In situ arsenic oxidation and sorption by a Fe-Mn binary oxide waste in soil.

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Graphical abstract

Highlights

- A Fe-Mn binary oxide waste is used to remediate As contaminated soils.
- As(III) and As(V) adsorption capacities of 70 mg g\(^{-1}\) and 32 mg g\(^{-1}\) were determined.
- The bioaccessibility of total As was significantly reduced by 7.80 %
- Arsenic in the contaminated soil effectively binds to the exogenous binary oxide.
- As(V) was sorbed by mononuclear bidentate corner-sharing with Fe.

Abstract

The ability of a Fe-Mn binary oxide waste to adsorb arsenic (As) in a historically contaminated soil was investigated. Initial laboratory sorption experiments indicated that arsenite [As(III)] was oxidized to arsenate [As(V)] by the Mn oxide component, with concurrent As(V) sorption to the Fe oxide. The binary oxide waste had As(III) and As(V) adsorption capacities of 70 mg g\(^{-1}\) and 32 mg g\(^{-1}\) respectively. X-ray Absorption Near-Edge Structure and Extended X-ray Absorption Fine Structure at the As K-edge confirmed that all binary oxide waste surface complexes were As(V) sorbed by
mononuclear bidentate corner-sharing, with 2 Fe at ~ 3.27 Å. The ability of the waste to perform this coupled oxidation-sorption reaction in real soils was investigated with a 10% by weight addition of the waste to an industrially As contaminated soil. Electron probe microanalysis showed As accumulation onto the Fe oxide component of the binary oxide waste, which had no As innately. The bioaccessibility of As was also significantly reduced by 7.80 % (p < 0.01) with binary oxide waste addition. The results indicate that Fe-Mn binary oxide wastes could provide a potential in situ remediation strategy for As and Pb immobilization in contaminated soils.

Keywords: Arsenic, Fe-Mn binary oxide, remediation, soil, lead.

1.0 Introduction

Arsenic (As) is one of the most prevalent toxic and carcinogenic contaminants of global concern [1]. Due to its ubiquity and elevated concentrations in aquatic environments, particularly in the drinking waters of southern Asia, intensive research has been carried out on remedial strategies. The majority of environmental As contamination is geogenic from the weathering and erosion of As-bearing rocks, minerals and ores [2]. There has also been considerable release of anthropogenic As into soils from insecticides, herbicides, wood preservatives and mine wastes [3]. These releases have led to localised but highly As contaminated soils worldwide. Remediation of such soils has received less attention than that of potable waters. However, As contaminated soils are a serious environmental issue, as accumulation in this matrix impacts human health via food and water quality. To abate this threat in the UK, soil guideline values (SGVs) for total inorganic As have been developed with the lowest permissible value being 32 mg kg\(^{-1}\) dry weight in residential areas [4]. Yet, it is the
bioaccessibility of As in soils, opposed to the total concentration, that gives the most accurate approximation of risk to humans [5].

Arsenic is most commonly found in two inorganic forms in soil: arsenate As(V) and arsenite As(III). The speciation and stability of these forms vary depending upon minerology, point source of As, redox potential, pH, presence of microorganisms, organic matter, ion exchange, clay minerals and aluminum oxides[6]. Arsenite is more mobile, soluble and ~60 times more toxic than As(V) [7]. Under oxic conditions As (V) dominates (as H2AsO4– and HAsO42–) whereas under anoxic conditions As(III) prevails (as H3AsO30 and H2AsO3–) [6, 8].

