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Desorption of arsenic from clay and humic acid-coated clay by dissolved phosphate and silicate

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ABSTRACT

Arsenic (As) contaminated aquifers contain iron minerals and clays that strongly bind As at their surfaces. It was suggested that As mobilization is driven by natural organic matter (including fulvic acids (FA) and humic acids (HA)) present in the aquifers either via providing reducing equivalents for reductive dissolution of Fe(III) (hydr)oxides or via competitive desorption of As from the mineral surfaces. In the present study we quantified sorption of As(III) and As(V) to Ca^{2+}-homoionized illite (IL) and to kaolinite (Kao) as well as to HA-coated clays, i.e., illite–HA (IL–HA) and kaolinite–HA (Kao–HA) at neutral pH. Clay–HA complexes sorbed 28–50% more As than clay-only systems upon addition of 100 μM As(III)/As(V) to 0.5 g of clay or HA–clay with Ca^{2+} probably playing an important role for HA binding to the clay surface and As binding to the HA. When comparing sorption of As(V) and As(III) to clay and HA–clay complexes, As(V) sorption was generally higher by 15–32% than sorption of As(III) to the same complexes. IL and IL–HA sorbed 11–28% and 6–11% more As compared to Kao and Kao–HA, respectively. In a second step, we then followed desorption of As from Kao, Kao–HA, IL and IL–HA by 100 and 500 μM phosphate or silicate both at high (0.41–0.77 μmol As/g clay), and low (0.04 to 0.05 μmol As/g clay) As loadings. Phosphate desorbed As to a larger extent than silicate regardless of the amount of As loaded to clay minerals, both in the presence and absence of HA, and both for illite and kaolinite. At high loadings of As, the desorption of both redox species of As from clay–HA complexes by phosphate/silicate ranged from 32 to 72% compared to 2–54% in clay only systems meaning that As was desorbed to a larger extent from HA-coated clays compared to clay only systems. When comparing As(III) desorption by phosphate/silicate to As(V) desorption in high As-loading systems, there was no clear trend for which As species is desorbed to a higher extent in the four clay systems meaning that both As species behave similarly regarding desorption from clay surfaces by phosphate/silicate. Similarly, no significant differences were found in high As-loading systems in the amount of As desorbed by phosphate/silicate when comparing Kao vs. IL and Kao–HA vs IL–HA systems meaning that both clay types behave similarly regarding desorption of As by phosphate/silicate. At low As loadings, up to 80% of As was desorbed by phosphate and silicate with no noticeable differences being observed between different As species, different types of clay, clay vs clay–HA or the type of desorbant (phosphate and silicate). The results of this study showed that HA sorption to Ca^{2+}-homoionized clay minerals can increase As binding to the clay although the As sorbed to the clay–HA is also released to a greater extent by competing ions such as phosphate and silicate. Desorption of As depended on the initial loadings of As onto the clay/clay–HA. Based on our results, the effect of humic substances on sorption of As and on desorption of As by phosphate and silicate has to be considered in order to fully understand and evaluate the environmental behavior of As in natural environments.

1. Introduction

Arsenic (As) is a toxic element of great concern because of its large scale contamination in many areas of the world (e.g. the Bengal delta or China). Tens of millions of people in

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countries such as Bangladesh, Vietnam and India suffer from arsenicosis (As poisoning) by consuming As-contaminated groundwater (Smedley and Kinniburgh, 2000). The concentrations of As is in many cases significantly higher than 10 μg/L, which is stipulated by the WHO as safety limit of As in drinking water (Smedley and Kinniburgh, 2000).

Two inorganic species of As, As(III) (arsenite) and As(V) (arsenate), are mainly found in soil and groundwater, with As(III) being present under reducing conditions and As(V) in more oxidizing environments (Smedley and Kinniburgh, 2000; Warwick et al., 2005). At neutral pH, As(III) exists as H_3AsO_3 with pK_a values of 9.2, 11.3 and 13.4 whereas As(V) exists mostly as $H_2AsO_4^-$ and $HAsO_4^{2-}$ with pK_a values of 2.3, 6.8 and 11.6 respectively (Warwick et al., 2005). As(III) is considered to be more toxic (Smedley and Kinniburgh, 2000) and more mobile (Sharma et al., 2011) than As(V) at neutral pH conditions. However, both species co-exist in solution and the speciation depends upon the presence of microbes, reactive minerals, redox conditions, radicals and organic matter (Amstaetter et al., 2010; Jiang et al., 2009; Redman et al., 2002; Saltikov and Olson, 2002).

The mobility of As depends on solution pH and is controlled by sorption of the different neutral and negatively charged As species to the surfaces of clay and Fe(III) oxy(hydr)oxide minerals. Additionally, As mobility depends on the presence of compounds that compete for mineral sorption sites such as natural organic matter (NOM), phosphate and silicate. Interactions of As with natural minerals, such as Fe(III) oxy(hydr)oxides, have been studied previously in the presence and absence of NOM. These experiments demonstrated that NOM can desorb As, and also prevents As from sorbing to mineral surfaces in batch and column systems (Redman et al., 2002; Warwick et al., 2005; Weng et al., 2009). Phosphate has an analogous chemical structure to that of arsenate and therefore competes strongly with arsenate leading to its desorption from mineral surfaces (Hingston et al., 1971; Smith et al., 2002; Stachowicz et al., 2008; Violante and Pigna, 2002). Silica is environmentally relevant due to its presence in groundwater and its high affinity to mineral surfaces and it therefore also represents a potential competitive ligand for As (Davis et al., 2001; Luxton et al., 2006; Swedlund and Webster, 1999). When compared to phosphate, silica has been shown to be less effective in competing with As (Meng et al., 2001; Stollenwerk et al., 2007). However, while studies on the aforementioned interactions of As with Fe oxides in the presence of NOM have been of great interest, research on As–clay–NOM interactions has not received wide attention.

