Soil organic matter affects arsenic and antimony sorption in anaerobic soils

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Abstract

Soil organic matter (SOM) affects arsenic (As) and antimony (Sb) mobility in soil under waterlogged conditions by acting as an electron donor, by catalyzing redox–cycling through electron shuttling and by acting as a competing ligand. This study was set up to disentangle these different effects of SOM towards As and Sb sorption in anaerobic soils. Nine samples were taken at different depths in an agricultural soil profile to collect samples with a natural SOM gradient (<1 – 40 g soil organic carbon kg^{-1}). The samples were incubated either or not under waterlogged conditions in an anaerobic chamber for 63 – 70 days, and glucose (5 g C kg^{-1}) was either or not added to the anaerobic incubated samples as an electron donor that neither acts as an electron shuttle nor as a competing ligand. The solid-liquid distribution coefficients (K_D) were measured at trace levels. The K_D values of As decreased ~2 orders of magnitude upon waterlogging the SOM rich topsoil, while no additional changes were observed when glucose was added. In contrast, smaller changes in the As K_D values were found in the low SOM containing subsoil samples, unless glucose was added that mobilized As. The Sb K_D values increased upon reducing conditions up to factor 20, but again only in the high SOM topsoil samples. Surprisingly, the Sb immobilization during waterlogging only occurred in Sb amended soils whereas the geogenic Sb was mobilized upon reducing conditions, although total dissolved Sb concentrations remained low (<10 nM). The change in As and Sb sorption upon waterlogging was similar in the SOM rich topsoil as in the low SOM subsoil amended with glucose. This suggests that the SOM dependent changes in As and Sb mobility in response to soil waterlogging are primarily determined to the role of SOM as electron donor.

Capsule: The change in arsenic and antimony mobility under waterlogged conditions is largely determined by the electron donor capacity of organic matter.

1. Introduction

Arsenic (As) and antimony (Sb) have potential hazardous effect on human health and environment (Filella et al., 2009; Mandal and Suzuki, 2002). The risk of both elements to the environment is determined by their toxicity and mobility in soil, and the redox potential (E_h) exerts a strong influence on this mobility. First, the chemical speciation of both As and Sb is pH and E_h dependent, i.e., at environmental relevant pH (4 – 9), arsenic dominates as the oxyanions $H_2AsO_4^-$ and $HAsO_4^{2-}$ in oxidized systems (As(V)), while in more reduced systems, the neutral species $H_3AsO_3^0$ prevails (As(III)) (Masscheleyn et al., 1991; Wilson et al., 2010). The main Sb solution species at environmental relevant pH in oxidizing conditions is the $Sb(OH)_6^-$ anion (Sb(V)), while in reducing conditions the neutral $Sb(OH)_3^0$ dominates (Sb(III)) (Filella and May, 2003; Mitsunobu et al., 2010). Second, the mobility of each chemical species will be determined by its specific sorption characteristics to the reactive soil minerals or by the specific solubility products of possible precipitates. For example, all As and Sb species are strongly retained on iron (Fe) hydroxides by sorption reactions, however, the more oxidized species are in general more strongly retained at acidic pH, while the sorption of the more reduced species are more strongly retained at higher pH (Dixit and Hering, 2003; Leuz et al., 2006). In addition, at elevated concentrations of As and Sb in soils (i.e. > 1 g kg^{-1}) Ca-arsenates and Ca-antimonates can control the As and Sb solubility (Johnson et al., 2005; Martínez-Villegas et al., 2013). Furthermore, the highly insoluble tripuhyite ($FeSbO_4$) can control the Sb solution concentration at very low levels (~ 1 ng L^{-1}), however the formation of this secondary ferric antimonate mineral is likely slow, due to kinetic constraints (Leverett et al., 2012). Finally, under moderately reducing conditions, poorly soluble Sb(III)–oxides like valentinite and senarmonite (Sb_2O_3) could control the Sb solubility , while under sulphate–reducing conditions, Sb(III)–sulfides (i.e. stibnite) can form (Bennett et al., 2017; Filella et al., 2009).

Lowering soil redox potential, e.g. due to waterlogging, is typically associated with mobilisation of As, however exceptions and reverse trends have been documented (Frohne et al., 2011; Hamon et al., 2004; Stroud et al., 2011; Williams et al., 2011). In contrast, anaerobic conditions typically immobilise Sb and, again, some exceptions have been noted (Frohne et al., 2011; Hockmann et al., 2014b, 2014a; Mitsunobu et al., 2006; Okkenhaug et al., 2012). The mechanisms behind mobilization or immobilization of As and Sb upon reducing conditions are rather complex, because changing redox conditions not only affects the speciation of As and Sb, but also the properties of their sorbents which, in turn, influences strongly As and Sb mobility. For example, reductive dissolution of Fe(III) and Mn (III, IV) hydroxides can release previously bound As and Sb (Frohne et al., 2011; Hamon et al., 2004; Hockmann et al., 2014b; Lovley, 1997). In contrast, Fe(II)-induced transformation of ferrihydrite to more crystalline feroxyhyte and goethite under mild reducing conditions can immobilize Sb, likely by structural incorporation of Sb(V) into the freshly formed Fe(III) hydroxide crystal lattice (Burton et al., 2019).

Soil organic matter (SOM) can have a strong influence on redox-transformations of toxic elements and of soil minerals (Borch et al., 2010), with different underlying mechanisms. First, the presence of biodegradable carbon fuels i) aerobic respiration that will lead to anaerobic, thus reducing conditions, when oxygen supply is limited and ii) anaerobic respiration that enhances the reduction of redox-sensitive elements (Kulp et al., 2014; Oremland and Stolz, 2005). Next to this, humic substances play a role in redox cycling of As and Sb, or of their host minerals Fe and Mn hydroxides by coupling the redox cycles of the redox-sensitive elements to the redox cycles of quinone/hydroquinone functional groups present in the humic substances, either directly or indirectly due to electron shuttling between electron donors and acceptors (Jiang et al., 2009; Lovley et al., 1998; Qiao et al., 2019; Redman et al., 2002). Finally, competition for sorption sites at Fe and Al hydroxide surfaces between humic substances and

As (Bauer and Blodau, 2006; Dousova et al., 2015; Gustafsson, 2006; Redman et al., 2002; Verbeeck et al., 2017; Weng et al., 2009) or Sb (Karimian et al., 2019; Verbeeck et al., 2019), may render As and Sb more available in soils for redox transformations. Thus, SOM could influence redox-cycling of As and Sb and this can result in mobilisation or immobilisation of As and Sb when soils get waterlogged. Furthermore, different underlying mechanisms can be responsible for these changes in As and Sb retention, and this will likely depend on the local composition of the organic matter, i.e. less or more biodegradable or less or more highly reactive humic substances, similar as observed for aquifer sediments in the case of As (Guo et al., 2019; Kulkarni et al., 2017). However, less information is available on this topic for Sb and at background levels of both As and Sb in soils.