Adsorption reactions by Mn and Fe oxides in soils is considered the most important control on As mobility. Reactions between Fe and/or Mn oxides and As have been extensively studied and are well understood [9-15]. In the environment Mn and Fe occur together and are chemically similar. Recent laboratory experiments have showed that the combination of these metal oxides in the form of synthetic Fe-Mn binary oxides show significantly higher As immobilization than the pure phases alone [16]. A binary oxide produces a synergistic two-step oxidation and adsorption reaction whereby As(III) is oxidized to As(V) by the Mn oxide portion, and As(V) is consequently strongly sorbed onto the Fe oxide via the following reaction series [17]:

\[
\text{As(III)}(\text{aq}) + (-\text{SFe-Mn}) \rightarrow \text{As(III)-SFe-Mn} \quad (1)
\]

\[
\text{As(III)-SFe-MnMnO}_2 + 2\text{H}^+ \rightarrow \text{As(V)}(\text{aq}) + \text{Mn}^{2+} + \text{H}_2\text{O} \quad (2)
\]

\[
\text{As(V)}(\text{aq}) + \text{As(III)-SFe-Mn} \rightarrow \text{As(V)-SFe-Mn} + \text{As(III)}(\text{aq}) \quad (3)
\]
where \((-S_{\text{Fe-Mn}})\) represents an adsorption site on the Fe–Mn binary oxide surface. \(\text{As(III)}-S_{\text{Fe-Mn}}\) represents the As(III) surface species and \(\text{As(V)}-S_{\text{Fe-Mn}}\) represents the As(V) surface species.

Many As removal technologies are available and have been extensively reviewed elsewhere [18-20]. The use of Fe-Mn binary oxides may be most promising due to the simplicity and efficiency of both As(III) and As(V) removal [21]. However, studies into the use of binary oxides for As remediation are limited and have concentrated upon application to water using expensive synthetic mineral sources [22-24], with a few exceptions that consider waste sources [25, 26], and application to soil [27]. At present, there are no studies on the use of Fe-Mn binary oxide by-products to remediate historically As-contaminated soils. This is despite the fact that waste supplies of have been identified from water treatment plants and are available nationally [28]. This water industry by-product may provide an inexpensive and sustainable option for remediation, which synthetic sources cannot.

The objectives of this study were to: (1) provide a detailed mechanistic study on effectiveness of As(III) and As(V) adsorption onto the binary oxide waste, and, (2) determine whether the binary oxide waste can immobilize As using a model system with a historically As-contaminated soil. In addition, as the soil in this study is known to be co-contaminated with lead (Pb) [28], the effect of this competing cation on As sorption was also investigated. This is the first study, to our knowledge, that investigates a waste source of binary oxide for remediation using realistic remediation conditions.

2.0 Materials and methods
2.1 Materials. The Fe-Mn binary oxide waste used in this study was obtained from a Northumbrian Water Ltd. water treatment works (Co. Durham, UK, 54°51'03.9"N 1°54'00.5"W) and has been previously described in detail [28]. Briefly, the binary oxide consists of ferrihydrite (total Fe: 20,000 mg kg\(^{-1}\)) and birnessite (total Mn: 90,000 mg kg\(^{-1}\)) [29]. A synthetic poorly crystalline δ-MnO\(_2\) was prepared for comparative purposes according to [30].

2.2 Sorption experiments. Solutions of As(III) were prepared using sodium meta-arsenite (NaAsO\(_2\)) and As(V) with sodium arsenate dibasic heptahydrate (Na\(_2\)HAsO\(_4\) · 7H\(_2\)O) (ACS grade, Sigma Aldrich). Batch sorption experiments were conducted as in [28] using a 10 g l\(^{-1}\) binary oxide waste concentration (<90 μm particle size) at a pH of 7. The effect of pH on As sorption was investigated at pH 5.5, 6.5 and 7.5 were maintained with either 1 M NaOH or 1 M HCl using 10 g l\(^{-1}\) binary oxide waste concentration unsieved. Experiments investigating the effect of Pb on As sorption were carried out as above but included Pb at a total concentration of 50 mg l\(^{-1}\) as per [28]. All solutions from experiments were analyzed for As(III), As(V), Mn(II) and Pb using a JY Ultima 2C ICP-OES and sorption data was fitted to the Langmuir isotherm [31]. The chemistry of moist residues was investigated by X-ray absorption spectroscopy (XAS, details below).

