



## Reducing conditions increased the mobilisation and hazardous effects of arsenic in a highly contaminated gold mine spoil

Albert Kobina Mensah<sup>a, g, 1</sup>, Bernd Marschner<sup>a</sup>, Jianxu Wang<sup>b, c</sup>, Jochen Bundschuh<sup>d, i</sup>,  
Shan-Li Wang<sup>e</sup>, Puu-Tai Yang<sup>e</sup>, Sabry M. Shaheen<sup>c, f, h, 2</sup>, Jörg Rinklebe<sup>c, \*, 3</sup>

<sup>a</sup> Department of Soil Science and Soil Ecology, Institute of Geography, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany

<sup>b</sup> State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 550082 Guiyang, PR China

<sup>c</sup> University of Wuppertal, School of Architecture and Civil Engineering, Institute of Foundation Engineering, Water, and Waste-Management, Laboratory of Soil, and Groundwater-Management, Pauluskirchstraße 7, 42285 Wuppertal, Germany

<sup>d</sup> University of Southern Queensland, UNESCO Chair on Groundwater Arsenic within the 2030 Agenda for Sustainable Development, West Street, Toowoomba 4350 Queensland, Australia

<sup>e</sup> Department of Agricultural Chemistry, National Taiwan University, 1 Sect. 4, Roosevelt Rd., Taipei 10617, Taiwan

<sup>f</sup> King Abdulaziz University, Faculty of Meteorology, Environment, and Arid Land Agriculture, Department of Arid Land Agriculture, Jeddah 21589, Saudi Arabia

<sup>g</sup> Council for Scientific and Industrial Research- Soil Research Institute, Academy Post Office, Kwadaso- Kumasi, Ghana

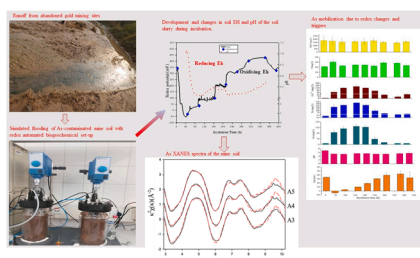
<sup>h</sup> International Research Centre of Nanotechnology for Himalayan Sustainability (IRCNSH), Shoolini University, Solan 173212, Himachal Pradesh, India

<sup>i</sup> Department of Earth and Environmental Sciences, National Chung Cheng University, 168 University Road, Min-Hsiung, Chiayi County 62102, Taiwan

### HIGHLIGHTS

- As mobilisation in mine spoil was higher at low  $E_H$  (<200 mV) than high  $E_H$  (>200 mV).
- As mobilisation was mainly governed by Fe chemistry.
- As (V) in sediments persisted during moderately reducing conditions.
- Lower Fe/As molar ratios at low  $E_H$  show potential As migration to water.
- As mitigation measures at the minefield should limit reducing conditions.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

Editor: Lingxin Chen

#### Keywords:

Toxic elements  
Gold mining  
Flooding  
Mobilization  
Hazardous effects

### ABSTRACT

Arsenic (As) redox-induced mobilisation and speciation in polluted gold mine sites in tropical climates largely remains unknown. Here, we investigated the impact of changes in soil redox potential ( $E_H$ ) (−54 mV to +429 mV) on mobilisation of As and its dominant species in an abandoned spoil (total As = 4283 mg/kg) using an automated biogeochemical microcosm set-up. Arsenic mobilisation increased (85–137 mg/L) at moderately reducing conditions (−54 mV to +200 mV), while its reduced (6–35 mg/L) under oxic conditions (+200 to +400 mV). This indicates the high risk of As potential loss under reducing conditions. The mobilisation of As was governed by the redox chemistry of Fe. XANES and EXAFS analyses showed that sorbed-As(V)-goethite, sorbed-

\* Corresponding author.

E-mail addresses: [albert.mensah@rub.de](mailto:albert.mensah@rub.de) (A.K. Mensah), [bernd.marschner@rub.de](mailto:bernd.marschner@rub.de) (B. Marschner), [wangjianxu@vip.gyig.ac.cn](mailto:wangjianxu@vip.gyig.ac.cn) (J. Wang), [shaheen@uni-wuppertal.de](mailto:shaheen@uni-wuppertal.de) (S.M. Shaheen), [rinklebe@uni-wuppertal.de](mailto:rinklebe@uni-wuppertal.de) (J. Rinklebe).

<sup>1</sup> ORCID: 0000-0001-5952-3357

<sup>2</sup> ORCID: 0000-0002-5618-8175

<sup>3</sup> ORCID: 0000-0001-7404-1639

<https://doi.org/10.1016/j.jhazmat.2022.129238>

Received 18 March 2022; Received in revised form 23 May 2022; Accepted 24 May 2022

Available online 27 May 2022

0304-3894/© 2022 Elsevier B.V. All rights reserved.

As(III)-ferrihydrite, scorodite and arsenopyrite were the predominant As species in the mine spoil. As(V) dominated at oxic conditions and As(III) predominated at moderately reducing conditions, which may be attributed to either inability of arsenate bacteria to reduce As or incomplete reduction. Lower Fe/As molar ratios during moderately reducing conditions show that the mine spoil may migrate As to watercourses during flooding, which may increase the hazardous effects of this toxic element. Therefore, encouraging aerobic conditions may mitigate As release and potential loss from the mine field.

## 1. Introduction

Arsenic (As) is a toxic element whose presence in the environment presents severe hazardous effects and health threats to environment and humans (Mensah et al., 2021; Khan et al., 2020; Aftabtalab et al., 2022; Niazi et al., 2022). In the natural environment, As is principally present as arsenopyrite (FeAsS) in gold mine tailings, soils, spoils and wastes (DeSisto et al., 2017; Filippi et al., 2015; Mensah et al., 2020). Arsenopyrite may react with atmospheric oxygen when abandoned mine spoils are left untreated and subsequently left exposed to atmospheric conditions. These conditions may then create oxidative dissolution of sulphide-bearing minerals in the mine spoils, leading to soil acidity, release of sulphates, other dissolved metals and As (e.g., DeSisto et al., 2017; Itabashi et al., 2019). For instance, arsenopyrite dissolution in gold mine spoils leads to production and consequent liberation of  $\text{Fe}^{2+}$ , As(III), and  $\text{SO}_4^{2-}$  into the soil solution and the environment as reported by DeSisto et al. (2017).

In Ghana, poor handling of gold mine wastes (Mensah et al., 2021), abandonment of mine tailings, spillage, flood damages and subsidence of tailing spoils (Bempah et al., 2013) had resulted in mobilisation of As into rivers (Hadzi et al., 2018), estuaries (Klubi et al., 2018), soil (Hayford et al., 2009; Mensah et al., 2021), and the food chain (Bortey-Sam et al., 2015). These risks may thus be exacerbated under varying field and climatic conditions such as the soil pH, leaching, drainage, waterlogging, high rainfall, and intensive flooding events at the contaminated sites. Extreme rainfall and frequent flooding events may create reducing and oxidising conditions in the soil system, and eventually lead to mobilisation of toxic elements into the soil solution and contamination of the surrounding ecosystem (Padoan et al., 2020).

Mobilisation of As from As-contaminated soils and mine spoils could thus be influenced by redox chemistry of the sites. This happens to a large extent via the direct changes of soil redox potentials and/or through redox-induced impacts on soil pH, dissolved organic matter content, and soil chemistry dynamics of Al, Fe, Mn, and S (Shaheen et al., 2016; Yang et al., 2022a; b). These conditions may also in turn influence migration of As into soil and surface-, pore-, and ground-water (Huq et al., 2020; Hussain et al., 2019, 2022; Aftabtalab et al., 2022; Niazi et al., 2022), which leads to food chain contamination (Antoniadis et al., 2017). For instance, flooding and low redox potential conditions may reduce arsenate As(V) to arsenite As(III), cause high As mobilisation and heighten the associated risks (Renock and Voorhis, 2017). Also, reducing conditions may cause a reductive dissolution of Fe/Al/Mn-oxyhydroxides. Consequently, any As that is sorbed to these oxyhydroxides can be liberated into mobile forms (Frohne et al., 2011; Rinklebe et al., 2016). In other instances, As may be immobilised or precipitated due to adsorption onto or co-precipitation with the surfaces of Fe/Al/Mn-oxyhydroxides under oxidising conditions (Frohne et al., 2011; Yang et al., 2022a; Niazi et al., 2022). Additionally, Renock and Voorhis (2017) reported that under  $\text{SO}_4^{2-}$ -reducing conditions, mobilisation of dissolved As is affected through formation of As-sulphide complexes including realgar ( $\text{As}_4\text{S}_4$ ) and orpiment ( $\text{As}_2\text{S}_3$ ), which may reduce As solubility and subsequently slow its release. Under such conditions, there is stabilisation of As-bearing minerals with consequent decrease in As mobilisation from contaminated fields as reiterated by Lemonte et al. (2017) and Huq et al. (2020). Furthermore, organic carbon has greater ability to complex and become carriers of positive ions due to the presence of negatively charged surfaces (Grybos et al.,

2009, 2019). Thus, an increase in concentration of dissolved organic carbon (DOC) may lead to concomitant increase in As mobilisation under reducing redox environments or vice versa (e.g., El-Naggar et al., 2019; Frohne et al., 2011; Grybos et al., 2009; Lemonte et al., 2017). Lemonte et al. (2017), for instance, reported a stronger DOC-As correlation in coastal sediments inundated with river water in a historically As-contaminated industrial site in USA.

Chemical speciation using synchrotron-based X-ray absorption spectroscopy (XAS), including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) is a sophisticated approach to assess solubility of As (Itabashi et al., 2019; Yang et al., 2020), and to determine its true potential and environmental risks (Cancès et al., 2008; Mensah et al., 2020; Tang et al., 2016). Also, chemical speciation may aid to determine As stability under various redox conditions and oxidation states (Itabashi et al., 2019; Manning, 2005). In this regard, Bjorn et al. (2020) reported that synchrotron XAS applied to some African earth and geological samples aided to improve understanding of the fate and mobility of toxic elements in soils and waterways. For instance, to determine As pollution in active and abandoned gold mines in Ghana, we used As K-edge XANES (Mensah et al., 2020) to investigate the speciation of As in mine tailings. This indicated that the mobility, and thus the health risk of As in the gold mining region may be more associated with the behaviour of scorodite than arsenopyrite.