The objective of this study is to better understand the role of soil organic matter (SOM) on the change in As and Sb mobility upon waterlogging soils. The hypothesis is that the presence of SOM strongly affects the As and Sb mobility in waterlogged soils, and that the effects of SOM on the change in As and Sb mobility combines different mechanisms i.e. being an electron donor, electron shuttle or competitor for As and Sb species. To address this issue, the As and Sb solid-liquid distribution was measured at low As and Sb concentrations in experimentally waterlogged soils that i) have a natural gradient in SOM concentrations and ii) are amended with or without glucose as an electron donor with neither electron shuttling nor competitive effects on As and Sb sorption.

2. Materials and methods

2.1. Soil samples and standard soil analysis

A soil profile was excavated up to 3 m depth in a Stagnic Luvisol under agricultural grassland in NE France (Crespy-le-Neuf, 48°24’11’’N, 4°37’44’’E). Nine samples were taken from different depths, to obtain samples with a natural gradient in SOM concentration. The samples

were labelled P1_X with X the average sampling depth. All samples were sieved at 2 mm, air-dried, and homogenized with a mortar and pestle prior to soil analysis.

Amorphous Fe, Al and manganese (Mn) and associated As were determined in a 0.2 M ammonium oxalate extract at pH 3 (solid:liquid ratio 1:50, 2 hours equilibration in darkness; Schwertmann (1964)) by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700x, Agilent Technologies, Santa Clara, CA, USA). Total Fe (hydr)oxide concentration was determined by ICP-MS in a dithionite-citrate-bicarbonate (Fe_{DCB}) extract with an adapted method based on Mehra and Jackson(1953). In short, 1 g air dry soil was weighed into a dark 50 ml centrifuge tube, 1 g of solid dithionite ($Na_2S_2O_4$; Fischer Scientific, Merelbeke, Belgium) was added, followed by 50 ml of 0.3 M citrate – 0.1 M bicarbonate pH buffer. The samples were warmed at 40°C in the oven for 3 h and then shaken (end-over-end) for 24 h at 19°C. Finally, samples were centrifuged at 2500 g for 10 min and the supernatant was sufficiently diluted before total Fe analysis with ICP-MS. The total organic carbon (OC) concentration of the soil samples was determined by thermal oxidation at 900 °C, followed by gas chromatographic measurements of the CO_2 generated (EA 1110, CE instruments, Wigan, UK) after removal of carbonates with a 5% HCl solution. The dissolved organic carbon (DOC) concentration was determined in a 1:10 solid:liquid ratio 5 mM $Ca(NO_3)_2$ soil extract as the non-purgeable organic carbon (NPOC) by catalytic combustion and infrared detection of CO_2 (Multi NC-2100, AnalytikJena, Jena, Germany; Visco et al., 2005)). Soil pH was measured in a 5 mM $Ca(NO_3)_2$ extract with a 1:10 solid:liquid ratio.

The total As concentration of the soil was determined by measuring the As concentration in an *aqua regia* soil digest (3:1 ratio of concentrated $HCl:HNO_3$) with ICP-MS (helium gas was used in the collision cell to remove interferences). Total soil Sb concentration was determined by a four acid digestion, as described in Verbeeck et al. (2019) and here shortly repeated (full protocol in the Supplementary data). Fifty mg of soil was weighed into Savillex beakers with

screw caps (Savillex, Eden Prairie, MN, USA). Concentrated HNO_3 (65%), $HClO_4$ (70%) and HF (48%) were added consecutively, with digestion in a closed system and evaporation near dry between each acid addition step and the residual digest was dissolved in 2.5 M HCl. The Sb concentration in the digests was measured with ICP-MS at m/z = 121, without use of reaction gas or collision cell. A reference sample (PACS-2 marine sediment, National Research Council of Canada, Ottawa, Canada) with certified As and Sb concentrations was included each batch in duplicate. All soil properties were analysed in duplicate, except for soil Sb that was analysed without replicates.

2.2. Arsenic and antimony sorption under different redox conditions

The original samples that were collected moist in the field and stored at 4°C, were sieved at 4 mm. The field-moist soil samples had a gravimetric moisture content of on average 0.2 L kg^{-1} oven-dry soil. The As and Sb sorption was determined by measuring the solid-liquid distribution coefficient (K_D) on samples with four contrasting treatments: i) no treatment, initial samples at moisture content as sampled; ii) aerobic incubation at moisture content as sampled for 63 – 70 days; iii) anaerobic incubation under waterlogged conditions in an anaerobic chamber (95% N_2, 5% H_2) for 63 – 70 days; iv) anaerobic incubations under waterlogged conditions in an anaerobic chamber for 63 – 70 days, with the addition of glucose (5 g C per kg soil; α-D-glucose, Sigma-Aldrich, Darmstadt, Germany) as electron donor and carbon source to stimulate microbial respiration and subsequent reducing conditions. The relative long incubation time was chosen to mimic seasonal periods of waterlogging. The different treatments were made in duplicate.

2.2.1. Arsenic sorption

Arsenic K_D values were determined by single dose addition of the radio-tracer ^{73}As (as As(V), Oak Ridge National Laboratory, Oak Ridge, TN, USA). This method enables the measurement

of the solid-liquid distribution of As without changing the soil equilibrium (Degryse et al., 2009). For the initial samples, 2.5 g of field-moist soil was weighed out in a 50 ml centrifuge tube with addition of 24 ml of a 5 mM $CaCl_2$ background solution and 1 ml of a carrier-free ^{73}As stock (final activity of 5 – 26 kBq ml^{-1}, depending on estimated ^{73}As K_D values). Next, the samples were placed in an end-over-end shaker for 7 days. For the aerobic incubation, about 30 g of field-moist soil was incubated at 19±2°C in closed 50 ml centrifuge tubes and after 63 days, 2.5 g of the incubated, field-moist soil was weighed out in a 50 ml centrifuge tube with addition of 24 ml of a 5 mM $CaCl_2$ background solution and 1 ml of a carrier-free ^{73}As stock (final activity of 5 – 26 kBq ml^{-1}, depending on estimated ^{73}As K_D values). Next, the samples were placed in an end-over-end shaker for 7 days. For the anaerobic incubation, 5 g field-moist soil was weighed into a 50 ml centrifuge tube, either or not with glucose addition, followed by 50 ml deoxygenated 5 mM $CaCl_2$. Glucose was added by weighing 63 mg of glucose in the centrifuge tube before adding the soil (i.e. 5 g C kg^{-1}). The samples were shaken manually to homogenize the soil, the solution and the added glucose. Then, for both anaerobic treatments, the samples were pre-incubated in a water bath, completely submerged and at room temperature, for one week before placing them in an anaerobic chamber (95% N_2, 5% H_2; on-site constructed chamber) at room temperature. During the anaerobic incubation, the samples were not further shaken. Resazurin solutions (1 mg L^{-1}; Acros Organics, Thermo Fischer Scientific, Waltham, MA, USA) were used as an anaerobic indicator. Then, after 63 days of anaerobic incubation, the previously incubated soil samples were opened in the anaerobic chamber, 1 ml of the background solution was removed and replaced with 1 ml of ^{73}As spike (final activity of 3 kBq ml^{-1}). Next, the samples were mounted on an end-over-end shaker in the anaerobic chamber and shaken for 7 days.