2.3 XANES and EXAFS analyses. The XANES and EXAFS data were collected at the arsenic K (1866.7 eV) and Mn K (6539 eV) edges on Station B18 at the Diamond Light Source Ltd, Didcot, UK in fluorescence mode using a Ge 9-element detector. Pressed powder pellets of model compounds Na-arsenite [for As(III)], Na-arsenate [for As(V)] were analysed in Total Electron Yield mode. The data was analyzed using ATHENA [32]. For As data DL_EXCURV [33] was used for fitting over 3 – 12 Å\(^{-1}\) using full
multiple scattering analysis. The number of independent data points (Nind) used was 16 as determined using Stern's rule [34] The reduced Chi² function [35] and EXAFS R-factor was used to determine quality of fit.

2.4 Binary oxide waste lysimeter trial. Historically contaminated soils containing 3,200 mg kg⁻¹ As were collected from a former industrial site in Newcastle upon Tyne (54°57'39.7"N 1°33'10.0"W). The soil geochemistry has been previously described with total As concentrations ranging from 10 - 6502 mg kg⁻¹ and variable total As bioaccessibilities (42 % to 64 % [36]). In addition to As, the site is co-contaminated with Pb, having been a former lead and copperas works. The soil collected for this study contained 11,000 mg kg⁻¹ total Pb which is present as galena (PbS) that alters to Pb carbonate (PbCO₃)[28]. This represented mean concentrations for the site which have been shown to range from 174 – 33306 mg kg⁻¹ total Pb with corresponding bioaccessibilities of 25 – 58 % [36].

The lysimeter trial was conducted as per [28] where the sorption of Pb onto the Mn oxide component of the binary oxide waste in this study has previously been proven. In short, contaminated soils were amended with 10 % by weight binary oxide waste in triplicate. Controls were carried out without the addition of binary oxide waste. All soils were adjusted to 60 % water holding capacity to ensure that pore spaces were sufficiently saturated whilst maintaining aerobic conditions. This facilitated As oxidation and sorption reactions between the binary oxide waste and contaminated soil which are known to occur at the mineral-water interface [22]. In addition, all lysimeters were incubated outside for 10 months in plastic (PTFE) cylinders to allow for natural variations in weather. Geochemical analysis of lysimeter samples occurred at 0 and 10
months to determine (i) total As via aqua regia digestion (British Geological Survey, Keyworth, UK) and (ii) bioaccessibility of total As using the BARGE-UBM method[37]. Immobilization of As onto the exogenous binary oxide was visually determined by comparing a binary oxide waste grain before mixing with the As contaminated soil and after 10 months reaction time in the lysimeter using electron probe X-ray mapping. This was carried out on a Jeol 8100 Superprobe (WDS) with an Oxford Instrument Inca System (EDS) as per [28]. Energy data was collected between 0–20 eV using a 15 Kv accelerating voltage, 2.5 mA current and a spot size of 1 μm. The analyses were calibrated using a ZAF program against oxide standards of oxides and Specpure metals.

2.5 Statistical analysis. All statistics were carried out in SPSS 17 (SPSS, Inc. Chicago, IL). Significant differences were determined using a two-tailed independent sample t-test or one-way analysis of variance (ANOVA), with Tukey’s HSD test. Correlations were determined using the bivariate two-tailed Pearson correlation coefficient. Statistical significance was defined as p ≤ 0.05.

3.0 Results and Discussion

3.1 Batch sorption. Experiments were carried out to evaluate: (i) the influence of pH, (ii) the influence of Pb as a competing cation (iii) the binary oxide waste As sorption capacity, and, (iv) provide material for EXAFS and XANES analysis to elucidate final As oxidation state and binding mechanism.