Previous works that studied As mobilisation and its speciation mainly were in temperate countries and ecosystems such as flood plains (Frohne et al., 2011; Shaheen et al., 2014a, 2016), agricultural soils (Beiyan et al., 2017), and coastal sediments (Lemonte et al., 2017), with limited focus on tropical rainforest environments and As-contaminated abandoned mine spoils. Such detailed investigation focusing on the biogeochemistry and potential governing factors controlling the availability of As under varying soil redox conditions in Ghana will aid to effectively plan mitigation measures against As release into watercourses in gold mining areas.

Mobilisation and speciation of As in an As-contaminated abandoned gold mine tailings and spoils especially during extreme flooding events under intense rainfall conditions in Ghana has not been studied so far. Such scientific investigations should be of paramount environmental and public health concern to policy makers and scientists, but have so far not been explored. Our previous work (E.g., Mensah et al., 2020) attempted this by studying the potential mobilisation and species of As in abandoned and active mining spoils. However, this former work focused on surface soils and soil profiles, and did not study As mobilisation and speciation as affected by various reducing and oxidizing conditions that happen at the mine contaminated sites.

We hypothesize that redox variations in the highly As contaminated abandoned spoil will lead to changes in 1) the soil pH, 2) the binding forms of As with oxides, sulphur, and the proportion of aliphatic and aromatic carbon compounds of dissolved soil organic carbon (DOC), and 3) the distribution of As species in the soil; which highly affect As release and migration from the abandoned spoil to watercourses and increase its hazardous effects. To test and verify our hypotheses, we aimed to: i) quantify the impact of a wide range of  $E_H$  on the mobilization of As in an As-contaminated gold mine spoil in Ghana, ii) determine the impacts of the redox-induced changes on soil pH, Fe-Mn-Al-(oxyhydr)oxides), sulphate ( $\text{SO}_4^{2-}$ ), and DOC on the release dynamics of As, and iii) elucidate the impact of different redox conditions on speciation of As in the

sediment phase of the studied As-contaminated gold mine spoil.

## 2. Materials and methods

### 2.1. Study site, mine spoil soil sampling and characteristics

We collected mine spoil soil samples from an abandoned As-contaminated gold mine spoil in gold mining town in southwestern Ghana (a tropical rainforest climate/area). Detailed study area characteristics of the site are reported recently in Mensah et al. (2020). Gold mining forms the major source of occupation of the people, like in other gold mining regions in Ghana. However, unsustainable gold mining practices emanating from both legal large-scale, and artisanal and small-scale mines in the area have resulted in extensive land degradation, soil and water pollution, and loss of soil fertility and arable fields (Mensah et al., 2015, 2021).

Samples were collected from 32 random spots at a soil depth of 0–20 cm and bulked together into one composite sample. Air-drying of the soil sample was then done for 48 h; then they were crushed, homogenized, and passed through a 2-mm sieve. The samples were then characterized for their basic soil parameters according to standard methods provided by Sparks et al. (1996). Determination of spoil soil texture was done using the pipet and the laser particle diffraction analysis methods; and then the texture was determined using the laser scattering method according to Zobeck (2004).

The spoil had a total As content of 4283 mg/kg and is thus the dominant contaminant. The spoil was predominantly sandy with 62% sand, 36% silt and 3% clay. The spoil was weakly acidic (pH: 6.4) and was salt-affected with an electrical conductivity of 1.9 dS/m. The site was low in total carbon (1.2%) and total phosphorus (13.4 mg/kg). The basic properties of the mine spoil are included in the [supporting materials](#) (Appendix A; [Table S1](#)) and more details about the soil are published in Mensah et al. (2021).

### 2.2. Total contents and geochemical fractionation of As

Total content of As and other elements (Fe, Ca, Mg, Al, and S) in the mine spoil composite bulk soil sample was extracted using microwave (CEM, Kamp-Lintford, Germany) concentrated nitric acid digestion method at 120 °C for 15 min at 1600 W according to USEPA (2007); then contents were measured by the inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectroblue, Ametek Materials Analysis Division). Geochemical fractions of As (water-soluble (FI), exchangeable fraction (FII), amorphous and low crystalline Fe oxides (FIII), high-crystalline Fe oxide (IV), and As bound to sulphides and arsenides (FV)) in the mine spoil soil were extracted sequentially according to the five-step sequential extraction procedure by Wenzel et al. (2001). In this method, 1.0 g of dried fine soil was weighed into a 40-mL centrifuge tube, mixed with the appropriate solution, shaken, centrifuged, and filtered. From the filtrate, As contents in each fraction were determined on the ICP-OES. Details of the extraction procedure and solutions used at each step are reported in the [supporting information](#) (Appendix A; [Table S2](#)). All procedures were done in triplicates and As recovery rate was calculated according to Mensah et al. (2020).

### 2.3. Redox experiment

#### 2.3.1. Biogeochemical microcosm set-up and experimental conditions

We simulated flooding of the As-contaminated mine spoil soil in the laboratory using the automated biogeochemical microcosm (MC) experiment set-up. This equipment allows the simulation of anoxic/oxic conditions by adjusting the  $E_H$  automatically using addition of nitrogen to lower  $E_H$  or synthetic air/oxygen to increase  $E_H$ . The advantages and applications of redox measurement in a microcosm set-up were reported in previous studies (e.g., Frohne et al., 2011; Shaheen et al., 2014b, 2016; Yang et al., 2022a, b). Technical details of the set-up and how it

works were also reported by Yu and Rinklebe (2011). Three independent MCs were used as replicates in the experiment. Using 1:8 soil/water ratio, 210 g air-dried soil was poured into the glass vessel of the MC and 1680 mL of tap water added. 15 g of powdered wheat straw and 10 g glucose were added to the soil in each MC to serve as carbon sources for microorganisms. An air-tight lid was then used to seal the setup. Constant stirring of the soil suspension was done throughout the experiment period to achieve homogeneity. The system has platinum (Pt) electrode, a pH electrode, and a temperature sensor allow the continuous measurement of  $E_H$ , pH, and temperature every ten minutes. The measured  $E_H$ , pH and temperature values were recorded every 10 min by a data logger connected via a computer to the system. The measured EH values were relative to the standard hydrogen electrode (SHE) using the ORP-Probe reading (electrode  $E_t$ , mV) and the solution temperature as well as the Nernst-Equation, as published by Wolkersdorfer (2008). Nine pre-defined  $E_H$  windows between  $-54$  mV and  $+429$  mV were set and examined. The windows were achieved 24 h before sampling and were automatically kept with alternate flushing with  $N_2$  (to lower  $E_H$ ) and synthetic air/ $O_2$  (to raise  $E_H$ ). The  $E_H$  values measured 6 h before sampling for each window and their averages are reported in the [Supporting information](#) (Appendix A; [Table S3](#)).

#### 2.3.2. Sampling and analyses

Nine samples were collected during the incubation period. Initial sample was collected one hour after stirring the MCs. Here, a syringe was used to collect 90 mL of the soil suspension in the MC 24 h after attaining the pre-set  $E_H$ -window. Centrifugation of the collected sample was then done for 15 min at 5000 rpm. Samples were then filtered using the  $< 0.45$   $\mu$ m filter paper (Whatman Inc. Maidstone, UK) to extract the dissolved fraction as reported by Guo et al. (2007) and Rinklebe et al. (2020). After filtration through the  $< 0.45$   $\mu$ m filter paper, samples were sub-divided for subsequent analyses. The whole filtration process took place in a glove box (MK3 Anaerobic Workstation, Don Whitley Scientific, Shipley, UK) to avoid exposure to oxygen.

The first subsample was preserved by adding 0.10 mL of 65%  $HNO_3$ , stored at 4 °C and then later analysed for total element contents using the ICP-OES (Ultima 2, Horiba Jobin Yvon, Unterhaching, Germany). Dissolved organic carbon and DIC were determined in the second subsample; whilst anions such as chloride and sulphate were measured in the third subsample. The second and third subsamples were stored at  $-20$  °C till they were ready for analysis. The fourth subsample was used for determination of specific UV absorbance (SUVA). Contents of dissolved As, Fe, Mn, Al, and S in the samples were analysed using the ICP-OES. Contents of DOC and DIC were measured by a C/N-analyser (Analytik Jena, Jena, Germany). Specific ultra violet adsorption serves as an indicator of the chemical composition of the DOC (Shaheen et al., 2014b; Weishaar et al., 2003) and was determined with a UV/VIS spectrophotometer (CADAS 200, Dr. Lange, Germany) at 254 nm. SUVA of the samples was deduced by normalizing the measured 254-nm absorbance to the content of DOC according to Weishaar et al. (2003). Chloride and sulphate anion contents were determined using ion chromatography (Metrohm, 881 Compact IC Pro). Iron (II) in the soil solution was measured using the 1,10-phenanthroline method according to Harvey et al. (1955).

#### 2.3.3. Fe/As molar ratio

The Fe/element molar ratio of reduced soil solutions is an important parameter in assessing the risk of element transfer and migration into watercourses (Gu et al., 2019; Zak et al., 2004; Shaheen et al., 2022). Additionally, it demonstrates the capacity of Fe to immobilize element once re-oxidized at the soil/stream water interface (Gu et al., 2019). It has been used in other agro-environmental research to estimate migration of As from aquatic environments, agricultural lands and wetlands to freshwater (e.g., Baken et al., 2015; Forsmann and Kjaergaard, 2014; Gu et al., 2019). Thus, we used Fe(II)/As molar ratio to assess potential migration of As into watercourses that could be situated near the

abandoned As-contaminated gold mine site. Here, a Fe(II)/As molar ratio  $> 3.0$  will mean higher As precipitation as soil water enters aerobic conditions at the soil/stream water interface (Zak et al., 2004), and thus lead to reduced-As mobilisation. Also, Fe(II)/As molar ratio  $< 3$  will mean possible migration of As from the mining spoil into nearby watercourses during reducing conditions.