After 7 days of end-over-end shaking, the soil suspensions of all treatments were left to sediment, the supernatant was 0.45 µm filtered (Chromafil XtraPET -45/25) and the ^{73}As γ

activity (15–70 keV; Packard COBRA Auto-gamma A5003, GMI, Ramsey, MN, USA) was measured. The K_D value for ^{73}As adsorption (in L kg^{-1}) was calculated as

$$K_D\ ^{73}As = \frac{(\gamma_i - \gamma_f)/W}{\gamma_f/V}, \qquad (1)$$

where γ_i and γ_f are the total initial and final activity, respectively, of the added ^{73}As (Bq) in solution, *W* is the mass of soil (oven-dry; kg) and *V* is the volume of the solution (L).

2.2.2. Antimony sorption

Antimony K_D values were measured by a single dose addition of 41 µmol of stable Sb(V) per kg of soil. No radio-tracer was commercially available for Sb, however, the added Sb dose was chosen to examine Sb sorption in the linear range, as suggested by sorption isotherms (Fan et al., 2013; Martínez-Lladó et al., 2011; Verbeeck et al., 2019). In addition, the added Sb dose is very comparable with the oxalate-extractable As concentration in the soils, i.e. the concentration at which the solid-liquid distribution of both elements was evaluated is similar. The incubation procedure, sampling and spiking method were also very similar to that used for As. For the initial samples, 5 g soil (oven-dry basis) was weighed out in a 50 ml centrifuge tube in two treatments, namely, 50 ml of 5 mM $CaCl_2$ was added, to obtain a non-Sb spiked, control sample or 49.8 ml 5 mM $CaCl_2$ was added, followed by 0.2 ml of an Sb spike by a stock solution ($KSb(OH)_6$; Sigma-Aldrich, Darmstadt, Germany), to obtain a Sb-spiked sample. Next, samples were placed in an end-over-end shaker for 7 days. For the aerobic incubation, 5 g soil (oven-dry basis) was incubated at 19±2°C in closed 50 ml centrifuge tubes and after 56 days, the same proceeding as for the initial samples was done, namely adding 50 ml of 5 mM $CaCl_2$ for control samples or adding 49.8 ml 5 mM $CaCl_2$, followed by 0.2 ml of Sb spike by a stock solution. Next, samples were placed in an end-over-end shaker for 7 days. For the anaerobic incubation, 5 g soil (oven-dry basis) was weighed into a 50 ml centrifuge tube, either or not with glucose addition, followed by addition of 50 ml deoxygenated 5 mM $CaCl_2$. Glucose was

added and mixed with the soil suspension exactly as done for the As sorption assay, described above. Then, for both anaerobic treatments, the samples were pre-incubated in a water bath, completely submerged and at room temperature, for one week before placing them in an anaerobic chamber (95% N_2, 5% H_2; Coy Lab's Vinyl Anaerobic Chambers (Coy Laboratory Products Inc., Grass Lake, MI, USA)) at room temperature. During the anaerobic incubation, the samples were not further shaken. Resazurin indicator strips (Oxoid Resazurin Anaerobic Indicator, ThermoFischer Scientific, Waltham, MA, USA) were used as an anaerobic indicator. Then, after 56 days of anaerobic incubation, the previously incubated soil samples were opened in the anaerobic chamber, 0.2 ml of the background solution was removed and replacedwith 0.2 ml of Sb spike, and also for this treatment, non-Sb spiked samples were included. Next, the samples were mounted on an end-over-end shaker in the anaerobic chamber and shaken for 7 days.

After 7 days, the soil suspensions were allowed to settle, the supernatant was filtered over a 0.45 µm filter and the total Sb concentration in solution was measured by ICP-MS. The Sb K_D values (in L kg^{-1}) were calculated as

$$K_D\ Sb = \frac{\left(M_{sol,i} - \left(M_{sol,f} - M_{sol,c}\right)\right) \times V/W}{M_{sol,f} - M_{sol,c}} \qquad (2)$$

with $M_{sol,i}$ and $M_{sol,f}$ are the initial, resp. final concentrations of Sb in solution of the spiked sample and $M_{sol,c}$ is the concentration in solution of the naturally desorbing Sb, in a control, non-Sb spiked soil sample (µM). The $M_{sol,c}$ measurements are needed to correct the final concentrations of the spiked samples, so only the fraction of added Sb that is adsorbed is considered. Defined this way, the K_D values determine the sorption of added Sb, which, in case of linear sorption, equals the solid-liquid distribution of the native, labile background Sb as discussed elsewhere for the classification of K_D values (Degryse et al., 2009). Finally, *W* is the weight of soil (oven-dry; kg) and *V* the volume of the solution (L).

2.3. Solution composition

In addition to the measurements of ^{73}As γ activity and Sb concentration, also DOC, total As, Fe and Mn in solution (ICP-MS), As solution speciation and Fe solution speciation were measured, with the latter two only in the anaerobic incubated samples.

The As speciation analysis was done by a microcartridge method with an anion exchanger resin (Moreno-Jiménez et al., 2013). This speciation method is based on the hypothesis that the neutral $H_3AsO_3^{\circ}$ will not be retained by the anion exchanger, while the negatively charged $H_2AsO_4^-/HAsO_4^{2-}$ will be retained by the anion exchanger. The method is described in the Supplementary data, and Table S1 presents the results of a preliminary test with model solution of As(V)-As(III) mixtures. Only As speciation of the ^{75}As was measured, i.e. before and after eluting the anaerobic supernatant over the anion exchange columns, the ^{75}As was measured by ICP-MS, enabling us to measure the % of total soluble As that is present as As(III). The speciation analysis was always performed within one day after sampling and inside the anaerobic chamber. This method was also tested for Sb speciation analysis, but was found not suitable for this (data not shown). No other method was used, thus no Sb speciation was measured.

The Fe speciation analysis was done by the ferrozine method (Viollier et al., 2000), which measures dissolved Fe(II). For this analysis, an acidified subsample of the supernatant was used (0.1 M HNO_3). In acid conditions, Fe(II) oxidation is very slow (Davison and Seed, 1983), ensuring Fe speciation preservation. The Fe(II) measurements were performed within one day after sampling and outside of the anaerobic chamber.

Finally, the pH and redox potential (E_h) of the soil suspensions were measured with portable field electrodes (WTW pH 91, Xylem Analytics, Weilheim, Germany and VWR ORP15, Avantor, Central Valley, PA, USA), which are easy to use in the anaerobic chamber. This was

done after subsamples for the above described analyses were taken. The redox potential measurement was controlled with saturated quinhydrone solutions at pH 4 and 7 (at 20°C or 25 °C; Alfa Aesar, Thermo Fischer Scientific, Waltham, MA, USA).

2.4. Data analysis

Statistical analyses were performed with the software package JMP Pro 13.1 from SAS Institute Inc. (Cary, North Caroline, U.S.). The change in K_D values upon anaerobic incubation was calculated as the ratio of the K_D value measured during anaerobic incubation with the mean of the K_D value measured during the aerobic incubation of the corresponding soil sample. Correlation analysis between measured soil and solution characteristics was done by calculating the Pearson's correlation coefficient.