In countries such as Bangladesh and Cambodia, As-contaminated aquifers contain a significant amount of both clay minerals and NOM (Hossain, 2006). Clay minerals such as kaolinite and illite are found as a result of active weathering of silicates deposited from riverine load. NOM can stem either from organic carbon present in the aquifers, e.g. from underlying peat deposits, or can be transported into the aquifers from surface waters due to intense irrigation leading to large groundwater withdrawal (Burgess et al., 2010; Hossain, 2006; Smedley and Kinniburgh, 2000). Clay minerals are hydrous phyllosilicates containing alternating layers of octahedral and tetrahedral sheets. Clays are divided into 1:1 or 2:1 layer groups, two common clay mineral types found in the environment. Kaolinite (1:1 layer type) has the general formula $Al_2Si_2O_5(OH)_4$ and contains two alternating basal cleavage faces, the tetrahedral siloxane on one side and the octahedral alumina on the other. Illite (2:1 layer type) has the general formula $K_{0.88}Al_2(Si_{3.12}Al_{0.88})O_{10}(OH)_2$ with one alumina layer in between two tetrahedral siloxane layers (Sposito, 1994). NOM sorbs readily to these clay minerals and competes with As for the same sorption sites (Wang and Xing, 2005). Additionally, NOM sorbed to clay can also modify surface properties of the clay minerals (in particular their charge) and potentially enhances binding of As by increasing the number of surface binding sites (Martinez et al., 2010). Arsenic adsorption to kaolinite–OM aggregates was quantified by Saada et al. (2003a). They found increased As adsorption to clay–humic acid (clay–HA) aggregates compared to clay only systems. However, this study was limited to only one type of clay (kaolinite), one As redox species (As(V)), did not test various As loadings onto clay/clay–HA, and only studied adsorption (and not desorption) of As.

While As sorption to clay minerals in the absence of humic substances has been studied thoroughly (Goldberg, 2002; Saada et al., 2003a) there is a lack of knowledge regarding the interactions of arsenite and arsenate with clay minerals that are coated with humic material as is typically the case in the environment. Additionally, while it is known that phosphate, and to some extent silica, can desorb As from clay minerals (Stollenwerk et al., 2007), desorption of As sorbed to humics-coated clays by silicate and phosphate has not been quantified so far. Therefore, in the present study we used batch experiments to determine whether and to which extent HA sorbed to clay affected As sorption and As desorption by silicate and phosphate. The specific objectives of this research were: 1) to determine the effect of HA on sorption of As(III) and As(V) to kaolinite and illite by quantification of As(III)/As(V) sorption to clay only (kaolinite and illite) and to clay–HA complexes (kaolinite–HA and illite–HA) and 2) to determine desorption of As from kaolinite and illite only, and from kaolinite–HA and illite–HA systems by environmentally relevant concentrations of silicate and phosphate anions, at low and high As loadings on clay/clay–HA.

2. Materials and methods

2.1. Reagents

Stock solutions of 100 mM arsenate and arsenite (Na_2HAsO_4 and $NaHAsO_2$), and 2 mM stock solutions of phosphate (KH_2PO_4) and silicate ($NaSiO_2 9H_2O$) (all from Fluka, Germany) were prepared in deionized water. For As(III) experiments, arsenite, phosphate and silicate solutions were purged with N_2 for 5 min (repeated three times for each solution with 30 seconds of vacuum applied in between) before adding the respective components to the clay/clay–HA complexes. All arsenic, phosphate and silicate solutions were adjusted to pH 7 with 0.1 M HCl or NaOH before addition meaning that under our experimental conditions different species of arsenate and phosphate were present (i.e., dihydrogen phosphate/hydrogen phosphate and dihydrogen arsenate/hydrogen arsenate). For simplicity, we use the terms arsenate and phosphate throughout the paper to represent both species of arsenate and both species of phosphate. Pahokee peat humic acid (PPHA) and $CaCl_2$ were purchased from the International Humic Substances

Society (IHSS) and Fluka (Germany), respectively. PPHA solution (0.1 mg/mL equivalent to ~50 mg C/L) was prepared by dissolving PPHA powder in 10 mM $CaCl_2$ under vigorous stirring. The amount of cations in the PPHA was very low (e.g. only 16.5 μg Fe per g HA, Bauer et al., 2007). No precipitation of PPHA by Ca^{2+} was observed. The pH of the solution was readjusted to pH 7 using 1 M NaOH and stirred for 1 h before filtering with a 0.45 μm mixed cellulose ester (MCE, Millipore) filter. Clay minerals (kaolinite (KGa-1b) and illite (Imt-1)) were obtained from the Clay Mineral Society (University of Missouri, USA). In case of illite, the material was ground to <50 μm before using it for experiments. No further pretreatment of the minerals were conducted.

2.2. Preparation of homoionized clay

25 g of clay was suspended in 1 L of 1 M $CaCl_2$ (solid:liquid ratio of 1:40 w/v) and shaken at 150 rpm in a rotable shaker to obtain Ca^{2+}-homoionized kaolinite and illite. This process was repeated three times with 2 h of shaking in between. Excess calcium chloride was removed after the last homoionization step by washing with deionised water until $AgNO_3$ addition to the washing water indicated absence of Cl^-.

2.3. Synthesis of complexes of clay and PPHA (‘clay–HA’ complexes)

To quantify sorption of As to clay–HA complexes compared to clay only systems, clay–HA complexes were first prepared by adding the Ca^{2+}-homoionized clay to the 50 mg C/L PPHA solutions at a ratio of 1:40 (w/v, 25 g clay and 1 L of 0.1 mg/mL HA solution). The clay–HA suspensions were incubated for 48 h at 150 rpm in an overhead shaker at pH 7. After 48 h, the suspension was centrifuged at 5,000 rpm for 15 min. The supernatant was sampled for dissolved organic carbon (DOC) measurements to quantify the non-sorbed PPHA. To remove loosely bound humics from the clay–HA, the pellet containing the clay–HA aggregates was resuspended in 10 mM $CaCl_2$ and gently shaken by hand. The suspension was then again centrifuged at 5000 rpm for 15 min. The last step was repeated until the supernatant contained <0.5 mg/L DOC. In all clay–HA systems more than 95% of the PPHA added were adsorbed yielding a value of about 0.2% [~ 2 mg C per g clay] in the clay–HA complexes (data not shown). The synthesis of clay–HA complexes represents a slight modification of the protocol from Saada et al. (2003b). From this point on, for simplicity, illite and kaolinite only systems will be referred to as IL and Kao, whereas, illite–HA and kaolinite–HA complexes will be referred to as IL–HA and Kao–HA complexes or systems, respectively.