#### 2.3.4. Arsenic speciation in sediments

Arsenic species in the solid-phase sediments collected from the spoil at the lowest ( $-30$  mV), middle ( $+210$  mV) and highest ( $+429$  mV) redox potentials were measured using As K-edge XANES. Both As XANES and EXAFS spectra were collected at beamline TLS 07 A at the National Synchrotron Radiation Research Centre (NSRRC), Taiwan. Arsenic species dominant at  $-30$  mV,  $+210$  mV and  $+429$  mV were determined using linear combination fitting (LCF) with a set of As reference materials including sorbed-As(V) goethite, sorbed-As(III) ferrihydrite, scorodite and arsenopyrite (Yang et al., 2020). The spectral processing and analyses were performed with the Athena software (Ravel and Newville, 2005) and the best fit was chosen based on the R-factor values (lower R-values are better).

#### 2.4. Quality control and data treatment

Quality control of the extraction efficiency of pseudo-total content of As was performed using certified soil reference materials (BRM No. 9b and TML), and the average recovery was 100.0% and 102.0%, respectively. To guarantee high quality of the sequential extraction results, the sum of each As fractions was compared with the As pseudo total content, and the recovery was 102.4%. Blanks were prepared and measurements were done in triplicates during the analyses to ensure reliability of results. To guarantee high-quality results, standard solutions (Merck) for the elements were prepared and certified reference materials for the soil were used. Replicates with maximum relative standard deviation (RSD) values above 15 were not included during statistical analyses. Values with RSD above 15 and below detection limits were replaced by multiplying 0.125 with the detection limit concentration of the elements. Elements and their detection limits are indicated in the supplementary material (Appendix A; Table S4).

Mean  $E_H$  and pH values of samples measured 6 h before the pre-defined  $E_H$  windows were calculated. Statistical analyses were done using IBM SPSS Statistics 25 (NY, USA) and the figures were created with OriginPro 2021b version software (OriginLab Corporation, Northampton, USA). Pearson correlation, simple linear regression and step-wise multiple regression analyses were done among  $E_H$  and other potential redox-induced controlling factors to indicate relationships among these parameters and their influence on mobilisation of As.

### 3. Results and discussions

#### 3.1. Total content and geochemical fractions of As in the mine spoil

The mine spoil soil contained high mean pseudo-total As concentration at 4283.0 mg/kg (Appendix A; Table S1). This value exceeded two hundred- and fourteen- times the maximum allowable As content of 15–20 mg/kg in soils and exceeded sixty-six times the trigger action value (65 mg/kg) reported by Kabata-Pendias (2011). The high As content in the mine spoil might be related to accumulation over many years and stockpiling of the mine wastes from mining activities, many years of abandonment without treatment or reclamation, or presence of scorodite and arsenopyrite in the spoil (Mensah et al., 2020). High As contents in mine tailings (3150 mg/kg) have also been reported in the Altiplano-Puna plateau (Andean Highlands) in South-America by Tapia et al. (2019) and around abandoned gold mining spoil (3144 mg/kg) in Ghana by Mensah et al. (2021). Additionally, elevated As contents (150 mg/kg) in mine tailings have been found in Spain by García-Sánchez et al. (2010), but these authors reported values far lower than those

found in our present study.

Arsenic was mainly distributed in the residual/sulphide fraction (FV = 2591.0 mg/kg (Fig. 1), which accounts for 60.5% of total As) and the low crystalline iron oxide fraction (FIII = 1390.0 mg/kg (Fig. 1), which accounts for 32.5% of total As). This was followed by the exchangeable/specifically-sorbed As fraction (FII), non-specific sorbed As fraction (FI); and then, the high-crystalline Fe oxide fraction (FIV) (Fig. 1). This indicates that As was primarily associated with the amorphous iron oxide and the sulphide components of the arsenopyrite (FeAsS) minerals dominant at the contaminated site as reported by Mensah et al. (2020). The high residual fraction also proves that pollution from the mine spoil soil may come from geogenic source (Shaheen et al., 2017; 2020).

The potential mobile fraction (non-residual fraction) of As (calculated as the sum of FI to FIV) from the mine spoil soil was 1793.5 mg/kg, and accounted for 41% of the total As. This potential mobile fraction could become mobile under changing soil redox potentials and can pose environmental and human health risks (Shaheen et al., 2017). For instance, As in the potential mobile fraction may leach or become mobilised due to reductive dissolution of the Fe-bearing mineral as reported in previous studies (e.g., Shaheen et al., 2017). The content of the mobile fraction of As (FI + FII) was 392 mg/kg, representing 9% of total As. This mobile proportion of As in the mine spoil was contributed by the higher contents of As in FI (25 mg/kg) and FII (367 mg/kg). We thus believe that the highly mobile fraction (392 mg/kg) found in our study may cause potential health implications on the food chain, the soil, and as well as migration into surface and ground water sources in the abandoned mine spoil's surroundings.

#### 3.2. $E_H$ and pH changes

Development and changes in the average  $E_H$  and pH over time of soil slurry of the contaminated mine spoil for the three microcosms are shown in Fig. 2, and the data of the replicates are presented in the supplementary materials (Fig. S1). The  $E_H$  values varied between  $-54$  and  $+429$  mV and the pH ranged between 5.1 and 7.1 ( $n = 7911$ ) during the entire incubation study (Table 1). Flooding decreased the mine spoil soil pH from the initial 7.1 to around 5.1 under reducing conditions at  $E_H$  value of 118 mV (Fig. 2). Overall, the pH decreased during oxidizing conditions and increased during reducing conditions (Fig. 2). The sharp fall of pH under reducing conditions during the initial 80-hours after flooding the soil could be attributed to production of organic acids and  $CO_2$  from the activities of microbes and decay of organic matter from the organic straw material and glucose used during the incubation experiment. This observation is further confirmed by the greater proportions of DOC produced throughout the reduction phase. In this regard, Grybos et al. (2009) indicated that microbial metabolites

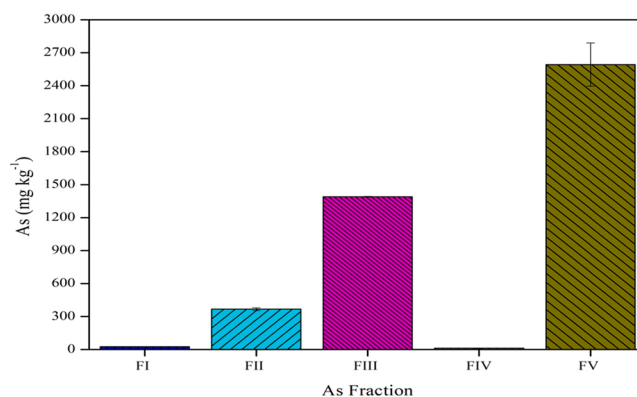
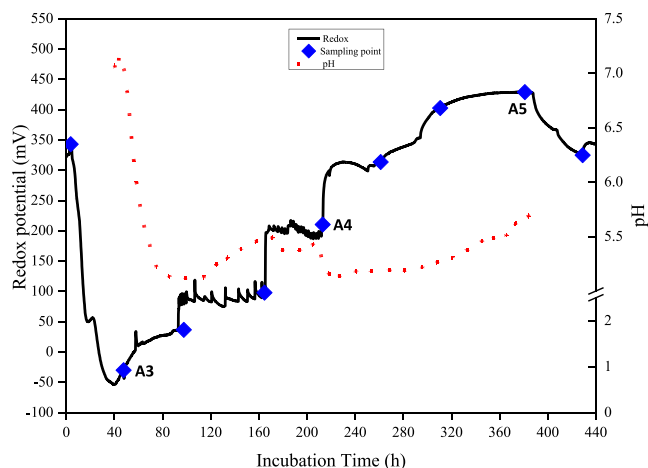


Fig. 1. Arsenic geochemical fractions in the As-contaminated mine spoil soil. Water-soluble and un-specifically bound As (FI); Specific-sorbed As/exchangeable fraction (FII); amorphous Fe oxide fraction (FIII); well-crystalline Fe oxide (IV); and As in residual fraction bound to sulphides (FV).



**Fig. 2.** Development and changes in  $E_H$  and pH of soil slurry of the contaminated mine deposit during the incubation period. Data recorded every 10 min in a data logger, values were reported for means of an underlying dataset ( $n = 7911$ ) of three replicate samples in the microcosms of the contaminated mine spoils. A3, A4, and A5 are samples analyzed for As speciation in sediments using XANES.

**Table 1**

Mean, minimum, maximum, and standard deviation of  $E_H$ , pH, As concentrations and potential governing factors (Fe,  $Fe^{2+}$ , Mn, Al, S, Cl<sup>-</sup>,  $SO_4^{2-}$ , DOC, and SUVA) in the dissolved fraction of the contaminated mine spoil soil.

Parameter	n	Unit	Minimum	Maximum	Mean	Median
$E_{H_{all}}$	7911	[mV]	-54	439	235	305
$pH_{all}$	7911		5.1	7.1	5.4	5.3
As	27		5.8	136.7	58.5	38.2
Fe	27		0.2	325.0	132.2	127.5
Mn	27		0.3	16.0	9.3	10.0
S	27		206.5	360.4	253.9	243.3
Al	27		0.02	0.5	0.2	0.2
$Fe^{2+}$	27	[mg/L]	1.4	172.3	61.9	51.7
Chloride	27		27.3	133.6	75.6	77.1
Sulphate	27		572.6	1087.3	922.2	948.0
DOC	27		1119	2558	1636	1538
SUVA	24	[m <sup>-1</sup> mg <sup>-1</sup> L]	0.05	0.24	0.10	0.09

DOC = dissolved organic carbon; SUVA = Specific Ultra Violet absorbance.

(made up of smaller and less-reactive molecules) contribute a significant portion of the soil DOC produced during the reduction phase of the redox cycle. These findings agree with those made by others (e.g., Shaheen et al., 2014b).