3. Results

3.1. Soil properties

The measured soil properties of the selected soil samples are presented in Table 1. The organic carbon (OC) concentration ranged from below detection limit (1 g OC kg^{-1} soil) to 39 g OC kg^{-1} and the dissolved organic carbon (DOC) measured in a 1:10 solid:liquid 5 mM $Ca(NO_3)_2$ soil extract ranged from below detection limit (0.5 mg DOC L^{-1}) to 18 mg DOC L^{-1}. The concentration of amorphous Fe and Al in the samples of upper soil layers, up to about 1 m depth, is higher than the concentration in samples from deeper soil layers. The total free Fe oxides, determined with an dithionite–citrate–bicarbonate extraction, however is more constant throughout the soil profile. This reflects in the amorphous Fe to total Fe oxide ratio (Fe_{ox}:Fe_{DCB}), that is ~50 % in the uppermost soil layer to only 3% starting from about 1 m soil depth. The detection limit for total soil As, determined by *aqua regia* digestion was 0.5 µmol As kg^{-1}, well below the As concentrations in the tested soil samples, that ranged 91 – 223 µmol As kg^{-1}. The detection limit of total soil Sb, determined by the four acid digestion, was 0.4

µmol Sb kg^{-1}, while the Sb concentrations of the tested soil samples ranged 3.4 – 4.9 µmol Sb kg^{-1}. The PACS-2 reference sample has a certified As concentration of 350 ± 20 µmol As kg^{-1} whereas 320 ± 15 µmol As kg^{-1} was measured. The certified Sb concentration in the reference sample was 93 ± 21 µmol Sb kg^{-1} whereas 81 ± 4 µmol Sb kg^{-1} was measured (means with 95% confidence interval). For all standard soil properties, the average coefficient of variation (CV) of duplicate analysis was <9%, only for the DOC, this was 0.7 – 69%, on average 30%.

3.2. As and Sb mobility under changing redox conditions

Initially, the ^{73}As K_D values ranged 4000 – 140 000 L kg^{-1} between soil samples, while Sb K_D values ranged 40 – 190 L kg^{-1} (Tables 2 and 3; full dataset presented in Table S2 and S3). During the aerobic incubation, the K_D values of both elements did not change compared to the initial samples. In contrast, large and contrasting changes in K_D values were noted upon anaerobic incubation. The ^{73}As K_D values decreased by a factor of 80, on average, and even up to a factor of 400 between aerobic and anaerobic incubated samples, with largest changes were found in the SOM rich upper part of the sampled soil profile (Figure 1a). In contrast, Sb K_D values increased by a factor of 5, on average, and up to a factor 20 after anaerobic incubation compared to the aerobic incubation, with largest changes were again found in the SOM rich upper soil layers (Figure 1b). The factor of change in K_D values upon anaerobic incubation, i.e. $K_{D,AN}$: $K_{D,A}$, was significantly smaller for the subsoil samples, i.e. collected at more than 1 m below surface, than for the surface soil samples, i.e. collected from the top 1 m, for both elements (Figure 2). Glucose addition enhanced the changes in K_D values in the subsoil samples for both elements whereas smaller and inconsistent effects were found in the topsoil samples upon glucose addition, i.e. no additional changes in ^{73}As K_D values were noted while the changes in Sb K_D were less pronounced than in the surface soils without glucose addition (Figure 2). The factors change of ^{73}As K_D values and Sb K_D values are similar upon reducing conditions when only soil organic matter (i.e. in surface soil) and when only glucose is present

(in glucose amended subsoil samples) (Figure 2), even when these factors change in K_D values were normalized for the amount of OC present, i.e., the type of OC (i.e. only soil organic matter or only glucose) did not influence the changes in As and Sb sorption upon anaerobic incubation (Table 4).

Upon anaerobic incubation, the As concentrations in solution increased strongly, i.e. from background concentrations of about 0.004 µM up to 1.5 µM soluble As, measured in the 1:10 solid:liquid 5 mM $CaCl_2$ soil extracts, and the As solution concentrations were strongly negatively correlated with the measured ^{73}As K_D values (r = -0.91; $p < 0.0001$; based on $\log_{10}$ transformed data; data not shown), i.e. decreasing ^{73}As K_D values result in higher As mobility in solution. During anaerobic incubation, the Sb concentrations in solution of the control, non-Sb(V) spiked soil samples increased, from background concentrations of 0.2 nM to 10 nM soluble Sb (Figure 3). This increase in solution Sb is matching the trend for As but contradicts that of the Sb concentration in solution of the Sb(V) spiked soil, i.e. Sb concentrations in solution of added Sb(V) decreased in reducing conditions, resulting in the increase in K_D values, as shown in Figure 1b. The increase in natural Sb concentrations was largest in the topsoil layers.

3.3. Solution composition

The As and Sb incubation tests ran at different times in different anaerobic chambers. In the As adsorption assay, more negative E_h values and higher Fe(II) concentrations were noted during anaerobic incubation than in the Sb adsorption assay, while Mn solution concentrations were comparable (Tables 2 and 3; full dataset in Tables S2 and S3). In general, solution properties remained constant in the aerobic incubated samples compared with the initial samples. Soil pH changed during anaerobic conditions but trends were inconsistent, i.e. increases and decreases were noted and the average absolute change in pH (ΔpH = |pH

anaerobic – pH aerobic|) was 0.4. Glucose addition acidified soils and the mean ΔpH (compared to the aerobic soils) was 1.1, maximally 2. The As speciation data show that As(III) concentrations ranged from below detection limit of the method (5 nM) to 1.2 µM. The % As(III) of the total solution As ranged from non-detectable to 110% between samples, with no clear effects of treatment (with or without glucose) or sampling location (subsoil or surface soil) on As solution speciation (Table 2 and Figure S1).

3.4. Correlations of As and Sb mobility with soil and solution properties under anaerobic conditions

The change in ^{73}As K_D upon anaerobic conditions ($K_{D,\,AN}$: $K_{D,\,A}$) was larger when Fe(II) and Mn concentration in solution increased (r = -0.82; p = 0.007 for Fe(II) and r = -0.95; p < 0.001 for Mn respectively; correlation based on $\log_{10}$ transformed data). These correlations were not present in the anaerobic + glucose treatment. In the glucose amended samples however, the change in ^{73}As K_D values was larger when the initial metal oxide concentration (quantified by Fe_{DCB} + Mn_{ox} + Al_{ox}) was smaller (r = -0.60; p = 0.009; correlation based on $\log_{10}$ transformed K_D changes).

The changes in Sb K_D values in the anaerobic treatment increased significantly when the Mn concentration in solution was higher and in samples with lower soil pH (r = 0.93, p = 0.0008 for Mn; r = -0.93, p = 0.0008 for pH; correlation based on $\log_{10}$ transformed data except pH). In the anaerobic + glucose treatment, only weak correlations were found (not shown). The soluble Sb concentration in the control, non-Sb spiked samples, increased with increasing DOC concentration in solution in the anaerobic treatment (r = 0.87, p = 0.005, correlation based on $\log_{10}$ transformed data; Figure 4).

Finally, in aerobic conditions, ^{73}As K_D values decreased with increasing OC concentrations (Figure 5). Upon reducing conditions, ^{73}As K_D values decreased in topsoil samples, resulting

in a more steep decline of As sorption with increasing OC concentrations of the samples. In addition, ^{73}As K_D values also decreased in glucose amended subsoil samples, but still, ^{73}As sorption remains higher in low OC samples than in high OC samples (Figure 5). This was not observed for Sb, only when Sb K_D values are normalized per molar concentrations of Fe_{ox}+Al_{ox}, these K_D values do decrease with increasing OC in the aerobic treatment (r = –0.61; p = 0.017).