2.4. Sorption experiments

Sorption isotherms for As were determined by equilibrating ~500 mg wet clay or clay–HA with 25 mL As(III) and As(V) solutions of concentrations between 1 and 100 μM (all solutions prepared in 10 mM $CaCl_2$ and readjusted to pH 7 if required) in 60 mL serum bottles with O_2-tight butyl rubber stoppers. The concentrations of As were chosen to represent environmentally relevant low and some relatively high concentrations of As found in the porewater of As-contaminated aquifers (Hossain, 2006; Smedley and Kinniburgh, 2000). We did not use concentrations higher than 100 μM As in the sorption isotherms for several reasons: (1) higher As concentrations would exceed the maximum (average) environmental As concentrations found in As contaminated aquifers, (2) the values of As sorbed per g clay obtained upon addition of 100 μM As to the clay and clay–HA systems represent values of As found in clay phases in As contaminated aquifers (Chakraborti et al., 2001), and (3) the goal of the sorption experiments was to determine whether humic substances sorbed to clay change As sorption/desorption and we had already found a significant difference in sorption of As to clay vs. clay–HA systems upon addition of 100 μM As.

For As(III) experiments, clay and clay–HA suspension were first deoxygenated by bubbling the suspension with N_2 once for 10 min and then again 5 min before adding anoxic As(III) solution in an anoxic glovebox. After equilibrating the mixtures for 72 h (at 150 rpm) on a horizontal shaker, samples were taken, filtered through a 0.45 μm MCE filter, and prepared for As total measurements (see analytical section). The reaction time of 72 h was determined to be sufficient from preliminary kinetic sorption experiments with As(III)/As(V) and both clay and clay–HA suspensions (data not shown). Sampling from As(III) sorption experiments was conducted in an anoxic glovebox. The pH change in all sorption experiments was less than 5% at the end of the experiments.

2.5. Desorption of As from clay and clay–HA by phosphate and silicate

To quantify desorption of As from clay and clay–HA complexes by phosphate and silicate, setups were chosen from sorption experiments where either 1 or 25 μM As (prepared in 10 mM $CaCl_2$, pH 7) was initially added to the clay and clay–HA complexes (see description of experimental setup in Fig. 1). These amounts of As loaded to clay/clay–HA represent average low and high amounts of As in solid phases (0.01–3.0 μmol As per g clay) in As-rich aquifers reported by several authors (Chakraborti et al., 2001; Mandal and Suzuki, 2002; Ullah, 1998). We would like to note that concentrations of 25 μM As were chosen to represent ‘high As loading’ for the desorption experiments, based on recent studies describing clay phases with high (average) As loadings (Chakraborti et al., 2001; Ullah, 1998). Therefore, whereas 100 μM As was chosen as the maximum concentration of As added to clay/clay–HA in the sorption experiments (described in Section 2.4), for desorption experiments 25 μM As was chosen for obtaining ‘high loading’. 100 μM and 500 μM phosphate and silicate (both prepared in 10 mM $CaCl_2$, pH 7) were separately added to each setup. The concentrations of phosphate and silicate chosen in this experiment to desorb arsenic represent average and high concentrations of the respective anions in solution found in some As contaminated aquifers and natural systems (Stollenwerk et al., 2007; Violante and Pigna, 2002). 96 h of desorption time was allowed for all setups before samples were taken and analyzed for total dissolved As (see analytical section). The desorption time of 96 h was determined to be sufficient from preliminary kinetic desorption experiments quantifying desorption of As(III) and As(V) over time from As(V)- and As (III)-loaded clay and clay–HA complexes (data not shown). The pH of all the setups remained neutral throughout the course of the experiments.

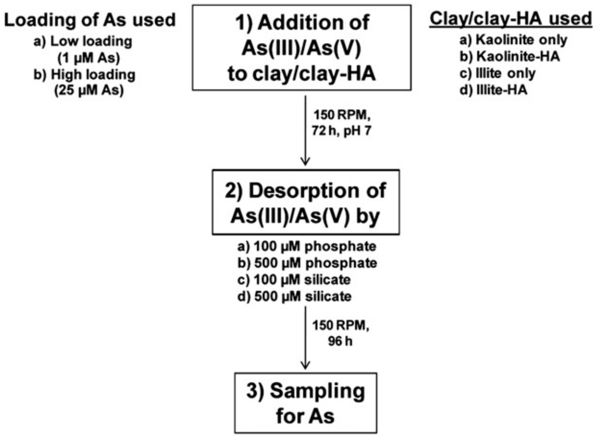

Fig. 1. Illustration of the experimental setup for arsenic desorption experiments: (1) Sorption of As(III)/As(V) to clay only (kaolinite and illite only) and clay–HA (kaolinite–HA and illite–HA complexes) was carried out either at low (1 µM) or at high (25 µM) As concentration, (2) Desorption of As(III) and As(V) from clay only and clay–HA complexes was carried out by addition of either 100 and 500 µM phosphate or 100 and 500 µM silicate, and (3) Quantification of desorbed/dissolved As after 96 h of incubation. It should be noted that all As(III) experiments involving As(III) (including addition reagents and sampling) were carried out in an anoxic glovebox.

2.6. Analytical methods

To quantify As in solution, 400 µL aliquots were taken from each experimental setup, centrifuged for 3 min (at 14,000 rpm), and the supernatant was acidified with 1 M HNO_3. The supernatant was analyzed for total As by ICP-MS. Selected samples were analyzed for As speciation by LC-ICP-MS (sample preparation protocol from Daus et al. (2002)). In all systems, there was less than 5% As oxidation or reduction in both As(III) and As(V) systems (data not shown), and therefore potential effects on sorption due to As redox changes can be disregarded. Al and Fe were not quantified in the supernatant and therefore the presence of clay–humics colloids in the supernatant and a slight overestimation of dissolved As concentrations can therefore not be ruled out. DOC was quantified from filtered solutions (0.45 µm MCE filter) by a TOC analyzer (highTOC II, Elementar Analysensysteme GmbH, Hanau, Germany). The absorbance was measured in a plate reader (FlashScan 550, Jena Analytik, Germany). Surface areas of clay minerals were measured with the BET method (Malvern, Germany).