### 3.3. Redox-induced mobilisation of As

#### 3.3.1. Arsenic mobilisation as affected by $E_H$ /pH dynamics

The minimum, maximum, and mean concentrations of As in the dissolved fraction of the flooded mine spoil are given in Table 1. Contents of dissolved As (85.0–136.7 mg/L) were obviously higher under moderately reducing conditions ( $E_H = -54$  mV to +200 mV) than of those (5.8–35.0 mg/L) under the oxidising conditions ( $E_H = +200$  mV to +429 mV; Fig. 3). Mobilisation of As indicated a significant correlation with  $E_H$  ( $r = -0.8$ ;  $P < 0.01$ ), whilst the impact of pH on As solubility was not significant (Supplementary materials; Fig S2). The high concentrations of dissolved As under low  $E_H$  pose a greater threat of exporting dissolved As from the soil to plants and waters under reducing conditions, which increase the potential environmental and human health risks (Niazi et al., 2022).

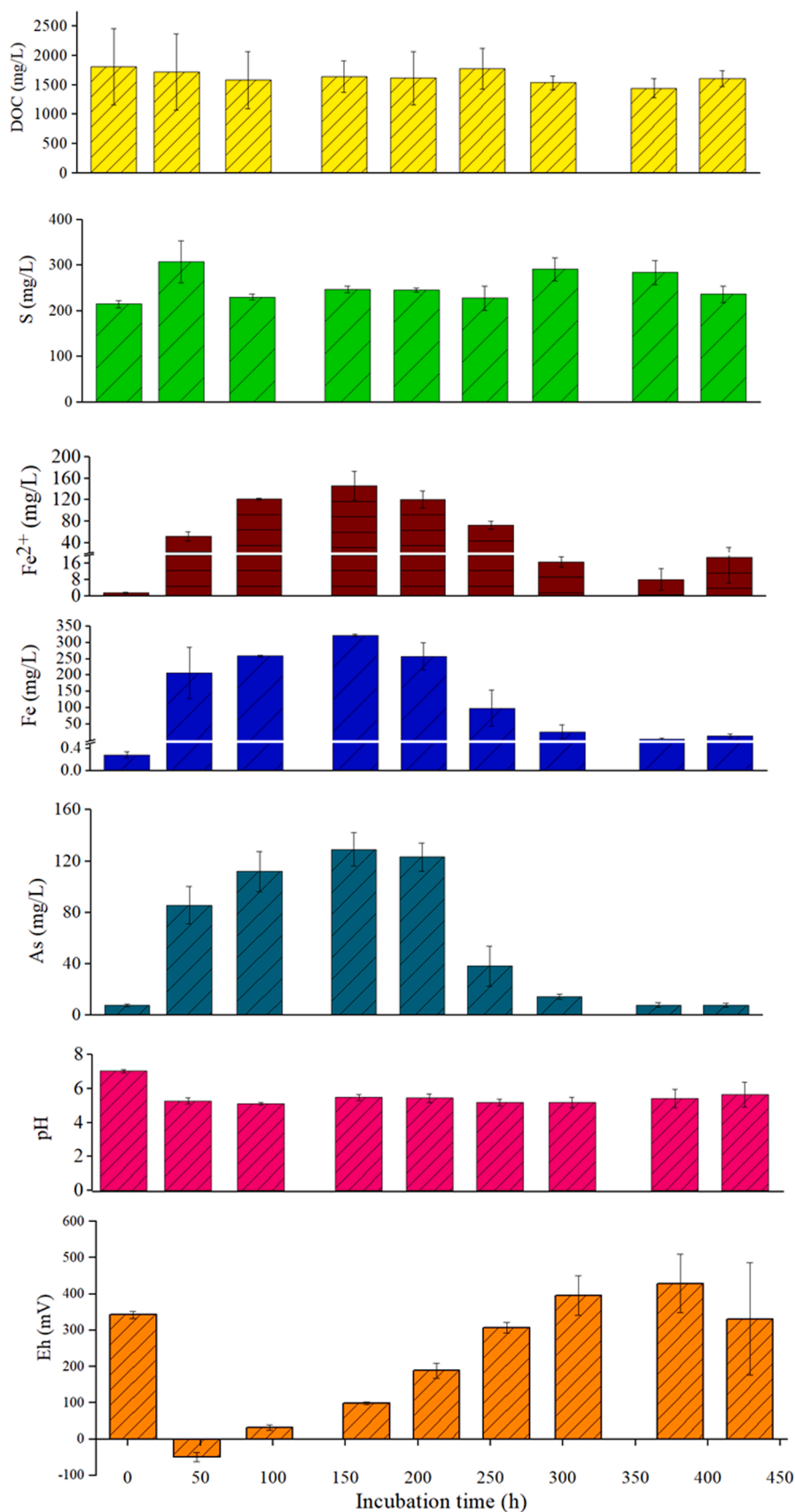
We assume that the higher release and mobilisation of As under reducing conditions than oxic conditions might be due to the redox-

induced alteration of As species. Under reducing conditions, mobile forms of As such as  $H_3AsO_3$ ,  $H_2AsO_3$ ,  $H_2AsO_3^{2-}$  and  $AsO_3^{3-}$  may dominate (e.g., Renock and Voorhis, 2017). Corkhill and Vaughan (2009) also reported the possibility of e.g.,  $As_2S_3$  and AsS, to dominate reducing conditions of FeAsS. However, our work found neither  $H_3AsO_3$ ,  $H_2AsO_3$ ,  $H_2AsO_3^{2-}$  and  $AsO_3^{3-}$ , nor  $As_2S_3$  and AsS under reducing conditions. The dominance of As reduced forms, e.g.,  $As_2S_3$  and AsS may impede solubility of As and consequently reduce its mobilisation (Eberle et al., 2020); as the impacts of sulphur on As mobilisation will be elaborated and discussed in Section 3.3.3.

Contrary to many findings (e.g., Corkhill and Vaughan, 2009; Renock and Voorhis, 2017), we found that As(V) dominated at the low  $E_H$  (-30 mV) and As(III) dominated at the highest  $E_H$  (+429 mV). At the  $E_H$  (+10 mV), sorbed-As(V) dominated and accounted for 34%. This was followed by sorbed-As(III) at 25%, arsenopyrite (23%) and scorodite at 18% (Table 2). Sorbed-As(III) and arsenopyrite are common As species reported under anaerobic conditions (e.g., Fakhreddine et al., 2020; Yang et al., 2020). We assume that in the solid-phase of our samples, it is possible that an oxidized portion of As (i.e., As(V)) may persist during the moderately reducing conditions ( $E_H = -30$  mV), as also reported previously by Fakhreddine et al. (2020) and Yang et al. (2022a). Similarly, Yang et al. (2020) found dominance of sorbed-As(V) (41%) and lower concentration of As(III) (35%) in a rice paddy/wet field in Taiwan. In contrast, the same study further found the dominance of As(III)–34% over As(V)–27% when the land was dry. These findings may be due to inability of arsenate bacteria to reduce all the As in secondary minerals (e.g., scorodite in our bulk soil sample) and thus may result in incomplete reductive dissolution during such moderate reducing conditions. For instance, microbes may chelate Fe, bind As onto mineral surfaces (Nair et al., 2007), or use arsenate as substrate for respiration (Lukasz et al., 2014). Further, strains of bacteria (e.g., siderophores) may impact arsenate reduction either through dissimilatory dissolution of As-minerals, exhibition of resistance to dissolved As compounds, or using dissolved arsenates as terminal electron acceptor (e.g., Drewniak and Sklodowska, 2013; Lukasz et al., 2014).

Likewise, at the highest  $E_H$  (+429 mV), sorbed-As(III) dominated at 41%, and arsenopyrite and scorodite were 25% and 21%, respectively (Table 2). This means that As(III) can be found in the studied soil solid phase even under oxic conditions. Thus, we may infer that the proportions of scorodite and arsenopyrite were relatively stable across  $E_H$  zones. The dominance of scorodite indicates oxidation of the As-bearing mineral (FeAsS) due to reintroduction and exposure to oxygen at higher  $E_H$  (Mensah et al., 2020). Primary As minerals such as arsenopyrites are mainly utilised under aerobic conditions through oxidative dissolution (Lukasz et al., 2014) but there may be limited kinetics or limited oxidation of As(III) to As(V) as explained by Yang et al. (2020) or oxidation of As(III) may be incomplete as suggested by Drewniak and Sklodowska (2013). In this regard, Wallis et al. (2010) found that arsenopyrite oxidation gave high concentration of Fe-OOH at higher  $E_H$  but limited oxidation of dissolved As(III) to As(V). Therefore, compounds of goethite-As(V), ferrihydrite-As(III), arsenopyrite and scorodite were the major As species found in the mine spoil.

Similarly, arsenopyrite and sorbed-As(III) dominated the moderate reducing conditions (+210 mV) at 29% and 30%, respectively. In turn, under reducing conditions, microbes can use arsenate adsorbed on the surface of iron minerals (e.g., scorodite or ferrihydrite) as a terminal electron acceptor in As respiration. However, complete transformation of As(V) into As(III) may be dependent on the concentration of the substrate and time duration under incubation (Lukasz et al., 2014). We thus hypothesise that the shorter incubation period in our study could not allow enough time to facilitate complete transformation. Lukasz et al. (2014) found that bacteria strains (e.g., *Pseudomonas* sp.) had lower arsenate reduction rate, and complete transformation of 2.5 mM (187.5 mg/L) of As(V) to As(III) needed between 72- and 96-hours during incubation. As such, As(V) persisted during anaerobic conditions and As(III) predominated the aerobic conditions during a 21-day



**Fig. 3.** Impact of different reducing and oxidising conditions on the release dynamics of arsenic (As) as affected by redox-induced ( $E_H$ ) changes on pH, Fe,  $Fe^{2+}$ , Mn, Al, S, Cl<sup>-</sup>, DOC and SUVA) in the contaminated mine spoil soil. Columns represent means and whiskers represent standard deviation of three replicates.