As (III and V) adsorption on the binary oxide waste was rapid within the first 2 h, achieving up to 93 % removal, with a maximum adsorption of 97 % achieved after the 24 h of contact time (Figure S1). This initial rapid phase followed by a decreasing
oxidation rate over time has been well documented due to surface passivation of the Mn oxide component [15, 38]. As the As(III) oxidation reaction proceeds via reaction (1), Mn(II) is released which can re-absorb onto the Mn oxide surface blocking sites for As(III) oxidation. In addition, experimental evidence also suggests that the oxidation of As(III) can proceed via two sequential one-electron transfer steps forming an intermediate Mn(III) product which may also sorb onto the Mn oxide surface or replace surficial Mn(IV) leading to further passivation [38].

Sorption capacities of both As (III) and As (V) were significantly higher in the waste than in the synthetic δ-MnO₂ (Figure S2) which is in agreement with previous reports [16]. Specifically, the binary oxide waste sorption capacities were 95 % for the As oxyanions while synthetic δ-MnO₂ showed sorption capacities of 7 % for both As(III) and (V). Arsenic sorption on the waste was higher at pH 5.5 and decreased to 8.5 (Figure S3). At lower pHs, it is thought that surface hydroxyl sites undergo increased protonation to form OH₂⁺ and stronger As sorption results from the increased number of these positively charged sites which are inherently more attractive to the negatively charged arsenate ions (H₂AsO₄⁻ and HAsO₄²⁻) in solution [39].

Fitting of the sorption isotherm data to Langmuir’s monolayer adsorption model determined the maximum adsorption capacity (q_max) of the binary oxide waste to be 70 mg g⁻¹ for As(III) and 32 mg g⁻¹ for As(V) (Figure S4). The significantly higher removal of As(III) than As(V) by Fe-Mn binary oxides is in agreement with previous studies [17, 26] and is attributed to the creation of fresh Mn oxide adsorption sites at the solid surface as a result of As(III) oxidation. The release of Mn²⁺ and Fe²⁺ cations into solution following q_max experiments showed a significant linear correlation between As(III) and Mn²⁺ (r² = 0.991) indicating the reductive dissolution of the Mn oxide phase due to the
oxidation of As(III) to As(V) (Figure S5, reaction 1). No correlations were observed between As(III) and Fe$^{2+}$ or As(V) and Mn$^{2+}$(data not shown).

The maximum sorption capacity for the waste in this study is slightly higher than other published values for Fe-Mn binary oxide by-products from water treatment plants which generally fall between 20 - 30 mg As g$^{-1}$ [40]. However, other Fe-Mn binary oxide wastes have been found to have significantly higher As sorption capacities. For example, Ocinski and colleagues [26] have reported $q_{\text{max}}$ for As(III) and As(V) as 132 and 77 mg As g$^{-1}$ respectively for a Fe-Mn oxide containing water treatment residual. These values are comparable to synthetic sources which can have maximal sorption capacities of 342 mg As(III) g$^{-1}$ and 250 mg As(V) g$^{-1}$ [41]. The significantly higher $q_{\text{max}}$ values for these synthetic and waste Fe-Mn binary oxides can be attributed to larger surface areas (120 m$^2$ g$^{-1}$ and 340 m$^2$ g$^{-1}$ respectively) than the waste in this study (34 - 44 m$^2$ g$^{-1}$[28]) which will provide more vacant sites for As sorption.

