analyses on the soil included total carbon, hydrogen and nitrogen, pH and total organic carbon by loss on ignition.

#### *Statistics*

Statistical analyses were carried out on the data using Minitab® v14. One-way and two-way ANOVA were used to determine any significant trends in the data. Posthoc testing using Fishers individual error rate was carried out to enable more detailed interpretation of the datasets. Multiple linear regression analysis was carried out on the whole dataset using principal component analysis (PCA) to determine any relationships between parameters.

### **Results**

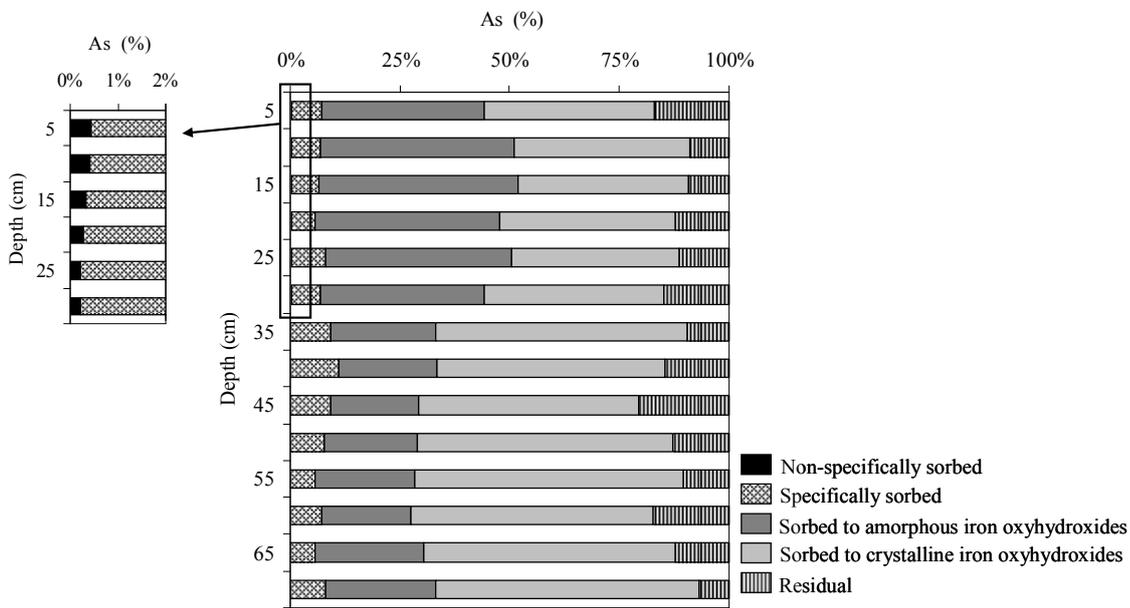
The results from the analysis of topsoil samples taken along the transect found that there was no variability in any of the soil chemical properties with location on the site (data not shown). This is consistent with the soil being under natural vegetation for a number of years. No variability in concentrations of total elements in the soil was found with changes in depth. However, results for the soluble ions and arsenic fractionation were found to have significant trends.

The distribution in arsenic amongst the five operationally defined phases was found to vary significantly with depth in the soil ( $P < 0.001$ ). The majority of arsenic at all depths in the soil profile was found to be sorbed to iron oxyhydroxides phases in the soil (Figure 2) with >70% of the total arsenic in the soil sorbed within these phases. The bioavailable fraction of arsenic in the soil, represented by the non-specifically sorbed phase was also found to vary significantly with depth ( $P < 0.001$ ) with the highest concentration (0.154 mg/kg) measured in the top 5 cm of the soil. Concentrations of non-specifically sorbed arsenic decreased between 5 and 35 cm and were thereafter less than the detection limit. The results for the specifically sorbed arsenic were also found to vary significantly in the depth profile however there was no consistent trend in the dataset. Residual arsenic was not found to vary with changes in depth.