**Table 2**

Linear combination fitting results for As K-edge EXAFS spectra of sediment samples collected under different  $E_H$  conditions. The data show the proportion of the reference spectra that resulted in the best fit to the sample data. Normalized sum of the squared residuals of the fit (R-factor =  $\sum(\text{data-fit})^2 / \sum \text{data}^2$ ).

Sample	A3	A4	A5
	%		
Sorbed As(V)	34(3)	24(3)	13(3)
Sorbed As(III)	25(2)	29(2)	41(2)
Scorodite	18(2)	17(3)	21(3)
Arsenopyrite	23(2)	30(3)	25(3)
R factor	0.01184	0.01429	0.01423

A3 = sample collected at EH of  $-30$  mV; A4 = sample collected at EH of  $+210$  mV; and A5 = sample collected at EH of  $+429$  mV.

Number in parentheses indicates uncertainty given by the Athena software.

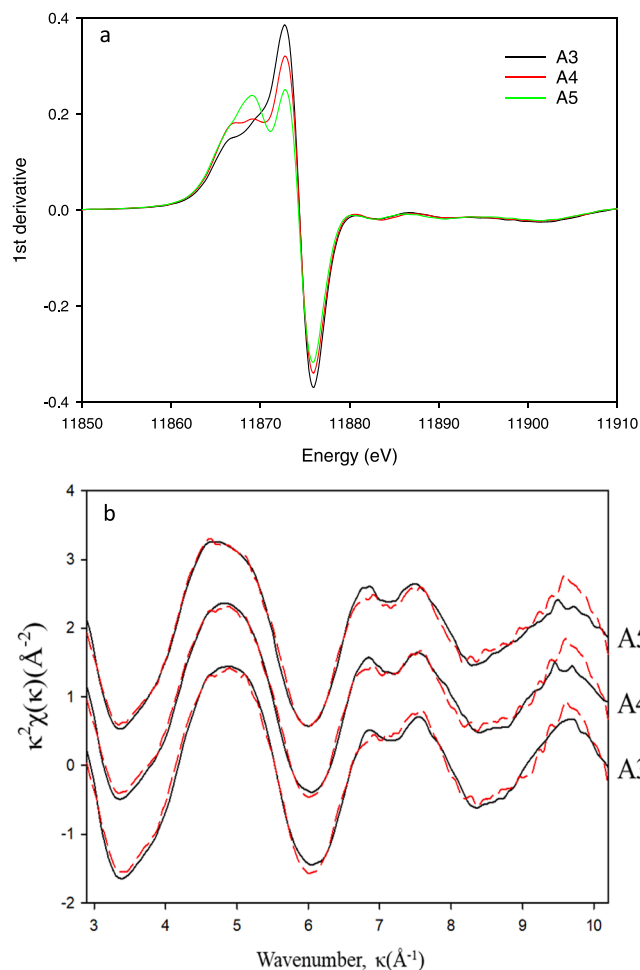
incubation (Lukasz et al., 2014). In conclusion, we infer that the high concentration of As and Fe observed during the anaerobic periods in our present study may be explained by direct dissolution of FeAsS or FeAsO<sub>4</sub> by metabolites (e.g., ligands and organic acids).

### 3.3.2. Arsenic mobilisation as affected by redox-induced changes of Fe-Al-Mn-(oxyhydr)oxides

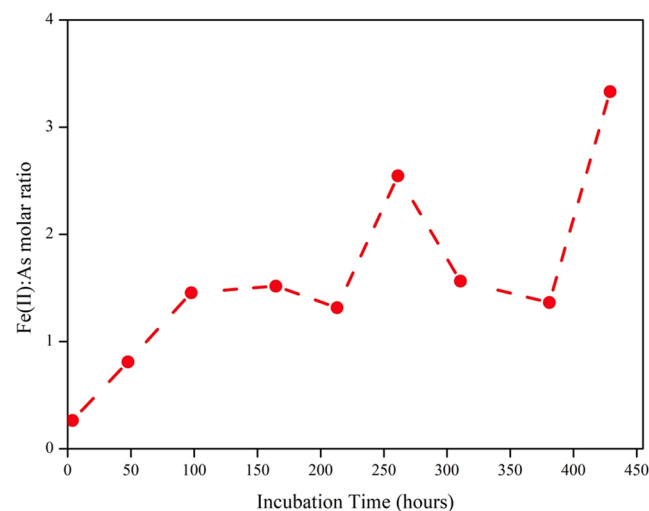
Concentration of dissolved Fe ranged between 0.23 and 325 mg/L, and a mean value of 132.2 mg/L (Table 1). Concentration of dissolved Fe increased under reducing conditions and reduced under oxidising conditions (Fig. 3). Thus, Fe negatively varied significantly with  $E_H$  ( $r = -0.8$ ,  $P < 0.01$ ; Fig. S2). We hypothesise that the negative association between  $E_H$  and Fe could be due to the flooding condition, which resulted in reductive dissolution of Fe<sup>3+</sup> oxides into Fe<sup>2+</sup> as explained by Gu et al. (2019) and Shaheen et al. (2022). It must be noted that flooding and water saturation in soils fill the soil pore spaces and thus may deplete the soil of oxygen. Consequently, soil microbes may change their terminal electron acceptors from that of oxygen to iron and thus resulting in reductive dissolution of Fe-oxyhydroxides (Gu et al., 2019). This observation is confirmed by the higher contents of Fe<sup>2+</sup> during the reducing phase of the redox incubation period.

Concentration of Fe<sup>2+</sup> ranged between 1.4 and 172 mg/L, with higher values observed under reducing conditions; and negatively correlated significantly with  $E_H$  (Fig. S2;  $r = -0.6$ ;  $P < 0.01$ ). This means that reductive dissolution of Fe-oxyhydroxides could result in excessive production of Fe<sup>2+</sup>, and may then consequently lead to mobilisation of sorbed-As on the surfaces of the mine spoil soil as explained in previous studies (e.g., Rinklebe et al., 2016; Shaheen et al., 2014b). Further, rise in pH during reducing conditions could also cause deprotonation of Mn/Fe/Al oxides as indicated by Gersztyn et al. (2013). This is demonstrated by the significant negative correlation between pH and Fe ( $r = -0.4$ ,  $P < 0.05$ ;  $n = 27$ ); pH and Fe<sup>2+</sup> ( $r = -0.4$ ;  $P = 0.05$ ;  $n = 27$ ) (Fig. S2). We assume that such phenomenon may cause carriers such as Mn/Fe/Al oxides to lose their ability to sorb As.

Results of the As K-edge XANES and EXAFS analyses to characterise the dominant As-bearing minerals in the mine spoil at different  $E_H$  are shown in Fig. 4. As shown in the first derivatives of XANES spectra, the peak at the edge of As(III) edge raised whilst that of As(V) decreased from A3 to A5. The LCF results of the mine spoil are also provided in Table 2. Results showed that As is strongly associated with Fe in the mining spoil at both reducing and oxidising periods, as also observed by Yang et al. (2020) and Yang et al. (2022a). The dominance of Fe bearing-As minerals (scorodite and arsenopyrite) in the mining spoil also supports the results from the sequential extraction, where greater percentage of As (32.5%) was bound to the amorphous Fe fraction; this was further reiterated in our earlier work on the mining spoil (Mensah et al., 2020).



**Fig. 4.** (I): The first derivatives of XANES spectra of the mining spoil at different redox potential. (II): Linear combination fitting results using the reference materials. The peaks of different colours represent the dominant arsenic species at various selected  $E_H$ . A3 =  $-30$  mV  $E_H$ ; A4 =  $+210$  mV  $E_H$ ; and A5 =  $+430$  mV  $E_H$ .



**Fig. 5.** Dynamics of Fe/As molar ratios in anaerobic incubation of the contaminated mine spoil soil. “As” in the Fe(II)/As ratio is the total dissolved As in the solution.

Additionally, the Pearson correlation, linear and stepwise regression analyses demonstrate that dissolved contents of As correlated positively with both total Fe (Adjusted  $R^2 = +0.9$ ,  $P < 0.01$ ;  $n = 27$ ) and  $Fe^{2+}$  (Adjusted  $R^2 = +0.8$ ,  $P < 0.01$ ;  $n = 27$ ) (Fig. S2). Thus, redox-induced impacts of Fe chemistry may explain 94% of the contributions to As mobilisation from the mine spoils. Like the dissolved As,  $Fe^{2+}$  contents in the soil suspension were higher during reducing conditions; and lower under oxidising conditions. The As-contaminated mine spoil soil reached highest levels of  $Fe^{2+}$  in the soil suspension at 146 mg/L under the reducing conditions ( $< 100$  mV), at which time dissolved As contents were concurrently at its peak at 129.2 mg/L (Fig. 3). Reductive dissolution of Fe oxides and subsequent As release has been reported in other studies (e.g. Gu et al., 2019). Rinklebe et al. (2016) and Shaheen et al. (2014a) have also reported that reductive dissolution of Fe(hydro)oxides under low  $E_H$  led to the release of associated As into the soil solution. Positive correlation between As and Fe, as well as influence of Fe on As solubility under redox conditions has been reported by other authors (e.g. Beiyuan et al., 2017; El-Naggar et al., 2019).

From the geochemical fractionation, we found that large amount of As was primarily associated with the amorphous iron oxide fraction (about 1500 mg/kg, 32.5% of total As; Fig. 1), whilst the bulk soil is principally made up of scorodite and arsenopyrites as dominant primary and secondary minerals, respectively (Mensah et al., 2020). Thus, it is expected that large parts of both the amorphous and well-crystalline FeO fractions will be reduced into soluble forms during flooding and consequently, As bound to their surfaces will become mobilised and available.