2.7. Statistical analysis

The desorption data was statistically evaluated (within each clay or clay–HA experimental setup) with a two-way analysis of variance using SPSS 12.0. Means separation was performed by Duncan's multiple range test at $P \leq 0.05$.

3. Results and discussion

3.1. Sorption of As to clays in clay and clay–HA systems

In As-contaminated aquifers, both clay minerals and natural organic matter (humic substances) were shown to be present (Hossain, 2006) and therefore As–clay interactions occur either in the presence of dissolved OM or with clay minerals coated with OM. To determine the effect of humic acids on As sorption to clays, we first quantified sorption of As to clay–HA (Kao–HA and IL–HA) complexes in comparison to clay only systems (Kao and IL) (Table 1, Fig. 2A to D).

3.1.1. Comparison of sorption of As to clay vs clay–HA complexes

HA adsorbed to clay affected As sorption considerably. After addition of 100 µM of As, As sorption was significantly lower in clay only systems compared to clay–HA systems (Table 1, Fig. 2A to D). The amount of As(III) sorbed increased by 50% in Kao–HA and by 28% in IL–HA systems compared to Kao and IL (HA-free) systems, respectively. Similarly, sorption of As(V) increased by 41 and 35% in the presence of HA compared to Kao and IL only systems, respectively. The increased sorption of As by clay–HA complexes compared to clay only is probably due to sorption of the humic acids to the clay surface that modifies the clay surface properties in a way that enhances the binding of As (Martinez et al., 2010). Possible mechanisms of As sorption onto the clay minerals and clay–HA complexes are illustrated in Fig. 3. Arsenic can either sorb directly to the clay mineral surface as an inner-sphere complex or as an outer-sphere ternary surface complex using Ca^{2+} as a cation bridge (Fig. 3). Complexation of As with OM in the presence of a cation bridge such as Fe has been shown previously in literature (Sharma et al., 2010; Wang and Mulligan, 2006) and it is possible that the negatively charged clay particles and As can interact with each other via Ca^{2+} as a cation bridge in our systems. In addition to binding to clay via cation bridges, As can also form ternary complexes with HA molecules that are bound to clay minerals provided that there are positively charged functional groups such as amines (Saada et al., 2003a) or phenolate groups (Buschmann et al., 2006) which can bind As. HA bind strongly to the clay mineral surface via cation bridges such as Ca^{2+} (Jekel, 1986; Saada et al., 2003b; Tipping and Higgins, 1982). Additionally, Saada et al. (2003a) found enhanced sorption of As onto clay–HA complexes with increasing nitrogen content. However, dialysis and ultracentrifugation experiments of As–HA colloids and dissolved complexes (Sharma et al., 2010) revealed that, at neutral pH, direct binding of As to HA (in the absence of bridging metal cations) was negligible even when high concentrations of As(V) and HA (100 µM As(V) and 50 mg C/L HA) were incubated together for 5 days. With regard to the potentially involved N-containing As binding sites, this is remarkable since the Pahokee peat HA that were

Table 1
Amount of As(III) and As(V) sorbed (µmol As/g clay) upon addition of 100 µM As(III) and As(V) to kaolinite and to illite only, or to kaolinite–HA and to illite–HA.

Setups	As(III)	As(V)
	µmol/g	µmol/g
Illite	1.22 (0.08)	1.06 (0.03)
Kaolinite	1.09 (0.10)	0.82 (0.12)
Illite–HA	1.65 (0.12)	1.37 (0.10)
Kaolinite–HA	1.54 (0.09)	1.23 (0.18)

The solid:solution ratio was 1:50 (m/v): 0.5 g clay/clay–HA and 25 ml of 10 mM $CaCl_2$. Background solution in all experiments was 10 mM $CaCl_2$. Arsenic was equilibrated with clay/clay–HA for 72 h at 150 rpm. All experiments were carried out in duplicates. Numbers in parentheses show errors calculated from duplicate setups.

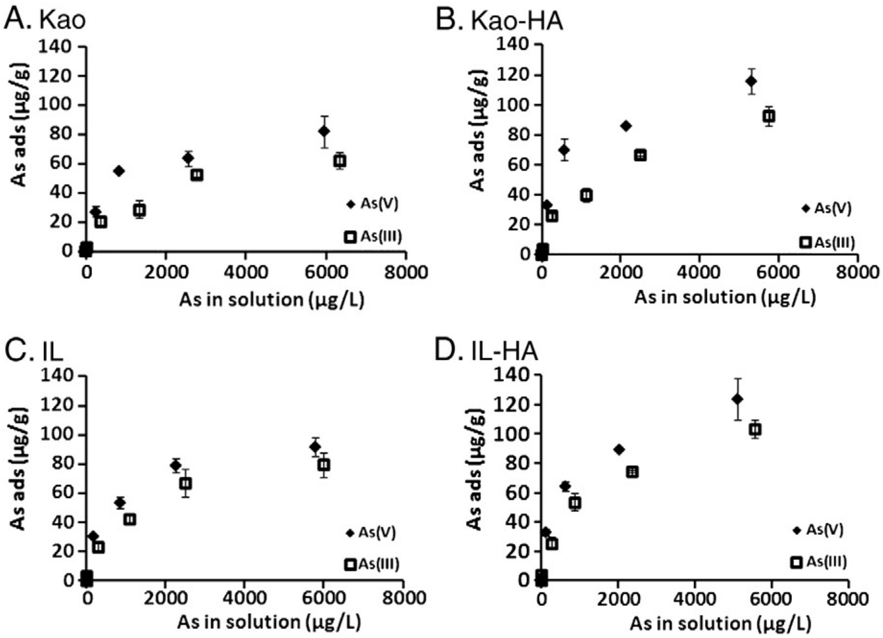

Fig. 2. Sorption isotherms of As(III) and As(V) to kaolinite (Kao – panel A), kaolinite–HA (Kao–HA – panel B), illite (IL – panel C), and illite–HA (IL–HA – panel D). The plots show the As concentration in solution after equilibrium has been reached (72 hours) vs the amount of As sorbed to the clay mineral surface in µmol As per g of clay mineral present. Error bars represent standard deviations calculated from three parallel samples.

