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1	Field and laboratory evidence for manganese redox cycling controlling iron and arsenic
2	retention in household sand filters
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#### 38 Abstract

39 Application of household sand filters (SFs) is widespread in low-income regions, such as West Bengal, Bangladesh and Vietnam, for removal of groundwater contaminants including Fe, Mn 40 41 and As. SF operation typically transitions from (oxic) unsaturated conditions to saturated 42 conditions creating oxygen-limited zones within sand layers. To ensure safe and effective use 43 of SFs, understanding filter performance and spatiotemporal changes of solid-associated Fe, 44 As, and Mn in different saturation conditions are crucial but remains unknown. Therefore, 45 column experiments were conducted to follow Fe, As, and Mn removal and their distribution 46 and speciation on sand grain surfaces under unsaturated and saturated conditions. On average, 47 99±0.2, 93±0.7, and 91±8% of Fe(II)<sub>aq</sub>, As(III)<sub>aq</sub>, and Mn(II)<sub>aq</sub> were removed under unsaturated 48 conditions. Under saturated conditions, Fe and As removal remained constant, whereas up to 49 5 mg/L of Mn(II)aq was leached from columns. µXANES analysis showed that solid-associated 50 Fe(III), As(V), and Mn(III)/(IV) dominated in unsaturated sand. However, under saturated 51 conditions, up to 46 and 15% of Fe(III) and As(V) were reduced and the presence of Mn(II) 52 was confirmed in the anoxic zones. The results suggest that Mn(IV) oxides formed during 53 unsaturated conditions, serving as hosts and oxidants for Fe and As in SFs under reducing conditions. 54

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56 Keywords: sand filters, biogeochemical processes, Fe, Mn, As

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58 Synopsis: Formation of Mn(IV) oxides under the oxic flow acted as the host and oxidant for
59 Fe(II) and As(III)/(V) under saturated conditions.

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#### 62 **1. Introduction**

63 Water filtration by household sand filters (SFs) is one the oldest point-of-use water treatment techniques that has been recommended by the World Health Organization (WHO) to provide 64 safe drinking water for people living in rural areas<sup>1,2</sup>. In the Red River delta, Vietnam, 65 66 groundwater is acutely contaminated by As; up to 3000 µg/L of As was detected in some places<sup>3</sup>. Household SFs have been used in this area to eliminate As(III) and other contaminants 67 such as Fe(II) and Mn(II) from groundwater for more than 30 years<sup>4,5</sup>. Groundwater is pumped 68 69 intermittently onto the top of the sand surface followed by gravitational trickling through the sand layer. Filtered water is collected in a lower compartment for cleaning and drinking<sup>5,6</sup>. 70 71 As(III), Fe(II) and Mn(II) are co-oxidized in the filter, followed by the precipitation of As(V)-

72 bearing Fe(III) (oxyhydr)oxides and Mn(III/IV) oxides on sand particle surfaces<sup>7,8</sup>.

The operation of the SF starts with unsaturated flow when sand layers maintain oxic conditions and is followed by saturated flow when an oxygen gradient is formed along the sand column creating semi-oxic (top layer) and anoxic zones (bottom layer). When the filters get clogged (every 3-6 months), 10-20 cm of the top sand is scraped off for unclogging. Thus, SFs are usually operated under alternating unsaturated and saturated flow for many years.

Under unsaturated conditions, Fe-, Mn- and As-species in the groundwater are almost completely oxidized (Fe(III), Mn(IV) and As(V)). Mn oxides are therefore constantly formed in SFs, forming distinguished black patches or layers in the filters<sup>6,9</sup>. The formation of Mn(IV) oxides is due to i) microbial activity of Mn(II)-oxidizing bacteria (MnOB)<sup>10,11</sup> and ii) abiotic oxidation of Mn(II) by O<sub>2</sub> catalyzed at Fe(III) (oxyhydr)oxide mineral surfaces<sup>12–14</sup>. Since Mn(IV) oxides are strong oxidants they can directly oxidize dissolved As(III) and Fe(II) in the groundwater (Eq 1, 2).

85  $MnO_2 + AsO_3^{3-} + 2H^+ \rightarrow Mn^{2+} + AsO_4^{3-} + H_2O$  (Eq. 1)

86 
$$2MnO_2 + Fe^{2+} + 5H^+ \rightarrow Fe(OH)_3 + 2Mn^{2+} + H_2O$$
 (Eq. 2)

87 Over a long operational time (several months to years), the filter surface gets blocked by 88 precipitation of carbonate minerals and metal (oxyhydr)oxides, thus inhibiting the abiotic oxidation of Fe(II) and As(III) by  $O_2^{15}$ . Under such conditions, Mn oxides might complement 89 90 the heterogeneous oxidation of As(III) and Fe(II) by O<sub>2</sub> (Eq 1, 2) to enhance As and Fe 91 retention in SFs. Indeed, under O<sub>2</sub>-depleted conditions, Mn(IV) oxides (either as abiotic or biogenic birnessite) prevented As mobilization in soil and sand columns<sup>16–18</sup>. However, until 92 93 now, there is no direct evidence that under O<sub>2</sub>-depleted conditions the presence of Mn(IV) 94 oxides can control the immobilization of As and Fe in household SFs. One of the issues is that 95 most studies have examined As, Fe, and Mn removal by sampling at specific timepoints to 96 confirm the high removal efficiency. There is inadequate data regarding long-time monitoring 97 of Fe, As, and Mn effluent over unsaturated (fully oxic) to saturated (O<sub>2</sub>-depleted) operational 98 phases in SFs. Obtaining such analyses at different timepoints (with different saturation status 99 and different redox conditions) is essential as it will reveal whether As removal mechanisms 100 change during redox fluctuations and can reveal the impact of Mn(III/IV) oxides on As and Fe 101 retention in SFs.

Therefore, in this study, series of column experiments were conducted in the lab and in the field in which sand columns were fed by sterile artificial and local native groundwater, respectively. We aimed at i) monitoring the performance of the sand filter applied to remove As, Fe, and Mn over time from unsaturated to saturated conditions, ii) quantifying the distribution of total As, Fe, and Mn along the depth of sand columns, and iii) identifying the location and speciation of As, Fe, and Mn on the surface of sand particles under unsaturated and saturated conditions.