The effect of Pb on As sorption was also investigated. Metal contamination in soils is rarely singular and the polluted site investigated in this study also contained high levels of Pb (11,000 mg kg$^{-1}$). In our previous work [28] the waste examined here was shown to effectively immobilise Pb from the same lysimeter trial via sorption to the Mn oxide component. When metals are present as multi-contaminants, competition for sorption sites can occur and adsorption may be affected. When both As and Pb were simultaneously added in solution, As removal by the binary oxide waste was impeded. A total of 58 % for As (III) and 37 % for As (V) was removed from solution over 24 hours at pH 5.5 whereas Pb underwent complete removal (100%, data not shown). To our knowledge this is the first report of suppression of As removal by Pb on a binary oxide. This data suggests the binary oxide waste has a preference for Pb$^{2+}$ but can still perform oxidation and adsorption of As, though inhibited.
It is well documented that the Mn oxide component of binary oxides perform the As(III) oxidation to As(V). The suppression of As(III) oxidation on Mn oxide surfaces by Pb(II) [42] and other metal cations such as Zn(II) [43], Fe(II) [44], Ni(II) and Co(II) [45] has been previously reported. These studies have concluded that decreased As(III) oxidation is due to competition from metal cations blocking the reactive sites on the Mn oxide surface. Mechanistically, metal sorption sites are located internally due to cation vacancies within MnO_6 octahedral layers, or, externally at lateral edges of MnO_2 sheets [46]. Until recently, it has been thought that sorption occurs predominately at internal cation vacancy sites. New evidence has shown that Pb(II) binds extensively to external Mn oxide edges [47]. It is at these same edge sites that binding of As(III) for electron transfer in oxidation reactions also occurs [38], resulting in competition. The preference for Pb sorption over As oxidation at lateral edges may be attributed to the contrasting behavior of cationic Pb versus neutral oxyanionic As. Mn oxides are known to have low points-of-zero charge which generally fall between a pH of 2 and 5, thus, at pH 5.5 the Mn oxide will exhibit an overall negatively charged surface which favors cation over oxyanion adsorption.

A mechanistic reason for a decrease in As(V) sorption on to the binary oxide is less evident as As(V) removal should be though immobilization onto the Fe oxide component of the binary oxide waste. It is possible that Pb(II) undergone sorption onto the Fe oxide component especially if the vacant sites in the Mn oxide fraction had reached saturation, thus blocking vacancies for As(V). Additionally, the experimental time frame in this study was only 24h and equilibrium may not have been reached. In the presence of competing cations, As(V) sorption onto Fe oxides has been reported to take 240 h [48]. Arsenate sorption onto mixtures of Fe and Mn oxides is limited by diffusion through the minerals [49]. As the binary oxide waste in this study is comprised
of banded Fe oxide and Mn oxide concentric layers, the presence of sorbed Pb to the Mn oxide component may have affected the diffusional transport of As(V) to the Fe oxide component.

3.2 XANES and EXAFS analyses before and after sorption. All binary oxide waste sorption samples had a consistent coordination environment regardless of pH, and, critically, whether the batch experiments were amended with As(III) or As(V). Indeed, analysis confirmed that the surface complexes formed on the binary oxide all contained As(V) rather than As(III). In all cases the first shell coordination environment comprised 4.0 oxygens at ~ 1.69 Å, consistent with the presence of a tetrahedral AsO$_4$ ion (Table S1). The consistency of these spectra confirms the assumption from sorption experiments that all adsorbed As was in the +5 oxidation state. Accordingly, it can be inferred that the Mn oxide portion of the binary oxide waste had oxidized the more reduced As species AsO$_3^{3-}$ to AsO$_4^{3-}$ during adsorption.

A comparison of representative spectra for the binary oxide waste and synthetic δMnO$_2$ from sorption experiments showed a characteristic asymmetry to the oscillation at c. 7 Å -1 in the synthetic δMnO$_2$ only, due to the contribution of the second shell of Mn atoms in δMnO$_2$ [12] (Figures 1 and 2). This noticeable second harmonic beat is absent in the waste spectra (Figure 1), indicating that the chemical association of As on the binary oxide waste is with Fe. A peak in the Fourier Transform at ~ 3 Å for the waste and at ~ 3 Å for the δMnO$_2$ was observed. Based on the literature to date, the nearest neighbour peaks suggest that As is sorbed in a bidentate corner-sharing configuration for both the binary oxide and δMnO$_2$ (Figure S6). This configuration is in agreement with previous studies [16]. Specifically, on the binary oxide waste we conclude that As is sorbed by mononuclear bidentate corner-sharing, with 2 Fe at c. 3.27 Å (Table S1,
This concurs with previous spectroscopic studies that have shown that the structure of the As(V) surface complex on Fe-Mn binary oxides is a bidentate bridging complex on singly coordinated surface sites similar to that on Fe(III) hydroxides[16]. The synthetic δMnO₂ also showed oxidation of As(III) to As(V) and concurrent sorption. However, in the synthetic δMnO₂ system, where no Fe is present, we find that As is sorbed on the Mn via mononuclear bidentate corner-sharing, with 2 Mn at c. 3.18 Å (Table S1).