4. Discussion

This work was set up to identify the effects of soil organic matter on the changes in As and Sb mobility upon reducing soils by flooding. The combination of a set of soils with i) a natural SOM gradient and ii) the effects of either or no glucose additions, allows to disentangle the different mechanisms by which SOM can mobilize or immobilize As and Sb under reducing conditions.

When reducing conditions develop, As sorption decreases while Sb sorption increases compared to aerobically incubated samples (Figure 1). This contrast between As and Sb was observed in several previous studies (Arsic et al., 2018; Couture et al., 2015; Fu et al., 2016; Mitsunobu et al., 2006). However, in our study, a striking difference in the extent of the changes in As and Sb sorption was found between the uppermost layers (<1 m soil depth) and the deeper soil layers (>1 m soil depth; Figure 2). This is most probably due to the lack of soil organic matter in the deeper soil layers, which normally enhance redox processes in soils by i) supporting aerobic respiration that induces reducing conditions in O_2 limited systems and ii) mediating redox cycling of As, Sb and their host minerals, by supporting anaerobic respiration or by enhancing these processes by electron shuttling. However, in our study, the different types of organic carbon present (i.e. soil organic matter, glucose and combining both) did only weakly affect the extent of change in As and Sb K_D values (Figure 2). In presence of only glucose, i.e. in the glucose amended subsoil samples, the changes in As and Sb mobility are

comparable to the changes when only SOM is present, i.e. in the surface soil samples without glucose amendment, even when these changes were corrected for the total amount of C present (Table 4). This indicates that no additional effects of SOM, and more specifically of humic substances, on the change in As and Sb sorption was observed compared to a mere carbon and energy source for microbial metabolism, like glucose. This does not implicate that changes of As and Sb sorption upon waterlogging cannot be facilitated by competitive or electron shuttling effects of humic substances, as shown by several authors in the case of As (Jiang et al., 2009; Qiao et al., 2019; Redman et al., 2002), but that the latter mechanisms likely contribute relatively less to the overall change in As and Sb mobility under reducing conditions compared to the carbon and electron donor effect of organic matter to stimulate microbial respiration.

The changes in ^{73}As K_D upon anaerobic incubation in presence of only native SOM, are most likely due to the reductive dissolution of Fe(III) and Mn (III, IV) hydroxides and subsequent loss of available sites for As sorption(Dixit and Hering, 2003; Villalobos et al., 2014). Different studies point out the associations between Fe, Mn and As release to soil solution in reducing conditions, due to the release of As by the reductive dissolution of Fe and Mn hydroxides (Weber et al., 2010; Xu et al., 2017). Interestingly, the change in ^{73}As K_D was more strongly correlated with dissolved Mn than with dissolved Fe(II) ($r = -0.82$; for Fe(II) and $r = -0.95$ for Mn). This suggest that reductive dissolution of Mn hydroxides is more important for changes in As mobility that dissolution of Fe hydroxides. However, As is usually more associated with the Fe hydroxides than the Mn hydroxides in soils due i) to the higher affinity of As to Fe oxides and ii) the usually higher abundance of Fe (hydr)oxides compared to Mn hydroxides (Suda and Makino, 2016), what is indeed observed in our study (on average a factor of 8 higher). Possibly, the measured Fe(II) concentrations in solution are not reflecting directly the reductive dissolution of Fe hydroxides due to complexation of the initially released Fe(II) with the exchange complex in soil, while this could be less important for Mn(II). Indeed, Fe(II) can

be more strongly complexed by soil organic matter than Mn(II) (Dudal et al., 2005). In addition, Fe(II) ions can be consumed during Mn(III, IV) hydroxide reductive dissolution (Postma and Appelo, 2000). The results of our study do not indicate that redox transformation between As(V) and As(III) resulted in the increased mobility of As in anaerobic condition, the As speciation in solution did not explain the observed changes in ^{73}As K_D values upon reducing conditions (Figure S1). This was also observed in a study by Hamon et al. (2004), i.e. the redox speciation of As could be largely As(V) or As(III) in anaerobic conditions and mobilisation/immobilisation of As under reducing conditions was a complex interplay between changes in redox speciation, reductive dissolution of Fe hydroxides and pH changes during the reducing conditions. When both sources of organic matter were present, i.e. SOM and glucose in the surface soil sample, no enlarged effect on the changes in As K_D values was observed, although more Fe(II) and Mn was released into solution than in the non-glucose amended anaerobic treatment (Table 2). In these strongly reduced soils, the change in As K_D values was likely not only controlled by mere dissolution of the metal hydroxides. Our data suggest that at higher total hydroxide concentration in the initial, aerobic soil, the changes in ^{73}As K_D values are lower (r = -0.60). When Fe and Mn hydroxides dissolve under reducing conditions, As(V)/As(III) can still adsorb on the non-dissolved, more recalcitrant oxides, like the more crystalline Fe oxides or the non-redox sensitive Al oxides, although likely to a lesser extent than on the amorphous Fe hydroxides (Dixit and Hering, 2003; Goldberg, 2002). However, it is difficult to estimate the amount of non-dissolved Fe oxides based only on the Fe(II) release, due to the complexation of Fe(II) and use of Fe(II) as a reductant, as discussed above, but also due to formation of Fe(II and/or III) minerals like siderite ($FeCO_3$) or like magnetite or mackinawite in sulfate reducing conditions, which in turn also can provide additional sorption sites for As (Burton et al., 2014, 2008; Tufano et al., 2008). Finally, this study corroborated the general trend that increasing OC concentrations are associated with a decrease in As sorption

(Figure 5). When organic anions sorb to Fe and Al hydroxides, competition and electrostatic repulsion result in lower As(V) in aerobic soils (Verbeeck et al., 2017). Interestingly, even under strongly reducing conditions (+ glucose treatments), As sorption remains higher in the low SOM containing soils (Figure 5), possibly indicating that the competition effects between SOM and As species for sorption sites to the reactive minerals in the higher SOM containing soils remain important in reducing conditions.