#### 110 **2. Materials and methods**

#### 111 **2.1 Column setup**

The glass columns (inner diameter 4.5 cm, length 25 cm) consisted of support layers filled with 2 cm gravel (particles size 6-8 mm, Flairstone, Germany) and 3 cm sterilized quartz sand (particle size 0.4-0.8 mm, Carl Roth GmbH, Germany) at the bottom, followed by a reactive layer filled with 10 cm of sand filter materials. Columns were intermittently operated in gravitational down-flow mode 2-3 times per day. Two similar column setups were running in the field (20°55′08.63" N, 105°53′47.61″ E, Van Phuc village in the Red River delta, Vietnam) (field site description see SI, section S1) and in the lab.

#### 119 **2.2 Column flow experiment**

#### 120 **2.2.1 Columns in the field**

In the field, the biotic columns contained the reactive layer (top 10 cm) filled with sand collected from the local sand supplier. 250 ml of natural groundwater was pumped directly on top of the sand columns each time. The inflow water contained 16.1 mg/L of Fe(II), 1.4 mg/L of Mn(II), and 240  $\mu$ g/L of As(III). The filtration rate, and the concentrations of Fe, Mn, As in the effluent were recorded at every feeding batches. The experiment ran over 1.5 months, equaling 169 pore volumes under temperature ranging from 20-25°C.

#### 127 **2.2.2 Columns in the lab**

In the lab, the duplicate biotic columns contained a reactive layer (top 10 cm) filled with sand collected from a frequently running household filter at the same location with the field experiment (sample collection is described in SI, section S1). Additionally, an abiotic control column was setup in the lab, with the reactive layer (top 10 cm) filled with sterile quartz sand (particle size: 0.4-0.8 mm, Carl Roth GmbH, Germany). To follow the dissolved oxygen (DO) in the sand columns (biotic and abiotic setups), six pieces of oxygen optode foil (PreSens, Germany) were glued inside at different depths along the columns. Sterile artificial 135 groundwater (AGW) was freshly prepared every week and contained 20.9±1.5 mg/L of Fe(II), 136 1.8±0.6 mg/L of Mn(II), and 307.0±24.4 µg/L of As(III). The preparation of AGW is described 137 in SI section S2 and Table S1. The pH of AGW was adjusted to 7.3 which is the average pH 138 value of groundwater in the Red River delta<sup>5</sup>. Every time, up to 150 ml of ARW was fed to the 139 columns. In total, the experiment was operated over two months equaling 141 pore volumes 140 and the columns experienced two clogging events at pore volumes 93 and 141. After the first 141 clogging event, 3 cm of top sand was scraped off the column to unclog the sand column, and 142 the experiment was continuously running until the second clogging. The column experiments 143 in the lab were performed at a temperature ranging from 20-25°C similar conditions as the field 144 experiment.

#### 145 **2.3 Aqueous analysis**

At every filtration time, inflow and outflow water was collected. To quantify dissolved As, Fe
and Mn, 2 ml of inflow and outflow water were filtered (0.22 μm cellulose filter, EMD
Millipore) and diluted with 1% HNO<sub>3</sub> before analysis by inductively coupled plasma mass
spectrometry (ICP-MS) (Agilent 7900, Agilent Technologies)

#### 150 **2.4 Solid phase analysis**

151 After the experiments, to prevent further oxidation of solid-associated Fe(II), As(III) and 152 Mn(II), filter materials were collected from 2-5 cm depth in the glovebox (100%  $N_2$ , <30 ppm 153 O<sub>2</sub>, MBRAUN UNIIab). Samples were stored anoxically in 100 ml Schott bottles in the freezer 154 (-20°C) until further analysis.

#### 155 **2.4.1 Elemental composition analysis**

156 12 ml of aqua-regia solution (9 ml of 37% HCl and 3 mL of 65% HNO<sub>3</sub>) were added slowly to 157 the Xpress Plus Teflon vessels containing 0.5 gram of dried sand materials. The samples were 158 digested in the Microwave Accelerated Reaction System, MARS 6 (CEM, USA) (details in SI 159 section S3). Afterwards, the digested samples were adjusted to a final volume of 50 ml by adding milliQ H<sub>2</sub>O under the fume hood. The samples were centrifuged at 16,873 g for 15 min (Thermo Scientific Sorvall LYNX6000). 100  $\mu$ l of the supernatant were collected and diluted 100-fold in 1% HNO<sub>3</sub>. Samples were stored at 4°C in the dark until analysis via the Agilent 7900 ICP-MS.

#### 164 **2.5.2 X-ray fluorescence imaging**

The distribution of As, Fe, and Mn on the surface of sand particles was visualized with X-ray fluorescence (XRF) mapping using beamline 7-2 at Stanford Synchrotron Radiation Lightsource (SSRL). Samples were freeze-dried and transferred to wells with 5 mm diameter on multi-well sample holders. Samples were embedded in Epotek 301-1 resin (Epoxy Technology). All preparatory steps were performed in a glovebox (100% N<sub>2</sub>, <30 ppm O<sub>2</sub>). Epoxied samples were polished to 5 mm thickness under oxic (ambient) conditions.

Beam line 7-2 is equipped with a bend magnet, capillary optics, and a double crystal (Si 111) monochromator. Samples were placed at a 45° to the incoming focused beam with a 50 µm spot size and a 100 ms dwell time per pixel. Samples were imaged at two energies 12,000 eV for obtaining As and total elemental maps, and 8000 eV for obtaining accurate Fe and Mn maps. Fluorescence intensities of selected elements were monitored with a four-element Vortex Silicon Drift Detector.