3.3. Binary oxide waste lysimeter trial. To determine the effectiveness of the binary oxide waste as an As remediation amendment a lysimeter trial was conducted using historically contaminated soil which contains high levels of As. Such a soil presents a realistic remediation opportunity wherein the contaminant has undergone appropriate ageing and is present in representative environmental forms.

The metal contamination at the historically contaminated site in this study has been shown to be extremely heterogeneous[28, 50]. Previously, we reported that bulk geochemical data from the site could not be used to determine remediation effects on lead (Pb) immobilization. This was due to such large variations between treatment replicates which resulted in the control soil replicates having a considerably larger average Pb values than soils which has undergone amendment for Pb immobilization [28]. Our current study also found the same large heterogeneity in As. The control soil had, from the outset of the experiment, a significantly lower average total As concentration (8280 mg kg⁻¹) to the binary oxide waste amended soils (11,200 mg kg⁻¹, p < 0.01). Such differences could not be explained by As addition via the binary oxide since the material only contained 3 mg kg⁻¹ of total As.
Examination of As in the historically contaminated soil showed that it occurs principally as grains of an Fe-As-O phase whose composition is typical of the poorly soluble and non-bioaccessible mineral scorodite (FeAsO$_4$·2H$_2$O), and in Fe-Pb oxides (Figure S8). This suggests the majority of As is incorporated into heterogeneously distributed mineral particles and only a small portion of As is present on exchangeable sites, characteristic of the behavior of this metalloid [51]. The contaminated soil in this study has a pH of 7.44 ± 0.1 [28]. At this pH, scorodite dissolution is incongruent yielding ferrihydrite and HAsO$_4^{2-}$ [52]. Consequently, it was assumed that any As released into the soil pore water will be present as As(V). The co-release of ferrihydrite during scorodite dissolution has been shown to reduce As(V) concentrations in pore waters due to adsorption onto the Fe oxide surface [53]. Due to this and the possibility of arsenate immobilization by other sorbates in soil, electron probe microanalysis (EPMA) was used to visually determine, based on elemental mapping, the chemical association of As on the surface of the with the binary oxide waste.

Elemental As mapping clearly showed that the binary oxide waste was As free prior to addition to the historically contaminated soil lysimeter trial (Figure 3). After 10 months’ reaction time in the lysimeter, As was visible on the binary oxide surface (Figure 4a), and many scorodite-like grains remained (data not shown). Further X-ray microprobe analysis of the binary oxide surface showed highly significant positive correlations between total As, which we presume to be present as As(V) and total Fe (Figure 4b, r = 0.848, p < 0.01), and no correlation between total As and total Mn (r = -0.36, p > 0.1, data not shown). These correlations strongly suggest that the As present upon the Fe-Mn binary oxide surface is bonded to the Fe oxide component and not the Mn oxide. In naturally occurring Fe-Mn binary oxides, Pb is found to be associated with the Mn oxide component and As with Fe which our results are in agreement with [54].
Mn oxides are known to be the dominant sorbent of Pb, that have been reported to preferentially sorb Pb over As, exerting an irreversible binding of Pb that is 40 times greater than Fe oxides [55-57].

