Chemistry of Arsenic in Soils of North-East

New South Wales

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Abstract

Ten soils from northern New South Wales, Australia, were sampled and assessed for their capacity to sorb arsenate (As\textsuperscript{V}) in relation to soil properties.

Multiple and simple linear regression analysis of the partition distribution coefficient (K\textsubscript{d}) of the soils and the soil properties revealed that As\textsuperscript{V} sorption in these soils is essentially controlled by the crystalline iron (Fe) oxide content of the soils (R\textsuperscript{2}=0.80***).

Following the preliminary investigation, four contrasting soils (C, H, I and J) were chosen to study the sorption of arsenite (As\textsuperscript{III}). The amount of As\textsuperscript{III} sorbed by three of the soils was less than that of As\textsuperscript{V}. This was attributed to differences in the surface charge density of the soils and the nature of the interactions between the charged surface and the nature of the As\textsuperscript{V} and As\textsuperscript{III} species present in solution.

Given that surface chemical properties of soils may influence the differences in the sorption characteristics of As\textsuperscript{V} and As\textsuperscript{III}, the effect of pH and ionic strength (I) on the sorption of As\textsuperscript{V} and As\textsuperscript{III} were studied. Contrasting effects of pH were observed for As\textsuperscript{V} and As\textsuperscript{III} sorption. For As\textsuperscript{V}, an increase in the pH of the soil resulted in a decline in sorption by the four soils studied. This was attributed to two interacting factors occurring in the soil solution. Firstly, there is the pH-pK\textsubscript{a} dependence of As\textsuperscript{V} species. Increasing the pH increases deprotonation of the neutral H\textsubscript{3}AsO\textsubscript{4} species up to pH 5 and each unit increase in pH leads to a 10 fold increase in the ratio of H\textsubscript{2}AsO\textsubscript{4}\textsuperscript{-} to H\textsubscript{3}AsO\textsubscript{4}. Higher pH also increases the negative potential in the plane of sorption and as a consequence of these two interacting factors, there is a decrease in As\textsuperscript{V} sorption as pH increases. In contrast to As\textsuperscript{V}, increasing pH increased the proportion of As\textsuperscript{III} sorbed at a pH > 6.0. Increasing I however, had little effect on the proportion of As\textsuperscript{III} sorbed. This may be
indicative of the importance of different sorption mechanisms of As$^{\text{III}}$ compared with As$^V$, but further research is needed to clarify the sorption mechanism of As$^{\text{III}}$.

The effects of selected anions [phosphate (P), sulphate (S) and dissolved organic carbon (DOC)] and selected cations [calcium (Ca) and sodium (Na)] were studied to determine their roles on the sorption of As$^V$ and As$^{\text{III}}$. There were large differences between the effects of the different ions on the behaviour of both As$^V$ and As$^{\text{III}}$. The addition of P (0 to 0.16 mmol L$^{-1}$) to the background solution decreased As$^V$ sorption in all soils although the extent of suppression varied with the soil physico-chemical properties. At low initial concentrations (< 0.33 mmol L$^{-1}$) of As$^V$ in solution, there was little effect of P on As$^V$ sorption with high sorbing soils. Under these experimental conditions, both ions were strongly retained by the soil colloidal particles. In contrast, the presence of P decreased the amount of As$^V$ sorbed in soils with low sorption capacity. In these soils, the effect of P appears to be pronounced even at low As$^V$ concentration (< 0.01 mmol L$^{-1}$). For As$^{\text{III}}$, the presence of P in solution decreased the sorption of As$^{\text{III}}$ in all soils, although the extent of the decrease varied between the soils studied. The difference in As$^{\text{III}}$ sorption in the presence of P was attributed to the widely different mineralogy of the soils and the mechanism of As$^{\text{III}}$ sorption. Arsenite has been shown to sorb predominantly on oxide surfaces which are also the active sorption sites for P. Enhanced sorption of P appears to saturate the sorption sites and decrease As$^{\text{III}}$ sorption and this competitive effect between P and As$^{\text{III}}$ may be more pronounced in low sorbing soils.

The effect of index cation on the sorption of As$^V$ also varied with soil type. Irrespective of the nature of the solution composition, Ca$^{2+}$ enhanced the sorption of As$^V$ by the soils studied. In contrast to As$^V$, the presence of Ca$^{2+}$ had little effect on the
amount of As$^{\text{III}}$ sorbed in the presence of P, supporting the earlier hypothesis that the sorption mechanism of As$^{\text{III}}$ may be different from that of As$^{\text{V}}$.

The presence of S had little effect on the sorption of As$^{\text{V}}$ and only decreased As$^{\text{III}}$ sorption in the low As sorbing soil. The hypothesis that competition between As$^{\text{III}}$ and S was effective only in the low sorbing soils, was examined by conducting a series of studies with increasing goethite content in Soil H. These studies confirmed that the extent of competition between As$^{\text{III}}$ and S was determined by the number of sorption sites available. In contrast to S, the presence of DOC in solution decreased the sorption of both As$^{\text{V}}$ and As$^{\text{III}}$. Increasing the concentration of DOC in solution had no further effect on the amount of As$^{\text{V}}$ and As$^{\text{III}}$ sorbed indicating that competitive interactions between As and DOC for sorption may be only one of the mechanisms by which DOC affects As sorption.

Kinetic studies, using a modified stirred-flow reaction chamber, were conducted to investigate the effects of varying the solution composition on the dynamics of As$^{\text{V}}$ sorption processes. The original chamber was modified by repositioning of and fitting of a filter to the inlet port, to prevent changes to the soil:solution ratio in the chamber caused by soil transferring to the inlet port during mixing.

As with the batch studies, the flow through reactor studies focused on the effects of I and different cations and anions on the kinetics of As$^{\text{V}}$ sorption by soil. A comparison of the different treatments demonstrates that the presence of different index cations and increasing I had little effect on the sorption capacity of As$^{\text{V}}$ by the soil. With all three treatments (0.03 mol L$^{-1}$ NaNO$_3$, 0.3 mol L$^{-1}$ NaNO$_3$ and 0.01 mol L$^{-1}$ Ca(NO$_3$)$_2$), the maximum sorption capacity of the soil ranged from 162 to 176 $\mu$g g$^{-1}$. In contrast, the presence of P decreased the amounts of As$^{\text{V}}$ sorbed by approximately 47% of the amounts sorbed. Increasing I from 0.03 to 0.3 mol L$^{-1}$ NaNO$_3$ appeared to increase the apparent
forward rate ($k_a$) of As$^V$ sorbed from 0.0001425 to 0.0002713 L mg$^{-1}$ min$^{-1}$. A similar increase in $k_a$ was observed when the index cation was changed from Na to Ca. The introduction of P decreased the sorption capacity of the soil by between 35 to 48% depending on the index cation in the background solution.

Desorption studies were conducted following As$^V$ sorption with 0.03 mol L$^{-1}$ NaNO$_3$ as the background electrolyte. Desorption of As$^V$ was characterised by a distinct irreversibility of some of the sorbed As$^V$, with no more than 17% of the sorbed As$^V$ being desorbed under the study conditions. The amount of As$^V$ desorbed followed the following pattern; 0.03 mol L$^{-1}$ NaNO$_3$ + P $>>$ 0.03 mol L$^{-1}$ NaNO$_3$ > 0.3 mol L$^{-1}$ NaNO$_3$. 