As, Fe and Mn maps were visualized in SMAK<sup>19</sup> with details in SI section S4. Locations with a simultaneous presence of high counts of As, Fe and Mn were identified and selected for  $\mu$ -X-ray Absorption Near Edge Structure ( $\mu$ -XANES) spectroscopy. Mn K-edge, Fe K-edge, and last As K-edge  $\mu$ XANES data were obtained in this order at the same locations (50-micron spot), starting with the lowest energy to prevent beam redox changes. Three to six spectra were obtained per spot, depending on spectra quality. The spectra were processed in Athena<sup>20</sup> with details in SI section S5.

184 **2.5.3 Scanning electron microscopy (SEM)** 

The morphology of precipitates coated on the sand particles surface was analyzed by SEM using a Zeiss Crossbeam 550L Scanning Electron Microscope (Zeiss, Germany). Filter materials collected from saturated and unsaturated columns were dried in an oven at 30°C, then placed on aluminum SEM sample holders onto carbon adhesive tabs. The samples were sputtercoated with 8 nm platinum with a BALTEC SCD 500 sputter coater. SEM micrographs were collected using the Secondary Electrons Secondary Ions (SESI) detector with an accelerating voltage of 5 kV.

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#### 194 **3. Results and discussion**

#### 195 **3.1 Long-term monitoring of As, Mn and Fe in the effluent**

#### 196 Field column experiment

197 Column experiments in the field were performed over 169 pore volumes in 1.5 months under 198 unsaturated conditions (flow rate ranged from 0.3-0.15 ml/s) (Figure 1A). The columns were 199 fed twice per day by natural groundwater containing 16.1 mg/L of Fe(II), 1.4 mg/L of Mn(II), 200 and 240 µg/L of As(III) (Table S2). Low concentrations of Fe, Mn, and As in the outflow 201 indicated high and stable removal efficiencies by the SFs. The relative effluent values ( $C/C_0$ ) 202 where C and  $C_0$  are effluent and influent concentration, respectively) for Fe, Mn, and As were 203 0.002, 0.08, and 0.07 (Figure 1) which corresponded to effluent concentrations of 38, 117, and 204 17.5 µg/L, respectively (Figure S3). The residual As concentration in the water after filtration 205 was higher than the WHO drinking water standard (10 µg/L). Our observation is consistent with other studies investigating full-scale household filters in the Red River delta<sup>6,7,9</sup>, 206 207 suggesting further As treatment steps are required for drinking purposes.

#### 208 Lab column experiment

209 To further investigate the effect of saturated versus unsaturated conditions on the filter 210 performance, we conducted a similar column experiment in the lab. The aim of the lab 211 experiment was to investigate the filter performance under saturated conditions. Therefore, a 212 slower flow regime than in the field experiment was selected, starting from 0.14 ml/s (the flow 213 rate in the field ranged from 0.3-0.15 ml/s) (Fig 1A). The abiotic control was performed with 214 sterile quartz sand added to the column instead of native sand materials collected from 215 household filters in Vietnam. Both abiotic and biotic setups were fed by sterile, anoxic, 216 artificial groundwater containing 20.9±1.5 mg/L of Fe(II), 1.8±0.6 mg/L of Mn(II) and 217  $307.0\pm24.4 \ \mu g/L \text{ of As(III)}$  (Table S2).

218 The performance of the biotic sand column was divided into two phases (Figure 1B). In the 219 first phase (93 pore volumes, before the first clogging), the sand column remained oxic with a DO in the porewater ranging between 4-6 ppm (Figure S4). Fe, Mn, and As were effectively 220 221 removed with relative effluent concentrations ( $C/C_0$ ) of 0.0004, 0.13 and 0.04, respectively 222 (Figure 1B). We noticed that the Fe and As removal efficiency in the lab setup was higher than 223 in the field probably due to the absence of Si and higher Ca in the AGW relative to natural 224 groundwater. Silicate has a weaker adsorption affinity to Fe(III) (oxyhydr)oxides compared to As(III) and As(V)<sup>21</sup>, therefore Si is only a weak competitor of As regarding adsorption on 225 226 Fe(III) phases during filtration. In contrast, Ca was shown to enhance As retention by forming 227 Ca-As(V) bonds on the sand particle surface  $^{22,23}$ .

During the second phase between the 1<sup>st</sup> and 2<sup>nd</sup> clogging (pore volumes 93-141) the column 228 229 was operated under semi-oxic conditions (DO of porewater <0.5 ppm) (Figure S4). After the 1<sup>st</sup> clogging, 3 cm of the top sand was scraped off, then the column was continuously run until 230 231 the second clogging event. Fe removal efficiency was comparable to phase 1 ( $C/C_0$  (Fe): 0.009), 232 while Mn breakthrough occurred throughout this phase as the Mn concentration in the effluent was constantly higher than in the influent with  $C/C_0$  ranging between 1 and 3.5 (Figure 1B). 233 234 Arsenic removal slightly changed from 8.9 to 12.6  $\mu$ g/L in the effluent (Figure S3). The drop 235 in DO along the sand column in the second phase compared to the first phase suggests a 236 formation of anoxic zones along the sand column. Under such conditions, it might lead to a reduction As-bearing Fe(III) (oxyhydr)oxides forming As(III) and Fe(II). Therefore, MnO<sub>2</sub> 237 238 could be involved in the oxidation of reduced As(III) and Fe(II) to varying extents (Ep 1, 2). 239 This explained an increase of mobile Mn(II) at the effluent and the high retention of Fe and As 240 in the sand column. In the abiotic control column, 99% of the Fe(II) was removed by abiotic 241 oxidation with O<sub>2</sub>, but As and Mn removal were limited to 70 and 66%, respectively (Figure 242 1C). These findings clearly show the important roles of microbial oxidation of Fe(II), As(III)

- and Mn(II) in order to complement the abiotic processes to maintain high removal rates of Fe,
  As and Fe in the sand column as shown before by Van Le et al<sup>9</sup>.
- 245



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Figure 1. Filtration rate (upper panel) and relative effluent concentration (C/C<sub>0</sub>, where C and C<sub>0</sub> are effluent and influent concentration, respectively) of Fe, Mn and As (lower panel) in the field-based biotic setups (A), lab-based biotic setups (B) and the abiotic control (C). The filtration rate as well as the concentrations of Fe, Mn, As in the influent and effluent were recorded at every feeding batches.