The changes in Sb K_D values upon anaerobic incubation in the presence of only native SOM or only glucose may be partly related to reduction of the added Sb(V) to Sb(III). . The reduced Sb(III) can be stronger retained to the residual, i.e. non-dissolved Fe(III) hydroxides at the pH of the incubated soils (7 – 8), as observed by Leuz et al. (2006) on goethite at pH >7. The added Sb(V) can be reduced biotically, by dissimilatory Sb(V) reducing bacteria (Kulp et al. (2014)) or abiotically, by interactions with freshly formed Fe(II) minerals in Fe(III) reducing conditions (Kirsch et al., 2008; Mitsunobu et al., 2008) or by interactions with reduced humic substances, when present (Karimian et al., 2019). Another mechanism that can explain increased Sb retention in mildly reducing conditions is the incorporation of Sb(V) into the crystal lattice of freshly formed Fe(III) hydroxides. Due to the similarities between Sb(V) and Fe(III) regarding ion size (0.60 – 0.65 Å) and coordination number (6), Sb(V) can substitute for Fe(III) during the Fe(II)-induced transformation of ferrihydrite into more crystalline Fe, which results in an increased fixation of Sb (Burton et al., 2019; Mitsunobu et al., 2013). Unfortunately, no redox or solid-phase speciation measurements of Sb are available to underpin these speculations. Other mechanisms that could explain increased Sb retention are however unlikely to prevail, i.e. during anaerobic incubation the pH of the samples only increased in some samples, which would result in less Sb sorption (Leuz et al., 2006; Rakshit et al., 2011; Tighe et al., 2005), which is contradictory to what was observed. When glucose was added during anaerobic incubation, pH decreased in almost all samples, however, the change in pH could not solely

explain the change in sorption, with largest changes in K_D values not present in samples with largest change in pH (Figure S2 in the Supporting Data). Next, it is very unlikely that increased Sb sorption in our soils is due to precipitation of Sb(III) with oxides or sulphides, as the Sb concentrations in solution of the spiked samples range 0.01 – 0.8 µM in both the anaerobic treatments, which is lower than the equilibrium Sb concentration of >1.8 µM of different Sb(III) minerals at pH 7 and pH 5, calculated with the Visual Minteq 3.1 speciation program (Gustafsson, 2019) for valentinite and senarmontite, both Sb(III) oxides and stibnite, an Sb(III) sulphide. Finally, when glucose was added to the anaerobic incubated samples, changes in Sb K_D values in surface soil layers are now smaller than in the subsoil layers (< factor 10, Figure 1) and even in the uppermost soil layer of this experiment, the K_D values did not change compared to the aerobic treatment. Also, in these samples, Fe(II) mobilisation is much larger than in the anaerobically incubated samples without glucose addition (up to 2 700 µM Fe(II); Table 3), so possibly loss of binding sites due to reductive dissolution of Fe hydroxides as a consequence of anaerobic respiration, counteracts the increased Sb(III) retention. These results are similar to what Hockmann et al. (2014b) observed, i.e. increased Sb retention under moderately reducing conditions, due to reduction of Sb(V) to Sb(III), followed by release of Sb in Fe-reducing conditions.

Finally, the changes in the geogenic Sb solution concentration upon anaerobic incubation were contradictory to the changes of the Sb K_D values, i.e. solution Sb concentration increased, while Sb K_D values decreased (Figure 1 and 3). Possibly, this can be explained by reduction of Sb(V) to Sb(III) and subsequent complexation of Sb(III) with DOC. The reduced Sb(III) is more strongly complexed with DOC than Sb(V) at pH values above 4 (Tella and Pokrovski, 2012, 2009) and this could explain the observed mobilisation of Sb in the control samples (up to factor of 10; Figure 3) upon anaerobic conditions, together with a small increase in DOC concentrations upon anaerobic incubation (up to a factor of 3; Table S3). This mechanisms is

likely not playing an important role in the changes of Sb mobility in the Sb spiked samples, due to the overall low complexation capacity of DOC for Sb(III), although higher than for Sb(V), in combination with low DOC concentrations (i.e., maximum 12 mg DOC L^{-1}) in the samples from this study. In the non Sb-spiked samples, the Sb:DOC ratio in solution of the surface samples (<60 cm soil depth) increased from ~ 0.3 nmol Sb per mg DOC to ~ 0.8 nmol Sb per mg DOC, upon anaerobic incubation. This Sb:DOC ratio is similar as reported by Buschmann and Sigg (2004), i.e. ~ 0.7 nmol Sb per mg DOC, at similar DOC and total Sb concentration (i.e. 5 mg DOC l^{-1} and 8 nM Sb). However, the total Sb concentration in the Sb-spiked samples is much higher, i.e. ~ 0.4 µM, resulting in a Sb:DOC ratio of ~100 nmol Sb per mg DOC in the aerobic incubated surface samples. Buschmann and Sigg (2004) report a maximum complexing capacity of 4 – 60 nmol Sb per mg DOC for Aldrich humic acid and Suwannee River humic acid, which is lower than observed in the samples of this study, which makes mobilisation of Sb with DOC at higher Sb concentrations likely not feasible. The complexation of Sb(III) to the reactive functional groups of soil organic matter could however be more important in soils with higher organic matter concentrations than in the soils used in this study, and the higher Sb(III) than Sb(V) complexation can result in an increased retention of Sb when reducing conditions arise (Besold et al., 2019).

5. Conclusions

Soil organic matter strongly alters the mobility of As and Sb in anaerobic soils. Changes of the As and Sb mobility under reducing conditions are significantly higher and thus more important towards As and Sb migration in the SOM rich surface soils compared to smaller changes in samples collected at >1 m below surface. In general, the extent of *change* in As and Sb mobility due to the presence of SOM in anaerobic conditions, can be largely explained by its effects as electron donor during microbial respiration. In addition, at low Sb concentrations, the complexation capacity of dissolved organic matter could increase Sb mobility. Finally, the

absolute K_D value of As under waterlogged conditions remains affected by SOM as a competitive ligand, i.e. lower mobility in low SOM containing soil, suggesting that SOM still acts as competitive ligand for As sorption even in strongly reduced conditions.

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Figures

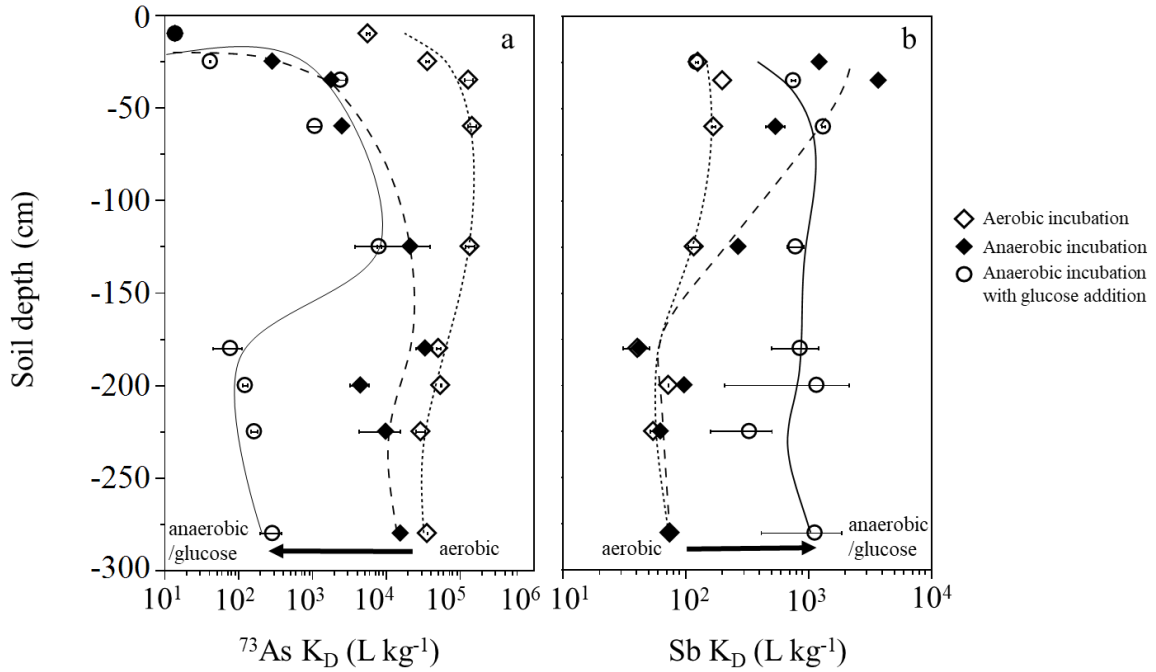

Fig. 1. When aerobic conditions change into anaerobic conditions (arrow), ^{73}As K_D values decrease (a) while Sb K_D values increase (b) and these changes in K_D are more pronounced in topsoil layers (0–60 cm below surface) than in the bottom of the soil profile. Upon glucose addition during anaerobic conditions, further decrease (As) or increase (Sb) of K_D values are more pronounced in the subsoil layers (>160 cm soil depth) than in the topsoil. Mean values with error bars presenting one standard error are presented (*n*=2). Lines are added to guide the eye.