used in the present study as well as in the study by Sharma et al. (2010) have a relatively high nitrogen content of 3.7% compared to the nitrogen content of 2.1% in the peat humic acids used by Saada et al. (2003a). Therefore, although amino groups are possible binding sites for As, binding of As to HA via metal cations in the HA itself is probably more important for As sorption in our systems (see illustration in Fig. 3). Furthermore, the clay minerals were homoionized with Ca^{2+}, which is also present in the background solution during the incubation of the clay with the HA and As. Aggregation of HA by Ca^{2+} on the clay mineral surface is therefore possibly leading to Ca^{2+}–HA structures at the clay surface via Ca^{2+} bridges thus increasing the number of binding sites for As and explaining the higher extent of sorption of As to clay–HA systems compared to clay only systems. This is supported by a study by Saada et al. (2003b), where the authors have experimentally shown that sorption of HA to clay minerals is enhanced in the presence of Ca^{2+} ions. The authors have suggested that Ca^{2+} ions enhance HA

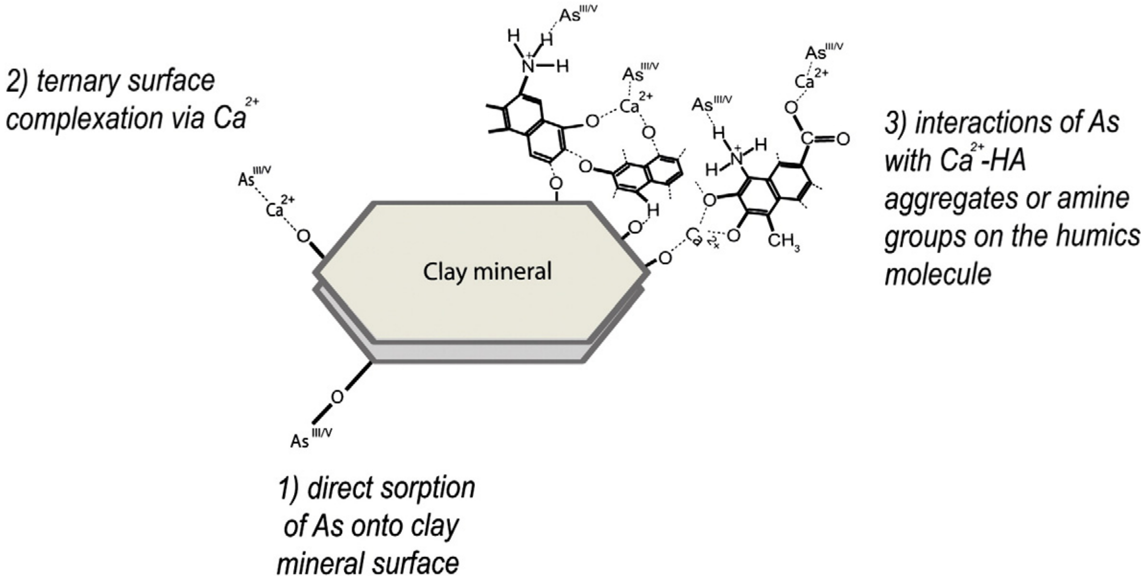

Fig. 3. Possible interactions between As(III)/As(V), clay minerals and humic acids (HA): (1) sorption of As(III) or As(V) directly to the clay mineral surface via an inner-sphere complex, (2) binding of As(III) or As(V) to the clay mineral surface via ternary complex formation with Ca^{2+} functioning as cation bridge (outer sphere complex), and (3) interactions of As with Ca^{2+}–HA aggregates or with amine groups from humic molecules sorbed to clay surface.

binding to clay by forming 'intra-molecular bridges' within the HA molecules as well as forming bridges between the clay and the HA suggesting that clay–Ca^{2+}–HA-complexes are formed. Binding of other anions (such as arsenate) could then be increased as a result of additional binding sites provided by the HA and Ca^{2+}. Such increased As adsorption to mineral surfaces in the presence of Ca^{2+} ions has also been described for natural clays (Smith et al., 2002).

One concern of the presence of Ca^{2+} is the potential formation of calcium arsenate mineral phases at high calcium and arsenate concentrations. Calcium arsenate precipitates such as $Ca_3(AsO_4)_2 \times 4H_2O$ were shown to form between Ca/As ratios of 1.5–2.0 and from suspensions that had pH values slightly higher than pH 7 up to a pH of 12 (Bothe and Brown, 1999). Based on the solubility product of $Ca_3(AsO_4)_2$ (6.8×10^{-19}, Cheng et al., 2009) and concentrations of Ca^{2+} (10 mM) and As (1 or 25 μM), the formation of calcium–arsenic precipitates at the clay surfaces is possible in our experiments. However, comparison of sorption isotherms for As(V) to the isotherms obtained with As(III) (Fig. 2) did not show any striking deviations from normal sorption behavior at high As(V) concentrations thus suggesting the absence to surface precipitation of calcium arsenates.

3.1.2. Comparison of sorption of As(III) vs As(V) to clay/clay–HA

Not only the presence of HA plus potentially bridging cations influenced As sorption to the clays, the As redox speciation also influenced As sorption behavior (Table 1). As(III) and As(V) were previously shown to sorb to different extents to different mineral phases such as ferrihydrite and goethite (Goldberg, 2002) and therefore a difference in the amount of As sorbed was also expected upon sorption to different forms of clay and clay–HA aggregates. We found that at neutral pH and after addition of 100 μM As(III) and As(V), respectively, As(V) sorbed to the clays to a greater extent (15, 20, 25 and 32%, respectively) than As(III) in IL, IL–HA, Kao and Kao–HA systems, respectively (Table 1). This sorption behavior of arsenite and arsenate is different compared to their sorption to iron minerals such as ferrihydrite or goethite where – at neutral pH – arsenite usually sorbs to a higher extent than arsenate (Dixit and Hering, 2003; Herbel and Fendorf, 2006; Raven et al., 1998). The greater adsorption of As(V) to the clays compared to As(III) in our systems can be explained by the electrostatic interactions between positively charged clay mineral surfaces (that were homoionized with 1 M Ca^{2+}) and the negatively charge deprotonated As(V) species at pH 7. The first two pKa values of arsenic acid (H_3AsO_4) are 2.2 (pKa_1) and 6.9 (pKa_2) while the first pKa value for arsenous acid (H_3AsO_3) is 9.2 (pKa_1). Therefore, at a circumneutral pH the positively charged clay surface would preferentially bind the negatively charged arsenate species compared to H_3AsO_3. This was also demonstrated in a separate study carried out by Smith et al. (2002), where they found that As(V) binds more to clay-rich soils in the presence of Ca^{2+} in comparison to As(III).