The relationships between Mn/Al and As were weak and non-significant (Fig. S2). This means that, although deprotonation at high pH (Gersztyn et al., 2013) might have resulted in decreased sorption ability of Mn/Al oxides during reductive dissolution of the mine spoil, these effects were not strong enough to be the main drivers of As mobilisation in the mine spoil. In addition, this insignificant effect might be due to the smaller concentrations of Mn/Al (Mn range: 0.3 – 16.0 mg/L,  $n = 27$ ; Al: 0.02 – 0.48 mg/L,  $n = 27$ ) in the mine spoil during the incubation period compared to the higher contents of the Fe (range: 0.2 – 325.0 mg/L,  $n = 27$ ) (Table 1). Therefore, there were lower contents of As associated with the Mn/Al oxides relative to contents associated with the Fe oxides. Thus, in such high Fe soil systems, and as reported by Lemonte et al. (2017), dissimilatory reduction of Fe oxides could become the primary driver of As release under reducing conditions.

Fe(II)/As molar ratios found in our study were all low (0.3 – 3.3), reaching maximum value at 3.3 at the end of the incubation period (Fig. 5). Additionally, lower Fe(II)/As molar ratios were found during reducing conditions and higher values were observed at oxidising conditions. The lower Fe/As molar ratios found under reducing conditions could be due to the higher amount of dissolved As released during its anaerobic redox cycle. Higher ratios found on the other hand under oxidising conditions might be related to the lower contents of dissolved As during the oxic redox-period as reported by Gu et al. (2019). Thus, we assume that higher release of As contributed to the lower Fe(II)/As molar ratio observed during the anoxic periods of the redox cycle in our study.

Therefore, since Fe(II)/As molar ratios (0.3 – 2.5) found in our study were less than 3, we assume that the abandoned As-contaminated mine spoil may migrate As from the site to adjacent surface waters, especially under anoxic conditions. This is because the Fe re-oxidation process may not precipitate enough Fe-oxyhydroxides to immobilize all the As present in the anoxic soil water as indicated by others (e.g., Baken et al., 2015; Forsmann and Kjaergaard, 2014; and Zak et al., 2004). In addition, the greater Fe(II)/As molar ratio found at the end of the incubation period (3.3, Fig. 5); oxidising condition with mean  $E_H = 331$  mV, implies that Fe re-oxidation may precipitate As. This condition may immobilise As from the mine site and thus lower the risk of migration into nearby watercourses.

### 3.3.3. Arsenic mobilisation as affected by redox-induced changes of sulphur

Mobilisation of As in a contaminated mine spoil soil can be affected by the presence of sulphides (Mensah et al., 2020). In our study, concentration of elemental sulphur ranged from 206.5 to 360.4 mg/L, with the maximum value occurring at the reduced redox potential ( $E_H = -96$  mV) (Table 1). Sulphate reduction is reported to be initiated by microbial communities at low  $E_H$  such as:  $< -150$  mV as indicated by Mansfeldt (2004). In this regard, we assume that sulphides could be formed under reducing conditions (e.g., Lemonte et al., 2017; Rinklebe et al., 2020); but sulphide contents found in our study were below detection (i.e. 1 mg/L) under both reducing and oxidising conditions. Additionally, formation of sulphate did not follow a specific pattern during the incubation period (Fig. 3). Neither sulphate nor sulphate reduction (formation of sulphides) affected the mobilisation of As in our study ( $r = -0.02$ ;  $P > 0.05$ ;  $n = 27$ ; Fig. S2).

We assume that much of the sulphides produced were retained on the surfaces of Mn/Al oxides and resulted in limited sulphide solubility, as indicated by the positive significant relationships between S and Mn ( $r = +0.7$ ,  $P < 0.01$ ;  $n = 27$ ); and S and Al ( $r = +0.5$ ,  $P < 0.01$ ;  $n = 27$ ) (Fig. S2). Thus, there was likelihood of  $S^{2-}$  formation under reducing conditions, but they might have been precipitated and retained in forms such as Mn-S, Al-S, or Mn/Al-As-S in the elevated  $Fe^{2+}$  anaerobic solution as reported by Lemonte et al. (2017). Thus, this precipitation and retention mechanism might have impeded S solubility and thus contributed to its non-significant effect on As mobilisation. This is further evidenced by greater parts of the total As from the geochemical fractionation (about 3000 mg/kg, 60.5% of total As; Fig. 1) that were retained in the sulphide components as residual fractions. Thus, the majority of As in the arsenopyrite and scorodite dominant minerals in the mine spoil may be retained in the residual fraction and is thus made unavailable during reducing periods. In this regard, we assume that greater proportions of total As might have been structurally incorporated into the residual fraction, and as indicated in other studies (e.g., Shaheen et al., 2017; Tack, 2010). The residual fraction of As is reported to be made up of greater proportions of FeAsS and FeAsO<sub>4</sub> arsenopyrite (e.g., Giacomino et al., 2010; Karak et al., 2011; Mensah et al., 2020). Consequently, this phenomenon makes As unavailable for potential release and possible environmental contamination.

### 3.3.4. Arsenic mobilisation as affected by redox-induced changes of soil organic carbon

Relatively, higher contents of DOC were observed at reducing conditions than at oxidising conditions. Contents of organic carbon did not follow a pattern during the incubation period; and thus, were not affected significantly by  $E_H$  changes. The DOC/SUVA-As correlation was non-significant (Fig. S2) and therefore, As mobilisation from the mine spoil was not impacted by redox-induced changes in the dissolved organic matter. As explained earlier in Section 3.2, the higher contents of DOC at the reduction phase of the initial redox cycle may either be due to production of CO<sub>2</sub> from microbial activities (Grybos et al., 2009), decay of the organic straw, or release of organically bound carbon to reductively dissolved Fe-hydroxides (Rinklebe et al., 2020).

Concentration of SUVA ranged between 0.05 and 0.24  $m^{-1} mg^{-1} L$ , with a mean value of 0.1  $m^{-1} mg^{-1} L$ . Contents of dissolved SUVA increased during reducing conditions (0.05  $m^{-1} mg^{-1} L$ ) and decreased under oxidising conditions (0.24  $m^{-1} mg^{-1} L$ ); and thus, indicated an inverse significant relationship with  $E_H$  ( $r = -0.5$ ,  $P < 0.05$ ). SUVA is a measure of aromaticity or organic molecules and compounds held on surfaces of soil DOC (Weishaar et al., 2003). The negative significant relationship between  $E_H$  and SUVA gives an indication of increased less molecular weight aromatic compounds of the DOC during reducing conditions and increased higher molecular weight aromatic compounds during oxidising conditions. Thus, we assume that there could be decreased DOC sorption of less aromatic organic molecules (low molecular weight and more labile organic constituents) during the reducing periods. This may account for the higher SUVA concentrations at lower



redox potentials. Higher SUVA contents under reducing soil conditions were also previously reported by McKnight et al. (2002) and further explained by Weishaar et al. (2003).

Multiple stepwise regression was further conducted among the changes in the factors ( $E_H$ , pH, Fe,  $Fe^{2+}$ , Mn, Al, S, Cl<sup>-</sup>,  $SO_4^{2-}$ , and DOC/SUVA) that could govern the mobilisation of As in our sample. Our multiple stepwise regression model showed sole contribution of Fe to the data variance, explaining 97% of the variation of As mobilisation at  $P < 0.001$ . The model of the multiple regression equation (Adjusted  $R^2 = +0.9$ ,  $P < 0.001$ ;  $n = 27$ ) is given as:

$$As \text{ mobilisation/availability} = 6.138 + 0.396 (Fe)$$

This implies that As mobilisation from the mine spoil under various redox conditions could be solely the function of changes in the content of total Fe and thus, a unit increase in Fe may significantly predict the release of As by + 0.4 units. Higher release and mobilisation of As notably happened at  $E_H < 100$  mV (Fig. 3). It must be reiterated that reductive dissolution of Fe oxides is reported to usually occur at redox potential values below 100 mV (Takeno, 2005).

In this instance, As potential mobilisation from the mine spoil could increase, with consequent groundwater pollution and food chain contamination in the mining environments as reported in other studies (e.g., Mensah et al., 2020). This is further confirmed by the positive relationship between  $Fe^{2+}$  and dissolved As (Fig. S2). Thus, we assume that, in such iron oxides-As dominated samples, dissolution of Fe oxides could become the main driver of As mobilisation from the mine spoil. This agrees with findings by Lemonte et al. (2017), who reported that dissolution of As-bearing mineral oxides was the main driver of As release from an As-contaminated river sediment (with 86% of total As occluded in hydrous oxides).

#### 4. Conclusions, environmental implications, and future prospects

This is the first work that has explored how redox chemistry affects mobilisation and species of As from highly contaminated mining spoils in humid tropical climate. We found that reducing conditions encouraged higher mobilisation of As than oxidising conditions. Furthermore, lower Fe(II)/As molar ratios found during anaerobic conditions prove possible migration of As from the site to adjacent watercourses especially during rainfall events and flooding regimes. Interestingly, As(V) dominated at moderately reducing conditions – 30 mV, which may be attributed to incomplete reduction at these conditions. Also, a detectable portion of As(III) was persisted during oxic conditions (> +200 mV).

The major As species in the mine spoil were goethite-As(V), ferrihydrite-As(III), arsenopyrite and scorodite. Thus, mobilisation and speciation of As in the studied Fe-As dominated mine spoil may solely be a function of the redox-induced chemistry of Fe and should be considered in its environmental impacts assessment and remediation. Tropical rainforest regions in Ghana may receive annual maximum rainfall of more than 2000 mm. We thus assume that under such tropical rainforest climates, extreme flooding events may be induced during intensive rainfall events. These flooding events may further create reducing conditions in such contaminated mine spoil, As solubility may then increase, and there could be high potential As mobilisation into available groundwater, soil and absorption into the food chain. Consequently, ecotoxicological risks and health impacts associated with As in the mine spoil may increase in the surrounding mining environments.

Our work has implications for future management and remediation of abandoned mine spoils in gold dominated regions and thus As remediation efforts should take into consideration the field wet and dry conditions prevailing at the contaminated sites. More specifically, it may be concluded that mitigation options should aim at limiting reducing conditions and encouraging aerobic conditions at the mine field. This cautious approach will thus reduce the pH, raise the redox potential, and consequently restrict As mobilisation from the mine spoil. In future, the

release dynamics of As in the subsoils under varying redox potentials could also be further explored. Further, various remediation measures and effects on the release of As under different redox environments from the mine spoil should be explored.