#### **3.2 Distribution of solid Fe, As and Mn in unsaturated and saturated columns**

To understand changes in Fe, As, and Mn distribution in different depth layers in the unsaturated column (field setup) and saturated column (lab setup), total Fe, As, and Mn associated with sand materials at every 2-5 cm depths were analyzed by ICP-MS after microwave digestion.

258 Fe, As, and Mn accumulated in the top 2-3 cm of the sand columns and their concentrations 259 decreased with filter depth. Since the groundwater in the Red River delta is enriched with 260 Fe(II), Fe showed the highest abundance in the sand column. Up to 18.5-22.0 g/kg and 26.5-261 28.8 g/kg were found in unsaturated and saturated columns, respectively (Figure 2A). 262 Manganese in the solid phase of the saturated sand column was between 744-991 mg/kg, twice 263 as much as in the unsaturated column (Figure 2B). Arsenic was enriched in the saturated 264 column with a concentration between 159 and 178 mg/kg, which was three times as high as As 265 in the unsaturated column (Figure 2C). Since the removal efficiency of the abiotic columns was lower than in the biotic ones, the Fe, As, and Mn retained in the sand was up to 10 times 266 267 less than in the biotic setups.

At the macro scale, both As and Mn linearly correlated with Fe with correlation factors R<sup>2</sup> from 268 269 0.82 to 0.99 in both unsaturated and saturated columns (Figure S5, S6), suggesting that As 270 adsorbed on Fe(III) (oxyhydr)oxides on the sand particles as reported before<sup>6,7</sup>. In contrast, As 271 and Mn was less co-located indicated by lower correlation factors which were 0.55 and 0.8 for 272 unsaturated and saturated columns, respectively. The element distribution in unsaturated and 273 saturated columns followed the same pattern. Thus, we hypothesize that the changes of Fe, As, 274 and Mn concentrations might occur due to changes in speciation and binding environment. It 275 has to be noted that new sand material was used for the field experiment (unsaturated conditions). In contrast, sand material collected from existing household filters was used for 276 277 the lab experiment (saturated conditions) to utilize the microbial activities in the sand.

Therefore, filter materials in the saturated column already contained higher amounts of Fe, As,
and Mn than the unsaturated column, which could lead to catalytic effects<sup>8,24</sup>.



Figure 2. Vertical distribution of Fe (A), As (B), and Mn (C) in abiotic control (black), unsaturated (orange) and saturated (brown) columns. All samples were analyzed in triplicate, and error bars indicate the standard deviation.

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#### **3.3 Morphology of precipitates and elemental distribution on sand particle surface**

Scanning electron microscopy (SEM) and micro-X-ray fluorescence ( $\mu$ XRF) were combined for assessing the sand particle size (Figures 3A and S7), the morphology of minerals (Figure 3 B, C, D), and the elemental distribution on the sand particle surfaces (Figures 4, S8, and S9). The results indicated a heterogenous elemental distribution and micro- to nano-sized mineral structures coating sand particle surfaces. Three mineral structures were identified including micro-platelets associated with nano-globular-aggregates (Figure 3C, D) and nano-flower shaped structures (Figure 3E, F). The nano-globules had a similar structure to Fe nanoaggregates found on the surface of sand particles in other Fe-Mn-based sand filtration systems<sup>25,26</sup>. We suggest that the flower-like nano morphology is similar to the birnessite structure reported in previous studies<sup>26,27</sup>. The identified mineral structures could originate from the filter materials or were newly formed during filtration. Further SEM imaging of the local raw sand materials should be included in future studies to better distinguish the origins of these precipitates.

299 Pixel fluorescence counts of Fe, As, and Mn collected from µXRF maps indicated a stronger correlation of Fe and Mn ( $R^2 = 0.5-0.6$ ) than Fe and As ( $R^2 = 0.2-0.4$ ) in both unsaturated and 300 301 saturated columns. However, at selected areas, both As and Mn were strongly correlated with 302 Fe with  $R^2 > 0.8$  (Figure 4E, 4F, S8, S9), while the correlation factor of Mn and As was lower  $(R^2 < 0.7)$  (Figure 4F). The Fe, As and Mn correlations at the micro scale were in line with the 303 304 findings at the macro scale. Additionally, Mn was associated with Fe(III) (oxyhydr)oxides in 305 the unsaturated sample ( $R^2 = 0.73$ ) (Figure S8), while in the saturated sample, Fe-Mn-rich areas were detected in fewer locations indicated by a lower correlation factor ( $R^2 = 0.6$ ) (Figure 4B). 306 307 Arsenic possessed a lower concentration than Mn and Fe and enriched as rims at the mineral's 308 surface-water (solid-water) interface (Figure 4C), that is also described in previous 309 studies<sup>7,28,29</sup>.

310 Additionally, other elements such as P, Ca, and Si also showed a strong partitioning into the Fe(III) (oxyhydr)oxide phase (Figure S10), probably influencing As removal in SFs. Iron was 311 312 well co-located with P in all samples as phosphate is preferentially adsorbed to Fe(III) (oxyhydr)oxide compared to As(V), As(III) and silicate<sup>21,30</sup>. Thus, low Fe/P ratios (0.05-1) of 313 the groundwater were an asset for high As retention. Tricolor maps of Si, Ca, and Fe indicated 314 315 a lower amount of Si and Ca associated with Fe (Figure S10). Most detected Si fluorescence 316 counts stemmed from the sample holder (made from quartz). Ca-rich sand crusts were found 317 separately from the Fe signal, probably precipitated as calcite in the filters.



**Figure 3.** Scanning electron micrographs showing the distribution of precipitates on the sand particle surface (A, B). The most dominant mineral structures were micro-platelets (green arrows) associated with nano-globular-aggregates (orange arrows) (C, D) and nano-flower shapes (blue arrows) (E, F).