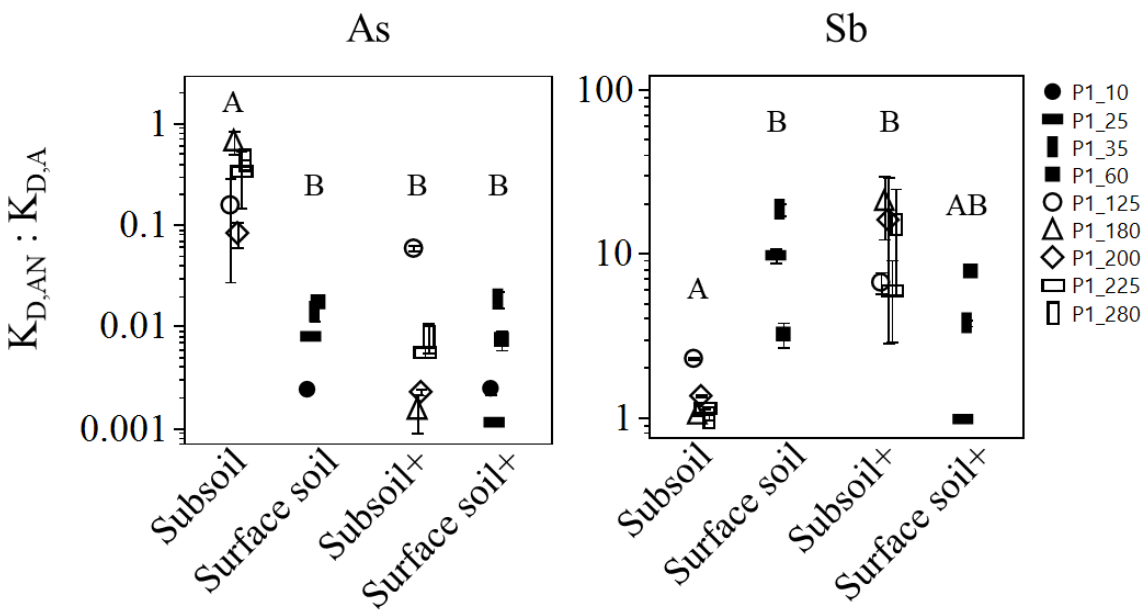

Fig. 2. Factor of change in ^{73}As K_D (left graph) and Sb K_D (right graph) between anaerobically and aerobically incubated surface soil and subsoil samples, with 1 m below surface the threshold between surface and subsoil. Samples were either or not amended with glucose (+), enabling to compare samples with very low OC (Subsoil), only with soil organic matter (SOM) (Surface), only with glucose present (Subsoil+) and with both types of OC present, i.e. SOM & glucose (Surface+). Mean data of replicate analyses are presented with error bars presenting one standard error (n=2). Letters connect groups with means which are not significantly different (α=0.05; Tukey HSD test on $\log_{10}$ transformed data).

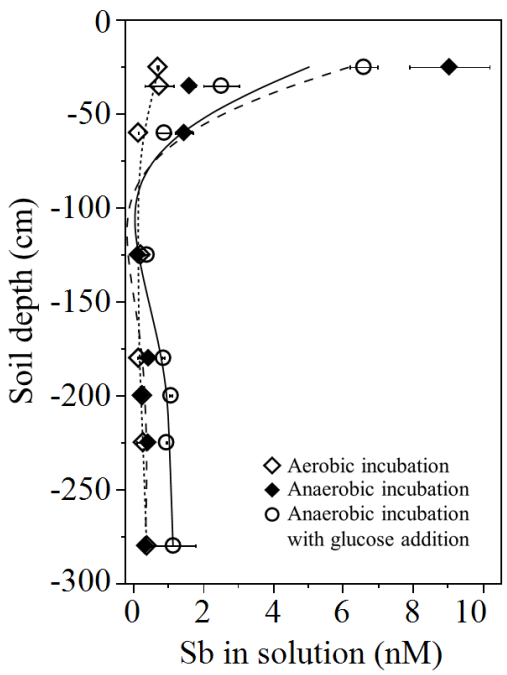

Fig. 3. Sb in solution in control, non-Sb spiked samples increases in topsoil layers when reducing conditions develop. Mean values with error bars presenting one standard error are presented (*n*=2). Lines are to guide the eye.

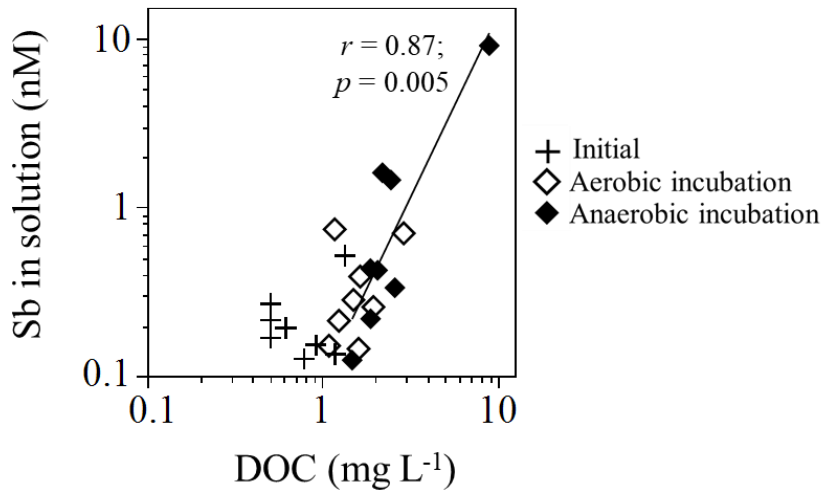

Fig. 4. The Sb concentration in solution increased with increasing DOC concentration in the anaerobic incubated samples (without glucose addition), suggesting mobilization of Sb by DOC. Mean datais presented (*n*=2). The regression line is presented to guide the eye.