#### Environment implications

An effective management of arsenic (As) polluted gold mine sites in tropical climates needs more insights into the factors, which govern the redox-induced mobilization of As, which remains unknown. We found that the mobilization of As increased under reducing conditions while it decreased under oxidizing conditions, which indicates a high risk of As loss under reducing conditions. These findings have substantial implications for management and remediation of abandoned mine spoils. More specifically, encouraging aerobic conditions shall mitigate As release and its potential loss from the studied mine field, and thus mitigating the associated environmental and human health risks.

#### CRedit authorship contribution statement

Albert Kobina Mensah, PhD: soil-sampling, treatment of samples, data collection, conducting and performing the redox experiments, laboratory analyses, data/statistical analyses, writing the first and revised drafts, addressing and responding to reviewers' comments, writing corrections according to the advice of the co-authors. Bernd Marschner, Professor, supervisor: concept, supervision, correcting and editing. Jianxu Wang, Professor: accurateness of data analysis, scientific advice, correcting and editing. Jochen Bundschuh, Professor: scientific advice, correcting and editing. Shan-Li Wang, Professor: accurateness of XANES and EXAFS data analysis, scientific advice, correcting and editing. Puu-Tai Yang, PhD: accurateness of XANES and EXAFS data analysis, scientific advice, correcting and editing. Sabry M. Shaheen, Professor: accurateness of calculations, correcting, writing, and editing. Jörg Rinklebe, Professor, supervisor: research idea, scientific and experimental concept, close experimental guidance, experimental, laboratory, technical and analytical facilities, supervision, writing, correcting, and editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

We are thankful to Ruhr University Bochum, Germany for providing financial support for the fieldwork in Ghana. Many thanks also go to the German Academic Exchange Service (DAAD) for providing research grant to facilitate Dr. Albert Kobina Mensah's PhD (Personal reference number: 91560903) in Germany. The redox experiment was conducted at the University Wuppertal. The authors are grateful to the beamline scientist, Dr. Shih-Chang Weng, for his assistance in EXAFS measurements conducted at National Synchrotron Radiation Research Centre (NSRRC) of Taiwan. We express our thanks to the team and to Mr. Claus Vandenhirtz as well as to Bettina Roehm of Ruhr University Bochum for their technical support.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2022.129238](https://doi.org/10.1016/j.jhazmat.2022.129238).

## References

- Aftabtalab, A., Rinklebe, J., Shaheen, S.M., et al., 2022. Review on the interactions of arsenic, iron (oxy)(hydr)oxides, and dissolved organic matter in soils, sediments, and groundwater in a ternary system. *Chemosphere* 286 (Part 2), 131790.
- Antoniadis, V., Levizou, E., Shaheen, S.M., Ok, Y.S., Sebastian, A., Baum, C., Prasad, M.N. V., Wenzel, W.W., Rinklebe, J., 2017. Trace elements in the soil-plant interface: Phytoavailability, translocation, and phytoremediation—a review. *Earth Sci. Rev.* 171, 621–645.
- Baken, S., Verbeeck, M., Verheyen, D., Diels, J., Smolders, E., 2015. Phosphorus losses from agricultural land to natural waters are reduced by immobilization in iron-rich sediments of drainage ditches. *Water Res.* 71, 160–170.
- Beiyuan, J., Awad, Y.M., Beckers, F., Tsang, D.C.W., Ok, Y.S., Rinklebe, J., 2017. Mobility and phytoavailability of As and Pb in a contaminated soil using pine sawdust biochar under systematic change of redox conditions. *Chemosphere* 178, 110–118.
- Bempah, C.K., Ewusi, A., Obiri-yeboah, S., Asabere, B., Mensah, F., Boateng, J., Voigt, H., 2013. Distribution of arsenic and heavy metals from mine tailings dams at obuasi municipality of Ghana. *Am. J. Eng. Res.* 2 (05), 61–70.
- Bjorn, P., Benoit, J., Fernandez, V., & Roychoudhury, A. N., 2020. Synchrotron X-ray radiation and the African earth sciences: a critical review. *Journal of African Earth Sciences* 172 (104012).
- Bortey-Sam, N., Nakayama, S.M.M., Ikenaka, Y., Akoto, O., Baidoo, E., Yohannes, Y.B., Mizukawa, H., Ishizuka, M., 2015. Human health risks from metals and metalloids via consumption of food animals near gold mines in Tarkwa, Ghana: estimation of the daily intakes and target hazard quotients (THQs). *Ecotoxicol. Environ. Saf.* 111, 160–167.
- Cancès, B., et al., 2008. Changes in arsenic speciation through a contaminated soil profile: A XAS based study. *Science of The Total Environment* 397 (1–3), 178–189.
- Corkhill, C.L., Vaughan, D.J., 2009. Arsenopyrite oxidation - a review. *Appl. Geochem.* 24 (12), 2342–2361.
- DeSisto, S.L., Jamieson, H.E., Parsons, M.B., 2017. Arsenic mobility in weathered gold mine tailings under a low-organic soil cover. *Environ. Earth Sci.* 76 (22), 1–16.
- Drewniak, L., Skłodowska, A., 2013. Arsenic-transforming microbes and their role in biomineral processes. *Environ. Sci. Pollut. Res.* 20 (11), 7728–7739.
- Eberle, A., Besold, J., Kerl, C.F., Lezama-Pacheco, J.S., Fendorf, S., Planer-Friedrich, B., 2020. Arsenic fate in peat controlled by the pH-dependent role of reduced sulfur. *Environ. Sci. Technol.* 54 (11), 6682–6692.
- El-Naggar, A., Shaheen, S.M., Hseu, Z.Y., Wang, S.L., Ok, Y.S., Rinklebe, J., 2019. Release dynamics of As, Co, and Mo in a biochar treated soil under pre-definite redox conditions. *Sci. Total Environ.* 657, 686–695.
- Fakhreddine, S., Prommer, H., Gorelick, S.M., Dadakis, J., Fendorf, S., 2020. Controlling arsenic mobilization during managed aquifer recharge: the role of sediment heterogeneity. *Environ. Sci. Technol.* 54 (14), 8728–8738.
- Filippi, M., Drahota, P., Machovič, V., Böhmová, V., Mihaljevič, M., 2015. Arsenic mineralogy and mobility in the arsenic-rich historical mine waste dump. *Sci. Total Environ.* 536, 713–728.
- Forsmann, D.M., Kjaergaard, C., 2014. Phosphorus release from anaerobic peat soils during convective discharge - effect of soil Fe: P molar ratio and preferential flow. *Geoderma* 223–225 (1), 21–32.
- Frohne, T., Rinklebe, J., Diaz-Bone, R.A., Du Laing, G., 2011. Controlled variation of redox conditions in a floodplain soil: Impact on metal mobilization and biomethylation of arsenic and antimony. *Geoderma* 160 (3–4), 414–424.
- García-Sánchez, A., Alonso-Rojo, P., Santos-Francés, F., 2010. Distribution and mobility of arsenic in soils of a mining area (Western Spain). *Sci. Total Environ.* 408 (19), 4194–4201.
- Gersztyn, L., Karczewska, A., Gałka, B., 2013. Influence of pH on the solubility of arsenic in heavily contaminated soils. *Environ. Prot. Nat. Resour.* 24 (3), 7–11.
- Giacomino, A., Malandrino, M., Abollino, O., Velayutham, M., Chinnathangavel, T., Mentasti, E., 2010. An approach for arsenic in a contaminated soil: Speciation, fractionation, extraction and effluent decontamination. *Environmental Pollution* 158, 416–423.
- Grybos, M., Davranche, M., Gruau, G., Petitjean, P., Pédrot, M., 2009. Increasing pH drives organic matter solubilization from wetland soils under reducing conditions. *Geoderma* 154 (1–2), 13–19.
- Gu, S., Gruau, G., Dupas, R., Petitjean, P., Li, Q., Pinay, G., 2019. Respective roles of Fe-oxhydroxide dissolution, pH changes and sediment inputs in dissolved phosphorus release from wetland soils under anoxic conditions. *Geoderma* 338, 365–374.
- Guo, L., Warnken, K.W., Santschi, P.H., 2007. Retention behavior of dissolved uranium during ultrafiltration: implications for colloidal U in surface waters. *Mar. Chem.* 107 (2), 156–166.
- Hadzi, G. Y., Essumang, D. K., & Ayoko, G. A., 2018. Assessment of contamination and health risk of heavy metals in selected water bodies around gold mining areas in Ghana. *Environmental Monitoring and Assessment* 190 (7), 406.
- Harvey, A.E., Smart, J.A., Amis, E.S., 1955. Simultaneous spectrophotometric determination of iron(II) and total iron with 1,10-phenanthroline. *Anal. Chem.* 27 (1), 26–29.
- Hayford, E.K., Amin, A., Osae, E.K., Kutu, J., 2009. Impact of gold mining on soil and some staple foods collected from selected mining communities in and around Tarkwa-Prestea area. *West Afr. J. Appl. Ecol.* 14, 1–12.
- Huq, M.E., Fahad, S., Shao, Z., Sarven, M.S., Khan, I.A., et al., 2020. Arsenic in a groundwater environment in Bangladesh: occurrence and mobilization. *J. Environ. Manag.* 262, 110318.
- Hussain, M.M., Bibi, I., Ali, F., et al., 2022. The role of various ameliorants on geochemical arsenic distribution and CO<sub>2</sub>-carbon efflux under paddy soil conditions. *Environ. Geochem Health.* <https://doi.org/10.1007/s10653-021-01196-3>.
- Hussain, M.M., Bibi, I., Shahid, M., Shaheen, S.M., Shakoor, M.B., Bashir, S., Younas, F., Rinklebe, J., 2019. Biogeochemical cycling, speciation and transformation pathways of arsenic in aquatic environments with the emphasis on algae. *Comprehensive Analytical Chemistry* 85, 15–51. <https://doi.org/10.1016/bs.coac.2019.03.007>.
- Itabashi, T., Li, J., Hashimoto, Y., Ueshima, M., Sakanakura, H., Yasutaka, T., et al., 2019. Speciation and fractionation of soil arsenic from natural and anthropogenic sources: chemical extraction, scanning electron microscopy, and micro-XRF/XAFS investigation. *Environ. Sci. Technol.* 53 (24), 14186–14193.
- Kabata-Pendias, A., 2011. Trace Elements in Soils and Plants, fourth ed. CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW.
- Karak, T., Abollino, O., Bhattacharyya, P., Kishore, K. D., Paul, R. K., 2011. Fractionation and speciation of arsenic in three tea gardens soil profiles and distribution of As in different parts of tea plant (*Camellia sinensis* L.). *Chemosphere* 85, 948–960.
- Khan, K.M., Chakraborty, R., Bundschuh, J., Bhattacharya, P., Parvez, F., 2020. Health effects of arsenic exposure in Latin America: an overview of the past eight years of research. *Sci. Total Environ.* 710, 136071.
- Klubi, E., Abril, J.M., Nyarko, E., Delgado, A., 2018. Impact of gold-mining activity on trace elements enrichment in the West African estuaries: the case of Pra and Ankobra rivers with the Volta estuary (Ghana) as the reference. *J. Geochem. Explor.* 190 (March), 229–244.
- Lemonte, J.J., Stuckey, J.W., Sanchez, J.Z., Tappero, R., Rinklebe, J., Sparks, D.L., 2017. Sea level rise induced arsenic release from historically contaminated coastal soils. *Environ. Sci. Technol.* 51 (11), 5913–5922.
- Lukasz, D., Liwia, R., Aleksandra, M., Aleksandra, S., 2014. Dissolution of arsenic minerals mediated by dissimilatory arsenate reducing bacteria: estimation of the physiological potential for arsenic mobilization. *BioMed. Res. Int.* 2014.
- Manning, B., 2005. Arsenic speciation in As(III)- and As(V)-treated soil using XANES spectroscopy. *Microchim. Acta* 151 (3–4), 181–188.
- Mansfeldt, T., 2004. Redox potential of bulk soil and soil solution concentration of nitrate, manganese, iron, and sulfate in two Gleysols. *J. Plant Nutr. Soil Sci.* 167 (1), 7–16.
- McKnight, D.M., Hornberger, G.M., Bencala, K.E., Boyer, E.W., 2002. In-stream sorption of fulvic acid in an acidic stream: A stream-scale transport experiment. *Water Resources Research* 38 (1), 1–6. <https://doi.org/10.1029/2001WR000269>.
- Mensah, A.K., Mahiri, I.O., Owusu, O., Mireku, O.D., Wireko, I., Kissi, E.A., 2015. Environmental impacts of mining: a study of mining communities in Ghana. *Appl. Ecol. Environ. Sci.* 3 (3), 81–94.
- Mensah, A.K., Marschner, B., Shaheen, S.M., Wang, J., Wang, S.L., Rinklebe, J., 2020. Arsenic contamination in abandoned and active gold mine spoils in Ghana: geochemical fractionation, speciation, and assessment of the potential human health risk. *Environ. Pollut.* 261, 114116.
- Mensah, A.K., Marschner, B., Antoniadis, V., Stemm, E., Shaheen, S.M., Rinklebe, J., 2021. Human health risk via soil ingestion of potentially toxic elements and remediation potential of native plants near an abandoned mine spoil in Ghana. *Sci. Total Environ.*, 149272.
- Nair, A., Juwarkar, A.A., Singh, S.K., 2007. Production and characterization of siderophores and its application in arsenic removal from contaminated soil. *Water Air Soil Pollut.* 180 (1), 199–212.
- Niaz, K., N., Hussain, M.M., Bibi, I., Natasha, Shahid, M., Ali, F., Iqbal, J., Shaheen, S.M., Abdelrahman, H., Akhtar, W., Wang, H., Jörg Rinklebe, J., 2022. The significance of eighteen rice genotypes on arsenic accumulation, physiological response and potential health risk. *Sci. Total Environ.* 832, 155004.
- Padoan, E., Kath, A.H., Vahl, L.C., Ajmone-Marsan, F., 2020. Potential release of zinc and cadmium from mine-affected soils under flooding, a mesocosm study. *Arch. Environ. Contam. Toxicol.* 79 (4), 421–434.
- Ravel, B., Newville, M., 2005. Athena, Artemis, Hephaestus: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron. Radiat.* 12, 537–541.
- Renock, D., Voorhis, J., 2017. Electrochemical investigation of arsenic redox processes on pyrite. *Environ. Sci. Technol.* 51 (7), 3733–3741.
- Rinklebe, J., Shaheen, S.M., Yu, K., 2016. Release of As, Ba, Cd, Cu, Pb, and Sr under pre-definite redox conditions in different rice paddy soils originating from the U.S.A. and Asia. *Geoderma* 270, 21–32.
- Rinklebe, J., Shaheen, S.M., El-Naggar, A., Wang, H., Du Laing, G., Alessi, D.S., Sik Ok, Y., 2020. Redox-induced mobilization of Ag, Sb, Sn, and Tl in the dissolved, colloidal and solid phase of a biochar-treated and un-treated mining soil. *Environ. Int.* 140 (April), 105754.
- Shaheen, S.M., Rinklebe, J., Rupp, H., Meissner, R., 2014a. Lysimeter trials to assess the impact of different flood-dry-cycles on the dynamics of pore water concentrations of As, Cr, Mo and V in a contaminated floodplain soil. *Geoderma* 228–229, 5–13.
- Shaheen, S.M., Rinklebe, J., Frohne, T., White, J.R., DeLaune, R.D., 2014b. Biogeochemical factors governing cobalt, nickel, selenium, and vanadium dynamics in periodically flooded Egyptian North Nile delta rice soils. *Soil Sci. Soc. Am. J.* 78 (3), 1065–1078.
- Shaheen, S.M., Rinklebe, J., Frohne, T., White, J.R., DeLaune, R.D., 2016. Redox effects on release kinetics of arsenic, cadmium, cobalt, and vanadium in Wax Lake Deltaic freshwater marsh soils. *Chemosphere* 150, 740–748.
- Shaheen, S.M., Kwon, E.E., Biswas, J.K., Tack, F.M.G., Ok, Y.S., Rinklebe, J., 2017. Arsenic, chromium, molybdenum, and selenium: geochemical fractions and potential mobilization in riverine soil profiles originating from Germany and Egypt. *Chemosphere* 180, 553–563.
- Shaheen, S. M., Antoniadis, V., Kwon, E., Song, H., Wang, S. L., Hseu, Z. Y., & Rinklebe, J., 2020. Soil contamination by potentially toxic elements and the associated human health risk in geo- and anthropogenic contaminated soils: A case study from the temperate region (Germany) and the arid region (Egypt). *Environmental Pollution* 262. <https://doi.org/10.1016/j.envpol.2020.114312>.