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**Figure 4:** Multiple energy  $\mu$ -XRF maps of sand filter materials from saturated columns operated in the lab.  $\mu$ -XRF maps of Fe (A), Mn (B), As (C) distributed on sand surfaces and their tricolor map (D). Correlations of Mn vs Fe (E), As vs Fe (F), As vs Mn (G) and their correlation co-efficiency (R<sup>2</sup>) were displayed for 4 selected areas from tricolor map.

#### 329 **3.4** Fe, As and Mn speciation in saturated and unsaturated sand columns

330 Filter materials were collected from different depth layers (2-5 cm) in unsaturated and saturated 331 columns. Redox states of Mn, Fe and As on selected areas from µXRF maps were analyzed by X-ray absorption near edge structure (µXANES) spectroscopy using linear combination fitting 332 333 (LCF) (Figure 5 A.B.C). µXANES spectra of different areas on the same sample were almost 334 identical indicating that the speciation distribution was homogenous and representative for that 335 sample. The proportions of Fe(II) and As(III) in each sample were converted to concentrations 336 for a better quantitative comparison between unsaturated and saturated columns (Figure 5D,E). 337 The results indicated that oxidized species such as Mn(III)/(IV), Fe(III), and As(V) dominated in unsaturated columns while reduced Mn(II), Fe(II), and As(III) were identified at a higher 338 339 relative contribution in saturated columns.

340 Under the unsaturated flow conditions, adsorption maximum positions of Mn, Fe and As were near 6563, 7134, and 11875 eV, respectively (Figure 5 A,B,C), indicating the presence of 341 342 Mn(III)/(IV), Fe(III), As(V) and in the sand columns<sup>31,32</sup>. LCF fitting results of Fe showed a 343 mixture of ferrihydrite and goethite contributed between 61 and 80% along the unsaturated 344 column except in the sample collected at 6-8 cm depth that contained only 36% of Fe(III) (Figure 5B, Table S4). Additionally, up to 87-93% of As(V) were detected along the 345 346 unsaturated columns (Figure 5C, Table S3). The speciation contribution of Mn, Fe and As in 347 unsaturated columns is comparable to the solid phase analysis results obtained from a series of household filters in Vietnam<sup>7,9</sup>. 348

Under the saturated conditions, Mn K-edge XANES spectra of samples taken from top (0-2 cm) and bottom (5-10 cm) layers showed an adsorption maximum at 6563 eV representing Mn(IV) and indicating a more diffused distribution than in the unsaturated sample (black arrow, Figure 5D). A shift of the edge position toward lower energy and a concomitant appearance of a shoulder at 6554 eV indicated the presence of Mn(II). Similarly, we also

observed an energy shift toward the positions of Fe(II) (7125 eV) from the Fe k-edge XANES spectra of 5-10 cm sand samples (arrow, Figure 5A). LCF fitting results confirmed that Fe(II) was contributing up to 44% to the total Fe pool equaling 11.6 g/kg (Figure 5D). This finding revealed an expansion of the Fe(III) reduction zone from 6-8 cm (in the unsaturated column) to 5-10 cm under saturated conditions. As(III) increased to 15% in the saturated sand column equaling 26-22 mg As(III)/kg which is 10 times more than the amount of As(III) in the unsaturated column.





Figure 5. Normalized K-edge µXANES spectra of Mn (A), Fe (B) and As (C) in filter materials
at different depths in the saturated and unsaturated columns. Experimental and linear

364 combination fit curves are plotted as black and red lines, respectively. The concentrations of
 365 solid-phase Fe(II) (D) and As(III) (E) in saturated and unsaturated columns were calculated by
 366 combining µXANES data and extraction data.

367

# 368 3.5 MnO<sub>2</sub> controlling the Fe and As retention under semi-oxic and anoxic zones in the 369 saturated sand columns

370 Under unsaturated conditions, Fe, As, and Mn were primarily present as As(V) adsorbed on 371 Fe(III) (oxyhydr)oxide and Mn(III)/(IV) oxide minerals. Under saturated flow conditions, we 372 found evidence that microbial Fe(III) and As(V) reduction led to elevated Fe(II) and As(III) in 373 the solid phase that might be oxidized by and/or associated with Mn(IV) oxides to different 374 extents. The mechanisms of As(III) and Fe(II) oxidation in the presence of Mn(III)(IV) oxides 375 and Fe(III) (oxyhydr)oxide are complex, involving many simultaneously occurring reactions. 376 Based on our observations, the following mechanistic reaction network is proposed to explain 377 Fe-, As- and Mn-redox speciation in the top and bottom layers of sand columns.

378 Under saturated conditions, the presence of Mn(II) and As(III) at the top layer (0-2 cm) 379 indicated Mn(II) and As(III) adsorbed to the surfaces of Fe(III) (oxyhydr)oxide and previously 380 formed Mn oxide minerals. Since the artificial groundwater contained high concentrations of 381 bicarbonate, solid-associated Mn(II) also could be present as MnCO<sub>3</sub> (rhodochrosite) as 382 previously reported<sup>33</sup>.

The oxidation of As(III) by Mn(IV) oxides in the top layer of the sand column was limited due to i) the high amount of Fe(II) of 21 mg/L as well as high Fe/As ratio of 68 in the groundwater so that Fe(II) outcompeted As(III) for adsorption and oxidation on Mn(IV) oxides surface<sup>34,35</sup> and ii) the formation of Fe(III) (oxyhydr)oxide minerals with adsorbed Mn(II) might cause a surface passivation of Mn oxides thus slowing down As(III) and Fe(II) oxidation<sup>34,36,37</sup>. Even

though Mn(IV) oxides might not directly oxidize As(III)<sup>16,34,37–39</sup>, these studies confirmed that the presence of Mn oxides maintain high As(V)/As(III) ratios in the solid phase, thus enhancing As immobilization. Additionally, the intermittent feeding of oxygenated water into the sand columns allowed O<sub>2</sub> re-penetration into the pore spaces to enhance oxidation processes in the top layers of the SFs<sup>28,40</sup>.

