Short Report

Evaluation of As(III) and Sb(III) Adsorption to Paddy Soils from Irrigated Rice Fields in Bangladesh

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O solo de várzea exerce um importante controle sobre os ciclos de arsênio e antimônio em ecossistemas de produção de arroz por meio de adsorção a partir da fase aquosa. Realizou-se um estudo de laboratório para avaliar a adsorção e o possível comportamento competitivo desses dois elementos contaminantes.

Paddy soil exerts a major control on the arsenic and antimony cycles in rice production ecosystems through adsorption from the aqueous phase. A laboratory study was conducted to assess the adsorption and the possible competitive behaviour of these two contaminant elements.

Keywords: paddy soils, arsenic, antimony, adsorption, geochemistry

Introduction

Arsenic (As) levels in drinking water and in irrigation water used for rice paddies can exceed the World Health Organisation (WHO) drinking water quality limit of 0.05 mg L^{-1} across many regions in South East Asia.[1,2] This is due to the dissolution of As-rich minerals in the groundwater hosting bedrock. In polluted groundwater, concentrations can exceed water quality limits to a factor of 900, reaching µg mL^{-1} concentration levels.[3] A key process that controls the As geochemistry in terrestrial ecosystems is the adsorption on soils and bedrocks.[4] Antimony (Sb) has been recognised to co-occur with As in iron and sulphide minerals associated with sedimentary and igneous mineral formations.[5,6] Due to the potentially similar aqueous chemistry to As as oxyanion and metalloid, Sb could well be involved in the As crisis,[7,8] for example by affecting As adsorption in groundwater systems and leading to higher As concentration in well waters. McCarthy *et al.* tested recently this hypothesis and analysed two hundred forty five tube well water samples from various regions in Pabna City, Bangladesh. They found that Sb concentration were ≤1 ng mL^{-1}, thus significant adsorption on the soils and subsequent removal from the aqueous phase was suggested.[1]

Paddy soil (Hydragric Anthrosol) is an environmentally engineered soil type formed and modified by human activity of irrigation and added organic materials. It constitutes rice fields across Bangladesh and adsorbs significant amounts of As from irrigation waters.[2,9] This process has been invoked as a possible explanation leading to elevated As content in rice,[10] however, the As dynamics in paddy soils are little understood.[11]

Given these recent findings, it is of great interest to assess the adsorption capacity of As and other potentially toxic elements on irrigated paddy fields and to understand potential processes affecting the adsorption and release of As from the soils. To this end, it was conducted preliminary adsorption studies determining the As(III) and Sb(III) adsorption on irrigated paddy soil and their potentially competitive behaviour. It is showed that As(III) sorption capacity is low, ca. 0.4 mg g^{-1}, and that Sb(III) has a stronger adsorption, potentially explaining the low Sb concentration in wells in Bangladesh. Antimony(III) does only affect slightly the As(III) adsorption.

Experimental

The paddy soil sample used originated from the Munshiganj district near Sreenagar, 30 km South of Dhaka City and 5 km North of the Ganges River, Bangladesh. The full description of the basic soil chemical parameters and the sample preparation are given elsewhere.[9] The soil was from prior contamination from irrigation and contained 15 µg g^{-1} As. The mineralogical composition

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of the paddy soil was identified using X-ray diffraction (XRD). Clay minerals, i.e., illite, chlorite, smectite and kaolinite dominated but quartz, k-feldspar and albite were also present.