- Shaheen, S.M., Wang, J., Baumann, K., Ahmed, A.A., Hsu, L.C., Liu, Y.T., Wang, S.L., Kühn, O., Leinweber, P., Rinklebe, J., 2022. Stepwise redox changes alter the speciation and mobilization of phosphorus in hydromorphic soils. *Chemosphere* 288, 132652.
- Sparks, D.L., Page, A.L., Helmke, P.A., Loppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E., 1996. *Methods of Soil Analysis: Chemical Methods, Part 3. ASA and SSSA*, Madison, WI.
- Tack, F. M. G., 2010. Trace elements: general soil chemistry, principles and processes. Hooda P (ed). *Trace elements in soils*. Wiley-Blackwell, pp. 9–37.
- Takeno, N., 2005. Atlas of Eh-pH diagrams. Geological Survey of Japan Open File Report 419, 102.
- Tang, J., Liao, Y., Yang, Z., Chai, L., Yang, W., 2016. Characterization of arsenic serious-contaminated soils from Shimen realgar mine area, the Asian largest realgar deposit in China. *J. Soils Sediment.* 16 (5), 1519–1528.
- Tapia, J., Murray, J., Ormachea, M., Tirado, N., Nordstrom, D.K., 2019. Origin, distribution, and geochemistry of arsenic in the Altiplano-Puna plateau of Argentina, Bolivia, Chile, and Perú. *Sci. Total Environ.* 678, 309–325.
- Wallis, I., Prommer, H., Simmons, C.T., Post, V., Stuyfzand, P.J., 2010. Evaluation of conceptual and numerical models for arsenic mobilization and attenuation during managed aquifer recharge. *Environ. Sci. Technol.* 44 (13), 5035–5041.
- Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* 37 (20), 4702–4708.
- Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. *Anal. Chim. Acta* 436 (2), 309–323.
- Yang, P.T., Hashimoto, Y., Wu, W.J., Huang, J.H., Chiang, P.N., Wang, S.L., 2020. Effects of long-term paddy rice cultivation on soil arsenic speciation. *J. Environ. Manag.* 254, 109768.
- Yang, X., Shaheen, S.M., Wang, J., Hou, D., Ok, Y.S., Wang, S.L., Wang, H., Rinklebe, J., 2022a. Elucidating the redox-driven dynamic interactions between arsenic and iron-impregnated biochar in a paddy soil using geochemical and spectroscopic techniques. *J. Hazard. Mater.* 422, 126808.
- Yang, X., Hinzmann, M., Pan, H., Jianxu Wang, J., 2022b. Pig carcass-derived biochar caused contradictory effects on arsenic mobilization in a contaminated paddy soil under fluctuating controlled redox conditions. *J. Hazard. Mater.* 421, 126647.
- Yu, K., Rinklebe, J., 2011. Advancement in soil microcosm apparatus for biogeochemical research. *Ecol. Eng.* 37 (12), 2071–2075.
- Zak, D., Gelbrecht, J., Steinberg, C.E.W., 2004. Phosphorus retention at the redox interface of peatlands adjacent to surface waters in Northeast Germany. *Biogeochemistry* 70 (3), 357–368.
- Zobeck, T.M., 2004. Rapid soil particle size analyses using laser diffraction. *Appl. Eng. Agric.* 20 (5), 633–639.