393 At the bottom layer (5-10 cm), under saturated flow, almost no dissolved oxygen was detected 394 (Figure S3), leading to an increase of Fe(III) reduction (up to 44% of Fe(II) detected in the 395 sand column). The main reason is the microbial reduction of As-bearing Fe(III) (oxyhydr)oxides, as demonstrated in our previous study<sup>41</sup>. The mobilized Fe(II) and desorbed 396 397 As(V)/(III) likely re-adsorbed to the remaining Fe(III) (oxyhydr)oxide and Mn(III)/(IV) oxide 398 minerals. While at the sand filter surface constantly new Fe(III) (oxyhydr)oxides formed, there 399 was a decrease in available binding sites for Fe(II) and As(III)/(V) on the Fe(III) minerals at 400 the bottom layer. These differences highlight the role of Mn(III)/(IV) oxides on the one hand 401 as secondary hosting phase and on the other hand as oxidant for Fe(II) and As(III). The stronger 402 correlation of Mn with Fe compared to As at the sand surfaces lead to the conclusion that Fe(II) 403 adsorbed on Mn oxides was instantaneously oxidized to Fe(III) sequestering As(V) and As(III) 404 into the solid phase. This finding is in line with previous studies on the role of Mn(IV) oxides controlling As mobilization in floodplain soils<sup>16,42</sup> and paddy soils<sup>43</sup>. In addition to the abiotic 405 406 reduction of Mn(IV) oxides by Fe(II), microbial reduction pathways<sup>44</sup> were probably involved 407 in the elevated Mn(II) concentrations in the effluent in our columns. Nevertheless, bulk XAS 408 for Fe, Mn, and As should be done in the future to obtain better insights into Fe, Mn and As 409 binding environment under unsaturated and saturated conditions.

#### 410 **4. Conclusions**

411 The operation of household SFs for removal of Fe, Mn and As from water is divided into two 412 phases, it starts with unsaturated flow when the sand column maintains oxic conditions and is 413 followed by saturated flow when an oxygen gradient is formed along the sand column creating 414 a semi-oxic (top) and anoxic zone (bottom). By conducting lab and field-based column 415 experiments, this study showed groundwater Fe(II) and As(III) were effectively immobilized 416 in sand columns under unsaturated (oxic) and saturated flow conditions. Mn(IV) oxides that 417 formed during the oxic flow were acting as a secondary hosting phase and oxidant for Fe(II) 418 and As(III)/(V). Consequently, removal rates of As(III) and Fe(II) were stable at 95 and 99% 419 respectively, while Mn(II) was leached from the sand column, and up to 5.5 mg/L was detected 420 in the effluent. Based on our findings, we therefore provide a few suggestions to improve the 421 performance of household/ small-scale SFs applied to remove Mn(II), As(III) and Fe(II) from 422 groundwater as follows. First, intermittent feeding is recommended rather than continuous 423 flow. The intermittent feeding allows the SFs to completely drain between filtration periods, 424 pulling new air into the pore spaces and reducing the hydraulic conductivity, thus prolong the time until filter clogging<sup>28</sup>. Second, backwashing as a method to unclog the filter surface is 425 426 more benefitial than scrapping off the top sand layer. The scrapping removes a substantial 427 amount of microorganisms accumulated at the top layer, which contribute to Fe, As and Mn oxidation<sup>9,17,45</sup> while backwashing can preserve better the SF's microbial community<sup>46</sup>. Third, 428 429 the risk of Mn contamination in the effluent should be reduced. In the household filters without 430 backwashing, the top layer of the SF will be removed once the SF is clogged, leading to 431 prolonged saturated conditions in the SFs and, consequently, Mn remobilization from the filter. 432 Even though Mn(II) is not as toxic as As(III) or As(V), long-term chronic exposure to elevated Mn levels can lead to several adverse health effects<sup>47–49</sup>. 433

434 Associated content

435 Supporting information: field site description, additional details of column experiments436 including pictures of the setups, and details information of methods used for solid phase

- 437 analysis (microwave digestion,  $\mu$ -XANES spectroscopy, visualization of multiple energy  $\mu$ -
- 438 XRF maps in SMAK, and As and Fe speciation obtained by LCF)

#### 439 **Author contribution**

A.V.L contributed to concept of the study, sampling campaigns, lab work, and manuscript
writing with support and feedback from A.K and E.M.M. A.K obtained funding and
conceptualized the study. Sample preparation, measurement, and data analysis for μXRF were
done by S.B, E.M.M. The ICP-MS analysis was conducted by S.D. The SEM/EDS was
conducted by S.F. The manuscript was revised by all co-authors.

445 Notes

446 The authors declare no competing financial interest.

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#### 463 **Reference**

- Freitas BLS, Terin UC, Fava NMN, et al. A critical overview of household slow sand
   filters for water treatment. *Water Res.* 2022;208(November 2021).
- 466 doi:10.1016/j.watres.2021.117870
- 467 2. WHO. Evaluating Household Water Treatment Options: Health-Based Targets and
- 468 *Microbiological Performance Specifications*. World Health Organization; 2011.
- 469 3. Berg M, Tran HC, Nguyen TC, Pham HV, Schertenleib R, Giger W. Arsenic
- 470 contamination of groundwater and drinking water in Vietnam: A human health threat.
- 471 Environ Sci Technol. 2001;35(13):2621-2626. doi:10.1021/es010027y
- 472 4. Luzi S, Berg M, Pham TKT, Pham H V, Schertenleib R. Household sand filters for
- 473 arsenic removal. www.arsenic.eawag.ch/publications (accessed 2019-01-29). Swiss

474 Fed Inst Environ Sci Technol (EAWAG), Duebendorf, Switz. 2004.

- 475 5. Berg M, Luzi S, Trang PTK, Viet PH, Giger W, Stüben D. Arsenic removal from
- 476 groundwater by household sand filters: Comparative field study, model calculations,
- 477 and health benefits. *Environ Sci Technol*. 2006;40(17):5567-5573.
- 478 doi:10.1021/es060144z
- 479 6. Nitzsche KS, Lan VM, Trang PTK, et al. Arsenic removal from drinking water by a
- 480 household sand filter in Vietnam Effect of filter usage practices on arsenic removal
- 481 efficiency and microbiological water quality. *Sci Total Environ*. 2015;502:526-536.
- 482 doi:10.1016/j.scitotenv.2014.09.055
- 483 7. Voegelin A, Kaegi R, Berg M, et al. Solid-phase characterisation of an effective
- 484 household sand filter for As, Fe and Mn removal from groundwater in Vietnam.
- 485 *Environ Chem.* 2014;11(5):566-578.
- 486 8. Hug SJ, Leupin O. Iron-catalyzed oxidation of Arsenic(III) by oxygen and by
- 487 hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction.