Results from bioaccessibility testing at 10 months further verify the immobilization of As upon the binary oxide waste. There was a statistically significant reduction of 7.80 % (p < 0.01) in the bioavailability of As in the stomach fraction between the unamended and 10 % by weight waste amended lysimeters (Table 1). A reduction in As bioaccessibility was also found in the stomach and intestine fraction (28.20 to 22.20 %) although it showed borderline significance (p = 0.1, Table 1). Taken together both EPMA and bioaccessibility results unequivocally indicated that As sorption to the binary oxide waste most probably from scorodite dissolution releasing As(V) into the soil pore water which has been sorbed onto the Fe oxide component of the binary oxide waste coating. These results build upon one previous study investigating the use of Fe-Mn binary oxides for remediation of As contaminated soils. An and Zhao [23] showed Fe-Mn binary oxide nanoparticles were capable of As(III) immobilization in soils while the current study only concentrated upon As(V). In the study of An and Zhao [23] water leachable As(III) in spiked soils was reduced by 91-96% and transferred from the soil pore waters onto the nanoparticles via either direct sorption of As(III) or oxidation of As(III) followed by direct sorption of As(V). While the study by An and Zhao investigated spiked soils, we have demonstrated that binary oxides can immobilize As under realistic remediation conditions, that is, by using a soil where contamination is present in the environmentally relevant form of scorodite. While Fe-Mn binary oxide coated nanoparticles are promising for As immobilization, they incur a cost for synthesis which a waste does not.
Building on our previous work [28] it is apparent that the binary oxide waste investigated in this study has the potential not only to remediate Pb \textit{in situ} as previously determined but also As, meaning that these wastes could be applied to multi metal contaminated soils for simultaneous immobilization. The waste used in this study presents a low-cost remediation option. Additionally, the literature shows there are many other waste forms of binary oxide by-products from the water treatment industry globally which have similar, or better, As sorption capacities that could be used for as soil amendments[26]. Based on our findings, we conclude that Fe-Mn binary wastes from water treatment plants could provide a sustainable, low cost remediation option for As and Pb removal from contaminated soils.

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\textbf{Competing financial interests statement.} The authors declare no competing financial interests.
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Figure captions

**Figure 1.** (a) As K-edge EXAFS, and (b) Fourier transforms of the EXAFS for the As-absorbed to the binary oxide waste (BOW) and the synthetic $\delta$MnO$_2$ at pH 5.5.

**Figure 2.** (a) As K-edge EXAFS, and (b) Fourier transforms of the EXAFS for the As-absorbed synthetic $\delta$MnO$_2$. Solid lines are data, dotted lines are fits. Numbers denoted the pH of the sorption experiment.

**Figure 3.** Electron microprobe X-ray maps of the binary oxide waste before addition to the As contaminated soil.

**Figure 4.** (a) Electron microprobe X-ray maps of the binary oxide waste after 10 months contact with the As contaminated soil. (b) linear correlation between Fe and As.

Table legends

**Table 1.** Stage related bioaccessibility of As in lysimeter soils after 10 months.
Fig. 1

Fig. 2
Fig. 3
Fig. 4

(a) [Images showing various elements and their measurements]

(b) [Graph showing correlation between As and Fe]

$r = 0.848$

$p < 0.01$
Table 1

<table>
<thead>
<tr>
<th>Soil</th>
<th>Total mean (mg kg(^{-1}))</th>
<th>BAF(^a) Stomach (%)</th>
<th>BAF Stomach and intestine (%)</th>
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<tbody>
<tr>
<td>0 % BOW(^b)</td>
<td>8280 ± 630</td>
<td>29.00 ± 0.90</td>
<td>28.20 ± 2.70</td>
</tr>
<tr>
<td>10 % BOW</td>
<td>11 200 ± 340</td>
<td>21.20 ± 0.60</td>
<td>22.20 ± 0.50</td>
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\(^a\) Stage-related bioaccessible fraction calculated as a fraction of the pseudo-total

\(^b\) ± Fe-Mn binary oxide waste (NBO)

\(^c\) ± 1 x standard error based upon 3 replicates