3.1.3. Comparison of sorption of As to different clay/clay–HA types (i.e. IL vs Kao and IL–HA vs Kao–HA)

In addition to the two different As redox species, the two tested clay minerals, kaolinite and illite, also showed noticeable differences with regard to As sorption (Table 1). For As(III), we found that sorption to IL and IL–HA systems was higher by 29.2 and 11.4% compared to Kao and Kao–HA systems, respectively. For As(V), the sorption maxima on IL and IL–HA were 11.9 and 7.1% higher than in Kao and Kao–HA systems. The sorption of As onto clay mineral surfaces depends on the structure and the surface area of the clay minerals (Lin and Puls, 2000). Aluminol binding sites of phyllosilicates were reported to be more reactive to sorption of organic compounds, anions and trace metals due to significant fractions of free oxygen atoms as compared to silanol sites (Benyahya and Garnier, 1999; Sposito, 1994)). Kaolinite is a 1:1 clay mineral with alternating octahedral and tetrahedral sheet with Si/Al ratio of 1 where as illite is a 2:1 clay mineral with the alumina layer in between the two silica layers with a Si/Al ratio of 2. This means that in kaolinite the more reactive Al–OH octahedral sheet is exposed whereas in illite the Al–OH sheet is masked between two less reactive SiO_4 sheets and therefore, more As is expected to sorb to kaolinite (Lin and Puls, 2000; Manning and Goldberg, 1997). However, in our systems we saw the opposite, i.e. higher sorption of As in IL and IL–HA systems. This can probably be explained by the fact that the specific surface area of illite ($26.8\ m^2/g$) is 3.7 times higher than that of kaolinite ($7.3\ m^2/g$). A previous study by Lin and Puls (2000) also described more As binding to illite compared to kaolinite and they also worked with illite and kaolinite clay minerals where the illite had a higher surface area than kaolinite.

3.1.4. Sorption of As to clays at low (1 μM) and high (25 μM) initial As concentrations

After having determined sorption isotherms with As concentrations from 1–100 μM, in a second step (as preparation for the desorption experiments) we loaded the clays and clay–HA complexes with two different concentrations of As. The concentrations of As added (i.e. 1 and 25 μM) were selected in order to yield an environmentally relevant low and high amount of As loading (0.01–3.0 μmol As/g clay) as observed by previous authors (Chakraborti et al., 2001; Hossain, 2006; Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2000; Ullah, 1998). We found that the loading of both As(III) and As(V) onto clay/clay–HA depended not only on the initial concentrations of As added, but also on clay type and As species (Table 2).

3.1.4.1. As sorption at low As loading (addition of 1 μM As to clay/clay–HA). At low As loading (addition of 1 μM As), no difference in the amount of As sorbed was found when comparing As(III) and As(V), clay vs clay–HA or Kao vs IL systems (Table 2). The values of As ranged from 0.04 to 0.05 μmol As/g clay for both species of As which means almost all As that was added sorbed to clay/clay–HA complexes. Since almost all As sorbed at low As loading, these experiments do not provide information on differences in adsorption affinity.

3.1.4.2. As sorption at high As loading (addition of 25 μM As to clay/clay–HA). Compared to the low As loading, at high As loading (addition of 25 μM As) there were differences between HA-loaded and HA-free clays, between kaolinite and illite, and between As(III) and As(V) following the same trends that were already observed when 100 μM As was added (for details see Section 3.1). Final As(III) loadings were 0.56, 0.71, 0.41 and 0.57 μmol As(III)/g clay and As(V)

Table 2
Amount of As(III) and As(V) sorbed (μmol As/g clay) upon addition of 1 μM As(III) or As(V) [low As loading] and 25 μM As(III) or As(V) [high As loading] to kaolinite and to illite only or to kaolinite–HA and to illite–HA.

Setups	Low As loadings		High As loadings	
	As(III)	As(V)	As(III)	As(V)
	μmol/g	μmol/g	μmol/g	μmol/g
Illite	0.04(0.02)	0.05(0.02)	0.56(0.05)	0.77(0.08)
Kaolinite	0.04(0.01)	0.04(0.01)	0.41(0.06)	0.73(0.08)
Illite–HA	0.05(0.02)	0.04(0.02)	0.71(0.03)	0.87(0.11)
Kaolinite–HA	0.05(0.02)	0.04(0.02)	0.57(0.04)	0.93(0.09)

The solid:solution ratio was 1:50 (m/v): 0.5 g clay/clay–HA to 25 ml of 10 mM $CaCl_2$. Background solution in all experiments was 10 mM $CaCl_2$. As was equilibrated with clay/clay–HA for 72 h at 150 rpm. All experiments were carried out in duplicates. Numbers in parentheses show errors calculated from duplicate setups.

loadings were 0.77, 0.87, 0.73 and 0.93 μmol As(V)/g clay in IL, IL–HA, Kao and Kao–HA systems, respectively (Table 2).