Arsenic(III) and Sb(III) solutions were prepared each day by dissolving sodium arsenite ($NaAsO_2$) and antimony potassium tartrate ($KSbO·C_4H_4O_6$), respectively, in deionised water. A 0.1 mol L^{-1} potassium nitrate (KNO_3) solution was prepared to control the ion strength. For the adsorption experiments, 100 mL solutions containing As(III) and Sb(III) were added to a previously acid cleaned plastic bottle, followed by 1 g of soil. This solid/solution ratios, as well as the concentrations used, were higher than typically found for paddy rice fields but represented a best compromise between experimental restrictions, i.e., analytical limit of detection for ICP-OES and natural conditions. The reaction bottle was closed airtight and placed on a mechanical shaking table rotating 150 rev min^{-1} at constant temperature 25 ºC and equilibrated for 48 h. Preliminary kinetic experiments were conducted for 72 h to determine the equilibrium time. Three 2.5 mL aliquots were extracted using a plastic syringe. The pH was measured in separate reaction bottles after 5 min and after the adsorption equilibrium was reached. Samples were filtered into separate test tubes and analysed using a Varian Vista Pro Series ICP-OES. The As(III) sorption isotherms were determined using concentrations between 4 and 20 µg mL^{-1}. The Sb(III) sorption isotherms were determined using concentrations between 2 and 19 µg mL^{-1}. Competitive adsorption between As(III) and Sb(III) was assessed for solutions with As:Sb concentration ratios of 5:1 and 2:1 to mimic natural conditions.[12] The concentrations of As and Sb in the spike solutions were analytically confirmed using ICP-OES.

Langmuir and Freundlich isotherms were obtained by fitting the linear data (Langmuir) and log transformed (Freundlich) data. The Freundlich adsorption isotherm satisfies an equation of the type $q_e = K_f C_e^{(1/n)}$ where C_e is the equilibrium concentration of sorbent in solution (As(III) and Sb(III) in mg L^{-1}), q_e is the equilibrium sorption capacity (As(III) and Sb(III) in g^{-1} sorbent), K_f and $1/n$ are constants, that are considered as relative indicators of adsorption capacity and intensity, respectively. The expression of the Langmuir model is given by $q_e = Q_{max}bC_e / (1 + bC_e)$ where Q_{max} is the maximum adsorption capacity (mg As(III), Sb(III) g^{-1} sorbent) and b is a constant (L mg^{-1}).

Results and Discussion

Figure 1 shows the As(III) removal rate from the experimental solution over a period of 72 h. The initial As(III)

concentration was 7.7 µg mL^{-1}. Temperature was maintained at 25 ºC. Three aliquots were taken from the same reaction bottle. The adsorption is initially fast and 232 µg As(III) are adsorbed in the first hour, which equals to 30% of the total As(III). Then the adsorption slows significantly down to a rate of about 18 µg *per* h. After 48 h, the adsorption approached equilibrium, with approximately 60% of the total As(III) adsorbed from the solution. A slight desorption seems to occur between 5 and 8 h after the start of the experiment but adsorption resumed thereafter. The equilibrium time determined is slightly longer than expected for As(III) on pure mineral surfaces.[13,14] However, organic coating of minerals can delay As sorption and As absorption on organic substances, clays, a major component of this paddy soil, and soils is slower.[15-18] The initial fast adsorption might indicate sorption on uncoated minerals present in the paddy soil. The temporal pattern itself observed is in line with studies of As(V) adsorption on soils where the retention rate was initially rapid followed by gradual or slower retention with increasing reaction time.[19]
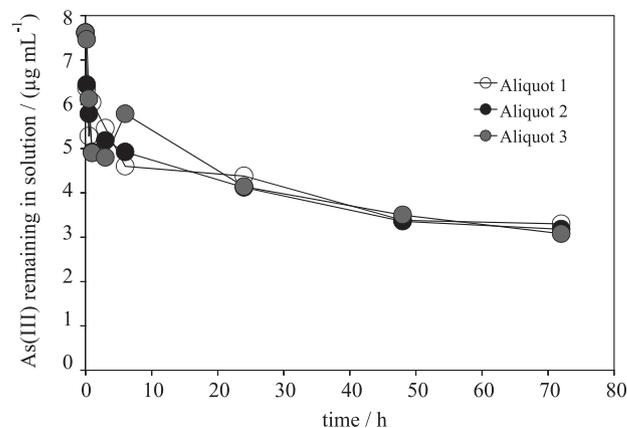
Figure 1. Arsenic removal from a 0.1 mol L^{-1} KNO_3 solution over 72 h. The initial concentration was 7.7 µg mL^{-1} As(III). Temperature was maintained at 25 ºC and the pH ranged between 6.25 and 6.75.