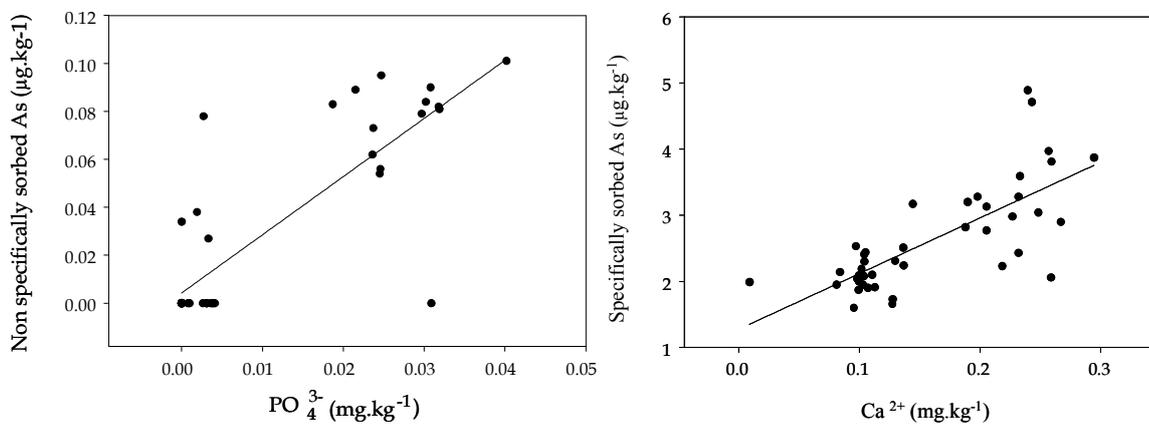
Results of the chemical characterisation showed a number of parameters varied significantly with depth. Phosphate ( $P < 0.001$ ), nitrate ( $P < 0.001$ ), potassium ( $P < 0.001$ ) and fluoride ( $P < 0.001$ ) were found to decrease with depth in the soil with the highest concentrations measured in the top 30 cm. Calcium ( $P < 0.001$ ) and sulphate ( $P < 0.001$ ) were also found to have significant trends with concentrations increasing with depth. The results for both chemical characterisation and arsenic fractionation analyses were subject to principal component analysis to determine any relationships within the dataset. Phosphate was found to have a significant positive correlation with non-specifically sorbed arsenic (Figure 3). A positive correlation was also found between calcium ions and specifically sorbed arsenic. No other relationships were found in the data.



**Figure 1.** Location of research site in Scunthorpe, NE England (53°36'N, 0°39'E).



**Figure 2.** Fractional distribution of arsenic amongst five operationally defined phases as a function of depth. Inset: enlargement of the non-specifically sorbed arsenic phase.



**Figure 3.** Regression analysis of (Left): phosphate ion concentration and non-specifically sorbed arsenic ( $r^2 = 0.695$ ;  $P < 0.001$ ) (Right): calcium ion concentration and specifically sorbed arsenic ( $r^2 = 0.542$ ;  $P < 0.001$ ).

## Conclusion

This study found that most of the arsenic in the soil was bound to crystalline and amorphous iron oxyhydroxides (>70%). These phases are generally not bioavailable and therefore suggest that the majority of the arsenic in the soil is low risk for leaching and uptake by plants under current conditions.

The arsenic in the non-specifically sorbed and specifically sorbed phases was found to vary significantly with depth in the soil. Regression analysis of the data suggested phosphate may increase arsenic mobility by increasing the concentration of non-specifically sorbed arsenic. In contrast calcium may have increased sorption of arsenic to the soil with a corresponding increase in the concentration of specifically sorbed arsenic. These results suggest that the application of soil amendments such as phosphate fertilisers and lime may have a significant impact on the fate of arsenic in these soils. This has major implications for the current land use on the site and highlights the need for further investigation into the biogeochemistry of arsenic.

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