3.2. Desorption of As from clay and clay–HA by phosphate and silicate

Many of the As contaminated regions in South Asia include extensive irrigation areas where crops are grown perennially. In these agricultural fields, phosphate is not only naturally present in minerals, as sorbed phases or as dissolved species, but it also can be present due to a widespread usage of phosphate fertilizers which enter the groundwater systems (Acharyya et al., 1999). On the other hand, high concentrations of groundwater silica (1–1000 μM) were found in As-contaminated soils and aquifers due to active weathering of silicate minerals (Iler, 1979; Meng et al., 2001). Anions such as phosphate, which has an analogous structure to that of arsenate, and silicate, which can effectively sorb to mineral phases were shown to desorb both arsenate and arsenite from minerals in soils (Meng et al., 2001; Stollenwerk et al., 2007).

3.2.1. Desorption of As by phosphate and silicate at high As loading

In our experiments, we found that not only sorption of As, but also desorption of As by phosphate and silicate, depends upon the amount of As initially loaded to clay and clay–HA systems.

3.2.1.1. Desorption of As by phosphate and silicate in clay vs clay–HA systems. At high As loading, desorption in clay only systems were significantly lower (at $P = 0.05$) than clay–HA systems (Fig. 4C and D). A concentration of 100 μM phosphate desorbed between 13–36% of As(V) and 25–31% of As(III) while 500 μM phosphate desorbed between 27–34% of As(V) and 42–48% of As(III) in clay only systems. In clay–HA systems, the amount of As desorbed by 100 μM phosphate increased to 36–45% for As(V) and 39–48% for As(III) (Fig. 4). When 500 μM phosphate were added to clay–HA systems, 27–60% of As(V) and 48–72% of As(III) was desorbed. Desorption of As by silicate at high As loading showed a similar trend as observed for the phosphate. In clay only systems, desorption by 100 and 500 μM silicate ranged from 2 to 10 and 8–19% respectively. In clay-HA complexes, the amount of As desorbed ranged between 14–32 and 20–39% by 100 and 500 μM silicate. The results from As desorption experiments compared to the initial amount of As loaded show that although more As can bind to clay–HA complexes than to clay only (without preloaded HA), the As is also desorbed to a greater extent from HA-covered clays in comparison to clay only systems. This can possibly be explained by the types of sorption sites on the clay mineral surface for these two systems. Inner-sphere complexes of As–clay or As–Ca^{2+}–clay are expected to be stronger than As bound to Ca^{2+}–HA–clay structures (Fig. 3). This means that As bound to clay via Ca^{2+}–HA will possibly be desorbed more easily than the arsenic that is bound directly to the clay mineral surface.

3.2.1.2. Desorption of As by phosphate vs silicate. When comparing desorption of As by phosphate to desorption by silicate, we found that 500 μM phosphate is more effective in desorbing As than 500 μM silicate in the systems with high As loading (Fig. 4). Additionally, 100 μM phosphate desorbed more As than 100 μM or 500 μM silicate with the exception of IL only systems for both As(V) and As(III) and Kao only systems for As(III). Phosphate being more effective than silicate has also been described previously for As desorption from clays (Stollenwerk et al., 2007). Overall, for both clay types and with/without HA, phosphate desorbed between 38 and 72% of the presorbed As whereas silicate desorbed only between 23 and 50% of As. Increasing the phosphate concentration from 100 to 500 μM increased the amount of As desorbed in all experimental setups. In contrast, increasing the silicate concentrations from 100 to 500 μM only increased desorption in As(V) experiments conducted with illite, in the other experiments it did not increase the amount of As desorbed.

3.2.1.3. Desorption of As in IL vs Kao and IL–HA vs Kao–HA. When comparing desorption of As for the two clays tested in this study, i.e. IL vs Kao, at high As loading in the absence of HA, desorption of As(III) and As(V) by phosphate or silicate showed no significant differences between the two clays (Fig. 4). This is remarkable since in the sorption experiments with 100 μM As, both redox species of As sorbed more to IL compared to Kao. This observation illustrates that determination of arsenic sorption isotherms for both As redox species does not necessarily allow predictions to be made as to which As species is detached from the surface of different clays more easily by competitive ligands.

In contrast to the HA-free clays, in IL–HA and Kao–HA some differences in desorption were observed between the two clays. Desorption of As in IL–HA systems was generally higher than in Kao–HA systems regardless of the As species, except for desorption of As(III) by 100 and 500 μM phosphate where higher amounts of As(III) were desorbed from Kao–HA than from IL–HA. Why more As(III) is desorbed from Kao–HA by phosphate than from IL–HA is currently unclear.

3.2.1.4. Desorption of As(V) vs As(III) in clay/clay–HA systems. When comparing As(V) to As(III), we found that the amounts of As(III) or As(V) desorbed by phosphate or silicate did not always follow a specific trend. We observed that in clay only systems, the amounts of As(V) and As(III) desorbed