Figure 2 shows the amount of As(III) and Sb(III) adsorbed from solution unto the paddy soil. The adsorption isotherms were adequately described using Freundlich and Langmuir models with $R^2 \geq 0.80$ (Table 1). The adsorption capacity of the paddy soil was reached for As(III) with approximately 0.4 mg g^{-1} As soil. The pH during the adsorption process did not drift and ranged between 6.25 and 6.75. This suggests that the soil acts as a natural pH buffer to the As(III) solution because H^+/OH^- ion exchange reactions take place during As adsorption on iron oxides and clays.[18,20,21] The adsorption capacity for the investigated paddy soil was low but in the same range like that observed for arsenate on clay rich soils and on clays itself.[19,22] The reason for the low adsorption was the presence of As(III)

Table 1. Langmuir and Freundlich model constants for the adsorption of Sb(III) and As(III) on paddy soil at 25 °C and 1 bar. The estimated error of the constants is ± 10%, determined from three replicate determinations of the isotherm

	Langmuir			Freundlich		
	Q_{max} / (mg g^{-1})	b / (L g^{-1})	R^2	K_f / (mg g^{-1})	1/n	R^2
As(III)	0.42	0.71	0.98	0.15	0.38	0.95
Sb(III)	3.34	0.17	0.80	0.47	0.84	0.96

in aqueous solution as uncharged $As(OH)_3$ complex that binds less strongly to mineral surfaces.[23] It was noted, that this adsorption capacity was an order of magnitude lower than that determined for oxisols (typical natural tropical soil) with 2.6 mg g^{-1} As(III) or for the iron and aluminium oxides associated with the oxisol, ranging between 3.3 and 7.5 mg g^{-1} As(III).[24]

The adsorption capacity of the paddy soil for Sb(III) was not achieved within the experimental concentration range used during our study and the adsorption increases continually. Approximately 80% of Sb was adsorbed onto the paddy soil. Again, the pH during the adsorption process did not drift, but the measured range was slightly larger than for the As(III) solutions and ranged between 5.4 and 6.4. Our results suggest that the paddy soil has a higher affinity for Sb(III) than for As(III) (Table 1). This observed difference in the adsorption capacity of Sb(III) and As(III) could explain the findings of a recent investigation into As and Sb concentrations in groundwater of Bangladesh,[1] where Sb concentrations were much lower than that of As.
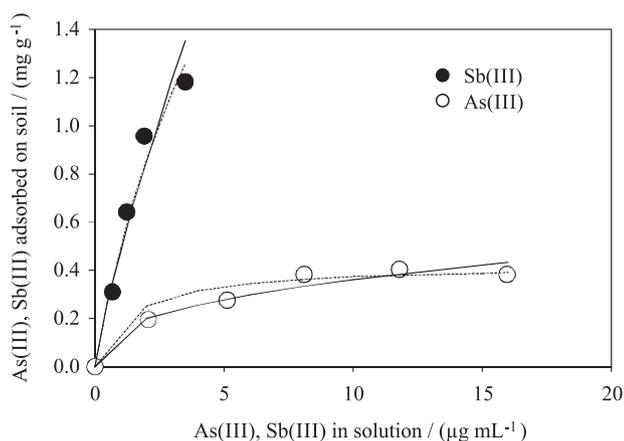
Figure 2. Adsorption curve for the As(III) and Sb(III) single element solutions added to the paddy soil. The error estimated for the concentration data was 5%, determined from triplicate measurements of the solutions.

Figure 3 shows adsorption curves for solutions with As(III) and Sb(III) only and with different As/Sb ratios. The ratios were chosen to represent natural ratios in aqueous soil solutions derived from weathering of rocks.[12] The other element did not affect the adsorption capacities of Sb(III) but seems to lower slightly the As(III) adsorption.