- 488 *Environ Sci Technol.* 2003;37(12):2734-2742. doi:10.1021/es026208x
- 489 9. Van Le A, Straub D, Planer-Friedrich B, Hug SJ, Kleindienst S, Kappler A. Microbial
- 490 communities contribute to the elimination of As, Fe, Mn, and NH4+ from groundwater
- 491 in household sand filters. *Sci Total Environ*. 2022;838(June):156496.
- 492 doi:10.1016/j.scitotenv.2022.156496
- 493 10. Hansel CM. *Manganese in Marine Microbiology*. Vol 70. 1st ed. Elsevier Ltd.; 2017.
- 494 doi:10.1016/bs.ampbs.2017.01.005
- 495 11. Tebo BM, Johnson HA, McCarthy JK, Templeton AS. Geomicrobiology of
- 496 manganese(II) oxidation. *Trends Microbiol*. 2005;13(9):421-428.
- 497 doi:10.1016/j.tim.2005.07.009
- 498 12. Ross DS, Bartlett RJ. Evidence for nonmicrobial oxidation of manganese in soil. *Soil*499 *Sci.* 1981;132(2):153-160.
- 500 13. Davies SHR, Morgan JJ. Manganese(II) oxidation kinetics on metal oxide surfaces. J
- 501 *Colloid Interface Sci.* 1989;129(1):63-77. doi:10.1016/0021-9797(89)90416-5
- 502 14. Morgan JJ. Kinetics of reaction between O2 and Mn (II) species in aqueous solutions.
  503 *Geochim Cosmochim Acta*. 2005;69(1):35-48.
- 504 15. Petitjean A, Forquet N, Boutin C. Oxygen profile and clogging in vertical flow sand
- 505 filters for on-site wastewater treatment. *J Environ Manage*. 2016;170:15-20.
- 506 doi:https://doi.org/10.1016/j.jenvman.2015.12.033
- 507 16. Ehlert K, Mikutta C, Kretzschmar R. Effects of manganese oxide on arsenic reduction
- 508 and leaching from contaminated floodplain soil. *Environ Sci Technol*.
- 509 2016;50(17):9251-9261. doi:10.1021/acs.est.6b01767
- 510 17. Bai Y, Chang Y, Liang J, Chen C, Qu J. Treatment of groundwater containing Mn(II),
- 511 Fe(II), As(III) and Sb(III) by bioaugmented quartz-sand filters. *Water Res.*
- 512 2016;106:126-134. doi:10.1016/j.watres.2016.09.040

- 513 18. Liu H, Xu R, Haggblom MM, et al. Immobile iron-rich particles promote arsenic
- 514 retention and regulate arsenic biotransformation in treatment wetlands. *Environ Sci*515 *Technol.* 2022;56(22):15627-15637.
- 516 19. Webb SM. The MicroAnalysis Toolkit: X-ray Fluorescence Image Processing
- 517 Software. *AIP Conf Proc.* 2011;1365(1):196-199. doi:10.1063/1.3625338
- 20. Ravel B, Newville M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray
  absorption spectroscopy using IFEFFIT. *J Synchrotron Radiat*. 2005;12(4):537-541.
- 520 21. Roberts LC, Hug SJ, Ruettimann T, Billah MM, Khan AW, Rahman MT. Arsenic
- removal with iron (II) and iron (III) in waters with high silicate and phosphate
  concentrations. *Environ Sci Technol.* 2004;38(1):307-315.
- 523 22. Voegelin A, Kaegi R, Frommer J, Vantelon D, Hug SJ. Effect of phosphate, silicate,
- and Ca on Fe (III)-precipitates formed in aerated Fe (II)-and As (III)-containing water
- 525 studied by X-ray absorption spectroscopy. *Geochim Cosmochim Acta*. 2010;74(1):164-
- 526
   186.
- 527 23. van Genuchten CM, Gadgil AJ, Peña J. Fe (III) nucleation in the presence of bivalent
  528 cations and oxyanions leads to subnanoscale 7 Å polymers. *Environ Sci Technol*.
- 529 2014;48(20):11828-11836.
- 530 24. Leupin OX, Hug SJ. Oxidation and removal of arsenic (III) from aerated groundwater
- 531 by filtration through sand and zero-valent iron. *Water Res.* 2005;39(9):1729-1740.
- 532 doi:10.1016/j.watres.2005.02.012
- 533 25. Gülay A, Tatari K, Musovic S, Mateiu R V., Albrechtsen HJ, Smets BF. Internal
- 534 porosity of mineral coating supports microbial activity in rapid sand filters for
- 535 groundwater treatment. *Appl Environ Microbiol*. 2014;80(22):7010-7020.
- 536 doi:10.1128/AEM.01959-14
- 537 26. Han YS, Kim SH, Jang JY, Ji S. Arsenic removal characteristics of natural Mn-Fe