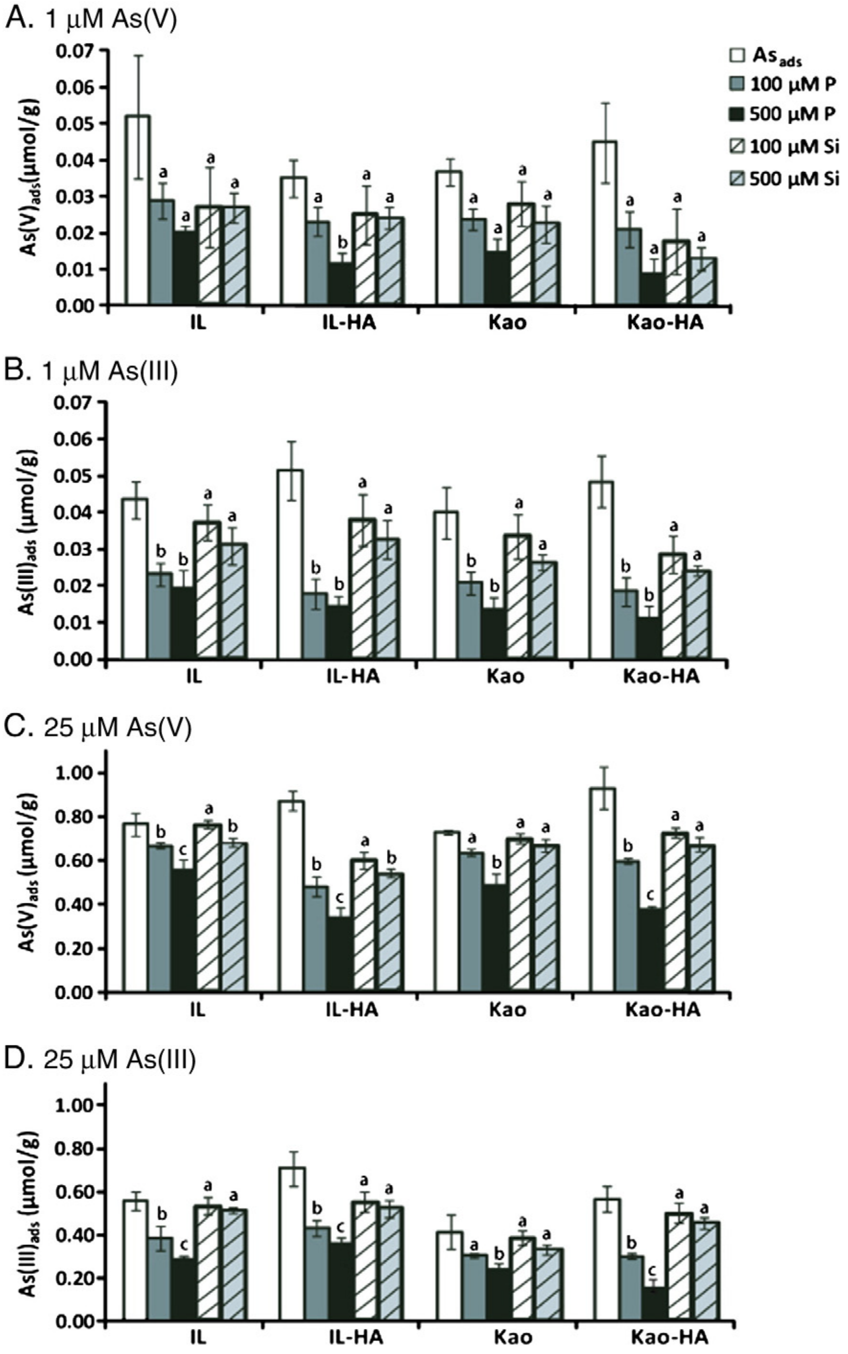

Fig. 4. Amount of As(III) and As(V) sorbed to IL, IL–HA, Kao and Kao–HA in the absence of phosphate and silica (white bars), and in the presence of 100 or 500 μM phosphate, and 100 or 500 μM silicate (phosphate and silicate experiments represented by colored and striped bars, respectively). Panels A–D denote experiments for As desorption with initially added (A) 1 μM As(V), (B) 1 μM As(III), (C) 25 μM As(V) and (D) 25 μM As(III). Error bars represent standard deviations calculated from two parallel samples. Different letters on the bars indicate statistically significant differences ($p = 0.05$) in As desorption by 100 μM and 500 μM phosphate and silicate within each clay system (i.e. within IL, IL–HA, Kao, Kao–HA experimental setups) according to Duncan's multiple range test. Note different scales of y-axes in C and D.

were not significantly different (Fig. 4). In contrast, in both IL–HA and Kao–HA systems, more As(V) was desorbed by silicate than As(III) and addition of phosphate desorbed more As(V) from IL–HA and more As(III) from Kao–HA. The reasons behind these desorption patterns are unclear.

3.2.2. Desorption at low As loadings

In addition to quantification of As desorption from clays at high As loading, we also quantified As desorption from clay and clay–HA at low As loading (Fig. 4). Significant differences in the amount of As(III) desorbed were found when phosphate containing systems (both at 100 and 500 μM phosphate) were compared to silicate in clay-only as well as in clay–HA systems with phosphate desorbing more As(III) than silicate. In As(V) systems, only 500 μM phosphate in IL–HA desorbed significantly more As(V) than silicate. This suggests that phosphate may desorb arsenite more effectively than arsenate at lower As loadings. When comparing As desorption by increasing concentrations of phosphate to increasing concentrations of silicate (i.e. 100 and 500 μM phosphate and silicate), desorption of As by 500 μM phosphate was significantly higher than As desorption by 100 μM phosphate in As(V) systems although this was not the case in As(III) systems. Between 100 and 500 μM silicate, there was no significant difference in the amount of As desorbed in any system. This suggests that an increase in concentrations of phosphate could desorb more As from clay/clay–HA and release the As into groundwater but increasing silicate concentrations are not necessarily expected to desorb more As from clay or clay–HA complexes at low As loadings. Besides the effect of increasing phosphate concentrations on As desorption, at low As loading, we did not find significant differences when we comparing As desorption in clay vs. clay–HA, IL vs. Kao or As(III) vs. As(V) setups.

4. Conclusions

In the present study, we quantified sorption and desorption of As in clay (illite and kaolinite) and clay–HA at neutral pH. The results demonstrated that HA sorbed to clay increased sorption of both As(III) and As(V) at neutral pH. Compared to As(III), higher amounts of As(V) sorbed to both clay and clay–HA. Illite and illite–HA generally sorbed more As than kaolinite and kaolinite–HA in the presence of high As concentrations. In desorption experiments, we demonstrated that higher relative amounts of As can be desorbed from clay–HA complexes by phosphate and silicate than from clay-only systems, particularly at high As loading. Phosphate was more effective than silicate in desorbing As confirming previous findings (Stollenwerk et al., 2007). At low As loading, sorption of HA to clay did not significantly impact the amount As sorption and desorption.

The results of our study suggest that in As-contaminated aquifers with high amounts of NOM and clay, formation of clay–NOM complexes can significantly increase sorption of As to clay. However, depending on the concentration of phosphate and silicate ions present in the soil solutions, As is expected to be effectively mobilized again from clay/clay–NOM. This process is particularly relevant in As-contaminated aquifers such as those of South Asia where high amounts of As, NOM, clay, phosphate and silicate are present. However, the stability of As sorbed to clay–HA complexes, and possible sorption mechanisms and desorption mechanisms by phosphate and silicate in these systems are not yet fully understood and more research on As–clay–NOM interactions in presence of phosphate and silicate is required to gain a better understanding of the sorption and desorption processes in As contaminated environments.

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