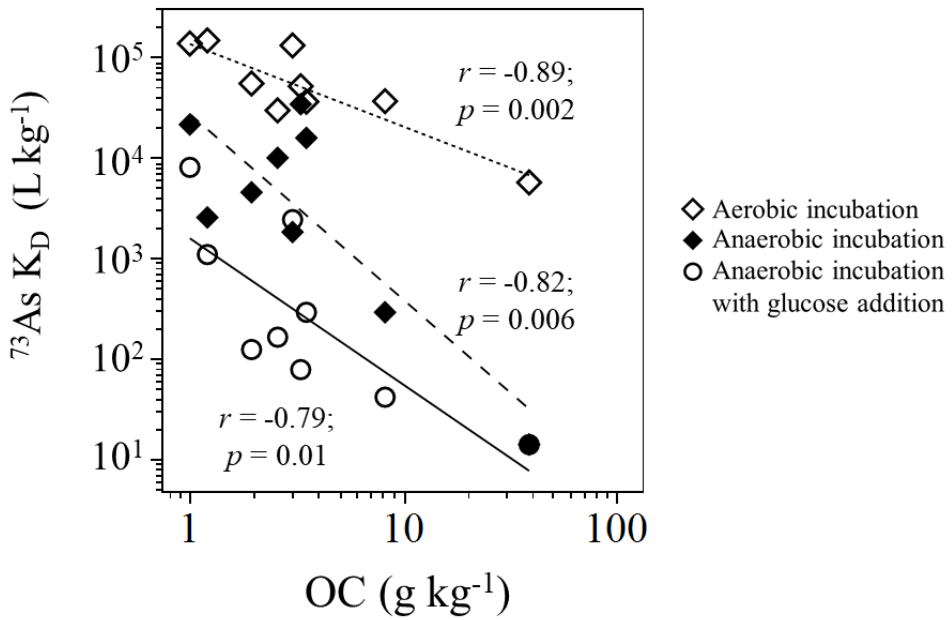

Fig. 5. ^{73}As K_D values decrease with increasing organic carbon content, in all treatments. Mean data are presented (n=2). Lines are regressions and presented to guide the eye.

Tables

Table 1

Soil properties of collected soil samples (*n*=9). Mean values from duplicate analyses are presented, except for total Sb, which was determined without replicates.

Sample	pH	OC[a]	DOC[b]	Fe_{ox}[c]	Fe_{DCB}[d]	Al_{ox}[c]	Mn_{ox}[c]	Fe_{ox}: Fe_{DCB}	As_{ar}[e]	As_{ox}[c]	Sb_{tot}[f]
		(g kg^{-1})	(mg L^{-1})	(mmol kg^{-1})					(µmol kg^{-1})		
P1_10	5.5	39	18	83	169	23	5.3	0.49	91	53	3.4
P1_25	6.6	8	3.7	47	258	25	7.0	0.18	111	47	4.5
P1_35	6.6	3	1.0	20	244	30	4.3	0.08	123	29	3.9
P1_60	7.1	1	0.8	11	269	34	1.5	0.04	117	29	4.4
P1_125	7.1	<1	<0.5	11	290	24	14	0.04	189	39	4.9
P1_180	6.9	3	<0.5	6	180	10	1.0	0.03	151	26	3.8
P1_200	7.6	2	<0.5	8	264	14	2.4	0.03	148	23	4.5
P1_225	7.0	3	<0.5	7	275	15	0.6	0.03	181	24	3.7
P1_280	7.5	4	<0.5	7	254	12	0.5	0.03	223	25	3.6

[a]organic carbon; [b]dissolved organic carbon; [c]oxalate extractable; [d]dithionite-citrate-bicarbonate extractable; [e]*aqua regia* extractable As; [f]Sb extracted with four acid digestion

Table 2

Properties of the 5 mM $CaCl_2$ extracts of soils before and after 70 days (an)aerobic incubation in the As adsorption/desorption assay. Median (minimum-maximum) of nine different samples of a soil profile are presented (*n*=9).

Treatment	^{73}As K_D	As in solution	As mobilized as As(III)	Eh vs SHE	pH	DOC	Fe(II) in solution	Mn in solution
	(L kg^{-1})	(µM)	(%)	(mV)		(mg L^{-1})	(µM)	
Initial	49 000 (4 000 – 140 000)	0.004 (<0.002 – 0.007)	n.a.	370 (200 – 410)	7.5 (6.1 – 7.7)	n.a.	n.a.	0.013 (<0.005 – 0.69)
Aerobic	50 000 (5 200 – 160 000)	0.004 (<0.002 – 0.027)	n.a.	150 (140 – 360)	7.7 (6.1 – 7.9)	n.a.	n.a.	0.011 (<0.005 – 0.35)
Anaerobic	3 300 (12 – 42 000)	0.011 (<0.002 – 1.5)	72 (n.d. – 96)	63 (-15 – 400)	7.0 (6.4 – 7.9)	n.a.	1.3 (<1 – 970)	8 (0.5 – 150)
Anaerobic + glucose	160 (12 – 7 900)	0.27 (0.047 – 1.5)	57 (2 – 110)	77 (-8 – 290)	6.7 (5.4 – 7.2)	320 (75 – 380)	1800 (57 – 5000)	120 (3 – 930)

n.a. = not available; n.d. = not detectable

Table 3

Properties of the 5 mM $CaCl_2$ extracts of soils before and after 63 days (an)aerobic incubation in the Sb adsorption/desorption assay. Median (minimum-maximum) of eight different sample of a soil profile are presented (*n*=8).

Treatment	Sb K_D	Sb in solution in control samples	Sb in solution in spiked samples	Eh vs SHE	pH	DOC	Fe(II) in solution	Mn in solution
	(L kg^{-1})	(nM)		(mV)		(mg L^{-1})	(µM)	
Initial	95 (37 – 200)	0.18 (0.08 – 0.58)	386 (186 – 857)	n.a.	7.1 (6.4 – 7.5)	1 (<0.5 – 2)	n.a.	0.006 (<0.005 – 0.12)
Aerobic	77 (30 – 200)	0.30 (0.10 – 1.6)	498 (204 – 1032)	300 (240 – 340)	7.7 (6.4 – 8.0)	2 (1 – 3)	n.a.	0.01 (<0.005 – 0.4)
Anaerobic	180 (42 – 4 100)	0.44 (0.12 – 10)	276 (12 – 812)	190 (100 – 360)	7.7 (7.0 – 8.0)	2 (1 – 12)	<1 (<1 – 7)	4 (0.5 – 200)
Anaerobic + glucose	700 (120 – 2 100)	1.0 (0.33 – 7.0)	63 (21 – 335)	180 (85 – 290)	6.4 (5.4 – 6.8)	340 (310 – 380)	1100 (51 – 2700)	100 (8 – 680)

n.a. = not available

Table 4 The factor of change in ^{73}As and Sb K_D values for subsoil samples (collected at >1 m soil depth), surface samples (collected at <1 m soil depth) and subsoil and surface samples amended with glucose (Subsoil/Surface+), normalized by the amount of C present in the soil sample during the anaerobic incubation (measured OC + added glucose-C when applicable).

	$K_{D, AN} : K_{D, A}$ (g^{-1} OC)	
	As	Sb
Subsoil	0.13^{A}	0.8^{A}
Surface soil	0.005^{B}	3.3^{A}
Subsoil +	0.002^{B}	1.7^{A}
Surface soil +	0.001^{B}	0.6^{A}

Mean values of soil samples per group (subsoil or surface soil) are presented and connected with the same letter when not significantly different from each other (α=0.05; Tukey HSD test on $\log_{10}$ transformed data).