538		binary coating on waste filter sand from a water treatment facility. Environ Sci Pollut
539		Res. 2022;29(2):2136-2145. doi:10.1007/s11356-021-15580-0
540	27.	Ying C, Lanson B, Wang C, et al. Highly enhanced oxidation of arsenite at the surface
541		of birnessite in the presence of pyrophosphate and the underlying reaction
542		mechanisms. Water Res. 2020;187. doi:10.1016/j.watres.2020.116420
543	28.	Wielinski J, Jimenez-Martinez J, Göttlicher J, et al. Spatiotemporal Mineral Phase
544		Evolution and Arsenic Retention in Microfluidic Models of Zerovalent Iron-Based
545		Water Treatment. Environ Sci Technol. 2022. doi:10.1021/acs.est.2c02189
546	29.	Root RA, Fathordoobadi S, Alday F, Ela W, Chorover J. Microscale speciation of
547		arsenic and iron in ferric-based sorbents subjected to simulated landfill conditions.
548		Environ Sci Technol. 2013;47(22):12992-13000. doi:10.1021/es402083h
549	30.	Hug SJ, Leupin OX, Berg M. Bangladesh and Vietnam: Different groundwater
550		compositions require different approaches to arsenic mitigation. Environ Sci Technol.
551		2008;42(17):6318-6323. doi:10.1021/es7028284
552	31.	Manning BA, Fendorf SE, Goldberg S. Surface structures and stability of arsenic(III)
553		on goethite: Spectroscopic evidence for inner-sphere complexes. Environ Sci Technol.
554		1998;32(16):2383-2388. doi:10.1021/es9802201
555	32.	Tournassat C, Charlet L, Bosbach D, Manceau A. Arsenic(III) Oxidation by Birnessite
556		and Precipitation of Manganese(II) Arsenate. <i>Environ Sci Technol</i> . 2002;36(3):493-
557		500. doi:10.1021/es0109500
558	33.	Schaefer M V., Plaganas M, Abernathy MJ, et al. Manganese, Arsenic, and Carbonate
559		Interactions in Model Oxic Groundwater Systems. Environ Sci Technol. 2020.
560		doi:10.1021/acs.est.0c02084
561	34.	Wu Y, Kukkadapu RK, Livi KJT, Xu W, Li W, Sparks DL. Iron and Arsenic
562		Speciation during As(III) Oxidation by Manganese Oxides in the Presence of Fe(II):

563		Molecular-Level Characterization Using XAFS, Mössbauer, and TEM Analysis. ACS
564		Earth Sp Chem. 2018;2(3):256-2684. doi:10.1021/acsearthspacechem.7b00119
565	35.	Gude JCJ, Rietveld LC, van Halem D. As(III) oxidation by MnO <sub>2</sub> during groundwater
566		treatment. Water Res. 2017;111:41-51. doi:10.1016/j.watres.2016.12.041
567	36.	Lan S, Ying H, Wang X, et al. Efficient catalytic As (III) oxidation on the surface of
568		ferrihydrite in the presence of aqueous Mn (II). Water Res. 2018;128:92-101.
569	37.	Ehlert K, Mikutta C, Kretzschmar R. Impact of birnessite on arsenic and iron
570		speciation during microbial reduction of arsenic-bearing ferrihydrite. Environ Sci
571		Technol. 2014;48(19):11320-11329. doi:10.1021/es5031323
572	38.	Wu Y, Li W, Sparks DL. The effects of iron (II) on the kinetics of arsenic oxidation
573		and sorption on manganese oxides. J Colloid Interface Sci. 2015;457:319-328.
574	39.	Han X, Li Y-L, Gu J-D. Oxidation of As(III) by MnO2 in the absence and presence of
575		Fe(II) under acidic conditions. Geochim Cosmochim Acta. 2011;75(2):368-379.
576		doi:https://doi.org/10.1016/j.gca.2010.10.010
577	40.	Bretzler A, Nikiema J, Lalanne F, et al. Arsenic removal with zero-valent iron filters in
578		Burkina Faso: Field and laboratory insights. Sci Total Environ. 2020;737:139466.
579		doi:10.1016/j.scitotenv.2020.139466
580	41.	Van Le A, Marie Muehe E, Drabesch S, et al. Environmental Risk of Arsenic
581		Mobilization from Disposed Sand Filter Materials. Environ Sci Technol. 2022;0(0).
582		doi:10.1021/acs.est.2c04915
583	42.	Dong G, Han R, Pan Y, et al. Role of MnO2 in controlling iron and arsenic
584		mobilization from illuminated flooded arsenic-enriched soils. J Hazard Mater.
585		2021;401(June 2020):123362. doi:10.1016/j.jhazmat.2020.123362
586	43.	Xu X, Chen C, Wang P, Kretzschmar R, Zhao FJ. Control of arsenic mobilization in
587		paddy soils by manganese and iron oxides. Environ Pollut. 2017;231:37-47.

- 588 doi:10.1016/j.envpol.2017.07.084
- 589 44. Cerrato JM, Falkinham JO, Dietrich AM, Knocke WR, McKinney CW, Pruden A.
- 590 Manganese-oxidizing and -reducing microorganisms isolated from biofilms in
- chlorinated drinking water systems. *Water Res.* 2010;44(13):3935-3945.
- 592 doi:10.1016/j.watres.2010.04.037
- 593 45. Hu W, Liang J, Ju F, et al. Metagenomics Unravels Differential Microbiome
- 594 Composition and Metabolic Potential in Rapid Sand Filters Purifying Surface Water
- 595 Versus Groundwater. *Environ Sci Technol*. 2020;54(8):5197-5206.
- 596 doi:10.1021/acs.est.9b07143
- 597 46. de Souza FH, Roecker PB, Silveira DD, Sens ML, Campos LC. Influence of slow sand
- 598 filter cleaning process type on filter media biomass: backwashing versus scraping.

599 *Water Res.* 2021;189. doi:10.1016/j.watres.2020.116581

- 47. Ljung K, Vahter M. Time to re-evaluate the guideline value for manganese in drinking
  water? *Environ Health Perspect*. 2007;115(11):1533-1538.
- 602 48. Oulhote Y, Mergler D, Barbeau B, et al. Neurobehavioral function in school-age
- 603 children exposed to manganese in drinking water. *Environ Health Perspect*.

604 2015;122(12):1343-1350. doi:10.1289/ehp.1307918

- 605 49. Rahman SM, Kippler M, Tofail F, Bölte S, Derakhshani Hamadani J, Vahter M.
- Manganese in drinking water and cognitive abilities and behavior at 10 years of age: a
- 607 prospective cohort study. *Environ Health Perspect*. 2017;125(5):57003.