Competitive behaviour between As and other oxyanions is well documented,[22,23,25] but here it was not found a significant effect.
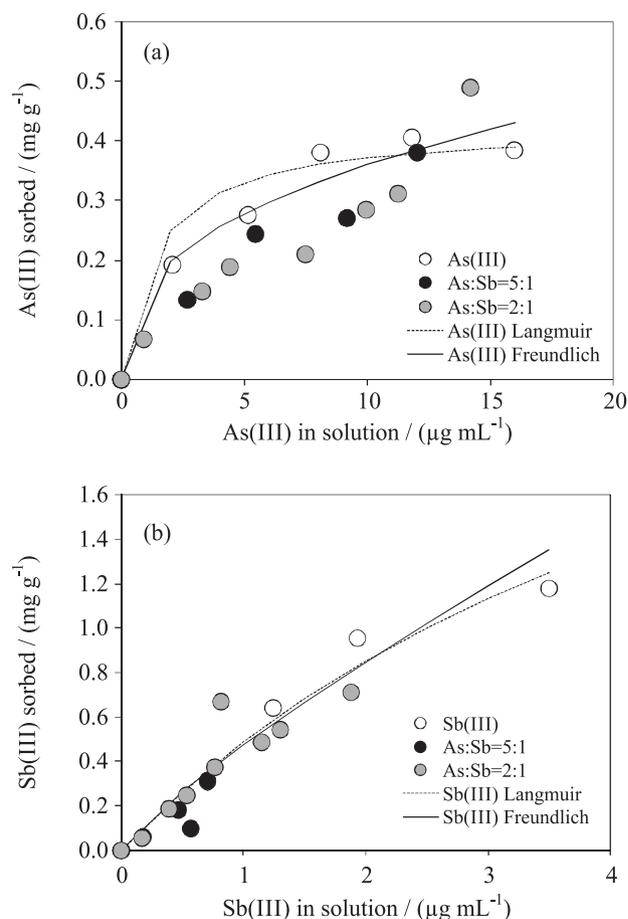
Figure 3. Adsorption curves for arsenic (a) and antimony (b) for pure elemental solutions and for mixtures of As:Sb of 5:1 and 2:1. The error of the concentration data was 5%, estimated from triplicate analysis of the solutions.

There was no evidence that Sb(III) was affected by the presence of As(III). The oxidation of Sb(III) or As(III) unlikely affected the observations given a line of evidences: (*i*) the oxidation rate of Sb(III) is lower at low pH[26,27] and all the experiments were carried at pH below 7, (*ii*) Sb(III) is oxidised by Fe and Mn oxyhydroxides only after a few days.[27] The experiments lasted only 48 h. In addition, the evaluated soil was dominated by clay minerals, which have

a lower oxidation potential than pure Fe and Mn oxides, (*iv*) As(III) is kinetically stable in the presence of clays and various iron oxides for reaction times well beyond the equilibrium time used in the present work,[24,28,29] (*v*) all experiments were conducted under airtight vessels with no significant air space between solution and caps. This prevented any fresh oxygen being supplied to the solution as tested in previous work in our laboratory.[30]

Conclusions

The preliminary work highlights interesting and important features. The adsorption equilibrium for As(III) on paddy soil was reached after approximately 48 h. This is slightly longer than observed on pure mineral surfaces, but in line with equilibrium times of As(III) during the adsorption on humic acids and humic acid coated minerals. The adsorption capacity of As(III) was reached for the paddy soil in this experimental set up using As(III) concentration solutions ranging between 4 and 20 $\mu g \ mL^{-1}$. It was approximately 0.4 mg As g^{-1} paddy soil, which falls within the range determined previously for clay rich soils. This was different for Sb(III) where the absorption capacity was not reached with the same initial concentrations. The adsorption isotherms for both metalloids were fitted well using Langmuir and Freundlich models. The calculated Sb(III) sorption capacity was about 10 times larger than that of As(III). Finally, the addition of Sb(III) to As(III) solutions seems to lower slightly the adsorption capacity of As(III), but this effect was not pronounced. No effect on the adsorption capacity of Sb(III) was observed. These observations could explain why Sb concentrations in groundwater of Bangladesh are smaller than these of As. The results would suggest that the Sb(III) soil-water interaction has little effect on the As(III) geochemistry in paddy soils. Ongoing work is assessing in more detail (*i*) the effect of cations and anions as confounding factor for the As(III) adsorption, (*ii*) the adsorption complexes using spectroscopic techniques; (iii) the potential importance of oxidation reactions for the processes studied using adequate analytical techniques,[31] and (*iv*) to conduct the same study at lower concentrations and wider ranges, in particular for Sb(III) to reach experimentally the equilibrium.

Acknowledgements

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