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Arsenic contamination in abandoned and active gold mine spoils in Ghana: Geochemical fractionation, speciation, and assessment of the potential human health risk[☆]

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ABSTRACT

This work aims to study the pseudo-total content, geochemical fractions, and species of arsenic (As) in the bulk soil and in the coarse and fine particles of top soil and soil profiles collected from active and abandoned gold mine spoils in Ghana. The human health risk for adults (male and female) and children has been assessed. To achieve our aims, we collected 51 samples, characterized them, determined the total As content, and sequentially extracted the geochemical fractions of As including water-soluble and un-specifically bound As (FI); specific-sorbed/exchangeable As (FII); poorly (FIII)- and well-crystalline (IV) Fe oxide; and residual/sulphide fraction (FV). In selected samples, As species were determined using synchrotron-based X-ray absorption near edge structure (XANES). Pseudo-total As contents varied from 1807 to 8400 mg kg⁻¹, with the extremes occurring at the abandoned mine spoil. Arsenic was almost 10-fold higher in the fine particles (<0.63 μm) than in the coarse particles. Arsenic was mainly associated with FIII and FV, indicating that the distribution of As in these spoils is governed by their contents of amorphous Fe oxides, sulphides and As bearing minerals. The XANES results indicated that scorodite (FeAsSO₄ = 65–76%) and arsenopyrite (FeAsS = 24–35%) are the two major As-containing minerals in the spoils. The potential mobility (PMF = ∑FI-FIV) of As in the fine particles of the top soil was higher (48–61%) than in the coarse particles (25–44%). The mobile fraction (MF) (FI+FII) and PMF of As in the coarse particles of the profiles increased with depth while it decreased in the fine particles. The median hazard index values indicated an elevated human health risk, especially for children. The high contamination degree and potential mobility of As at the studied mine spoils indicate high potential risk for human and environmental health.

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1. Introduction

Gold mining is one of the major anthropogenic activities responsible for releasing arsenic (As) into the environment, thus posing potential threats to environmental resources and raising health concerns for humans and animals (DeSisto et al., 2017; Martiñá-Prieto et al., 2018; Aguilar et al., 2019). Some reports (e.g., Quansah et al., 2015) estimated that more than 300 million people

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in 70 countries are affected by As contamination in sediments and groundwater. As contamination comes either from geogenic source due to natural oxidation, weathering or degradation of arsenic-rich minerals or from anthropogenic sources due to human activities including mining ores (Hussain et al., 2019). Cases of As pollution of groundwater and soils from mining activities are reported in Thailand, Ghana (Bempah et al., 2013), Brazil (Morais et al., 2019), South Africa (Abiye and Bhattacharya, 2019), Canada (DeSisto et al., 2016; Miller et al., 2019), Bangladesh (Palansooriya et al., 2020), Greece (Antoniadis et al., 2019a), Mexico (Posada-Ayala et al., 2016), and the United States (Ahoulé et al., 2015).

In Ghana, gold mining has resulted in widespread environmental degradation of water, landscape, soil and the ecosystem (Mensah et al., 2015; Owusu et al., 2019). The extraction process of gold is accompanied by generation of huge amount of wastes, among which is the creation of tailing dams and heaps. Gold mine tailings, though designated as protected areas in Ghana, are sometimes abandoned without reclamation or are poorly managed (Bempah et al., 2013). Especially in the western region, gold bearing ores are rich in As (Hayford et al., 2009), which may result in high As contents of the tailings, posing potential risks for the surrounding ecosystem and humans. For example, uncontrolled and poor management of mine tailings could disperse As into near watercourses, farms and agricultural fields, and become a threat to human health. For instance, collapse of mine tailing dams through erosion could impact negatively on water quality and affect livelihoods of the people living in mining areas (Abiye and Bhattacharya, 2019). In this respect, Bansah et al. (2018) reported that abandoned tailings can potentially be harmful to children who usually use the fields as playing grounds and can accidentally inhale or ingest the tailings material.

Assessing the potential soil and human health risks of toxic elements contamination is a global concern (Antoniadis et al., 2019a;

Rinklebe et al., 2019), particularly in mining soils (e.g., Armah and Gyeabour, 2013; Posada-Ayala et al., 2016; Wan et al., 2017). Studying the toxic elements fractions and species is a good tool to assess their potential mobilisation and associated environmental and human health risk (Cancès et al., 2008; Shaheen et al., 2017; Antoniadis et al., 2019b).

Presently, there is lack of scientific investigations on mobilisation, environmental and human health risk assessment of tailing spoils from gold mining activities in Ghana. We assume that the distribution of As among its geochemical fractions and its species in active mining spoils may differ as compared to the abandoned spoils. Also, we hypothesize that the soil particle distribution may affect the geochemical fractions and mobility of As in the top soil and profiles of the abandoned and active mining spoils. Therefore, the objectives of this study were: i) to quantify the spatial distribution of As in topsoil and profiles of active and abandoned mine spoils in Ghana, ii) to determine the dominant species of As in the active and abandoned gold mine spoils, iii) to determine the geochemical fractions and assess the potential mobilisation of As in the bulk soils and in the coarse and fine particles of the contaminated mine spoils, and iv) to assess soil and human health risks of children and adults exposed to As in contaminated gold mine spoils.

2. Materials and methods

2.1. Study area, soil sampling and characterisation

Samples were collected from a gold mining area in the western region of Ghana (05°26'00"N, 02°09'00"W; average elevation of 59 m; Fig. 1). The area is in the rain forest zone of Ghana and is characterized by a wet equatorial climate, with a mean annual rainfall of 1711 mm and mean annual temperature is 26.6 °C.

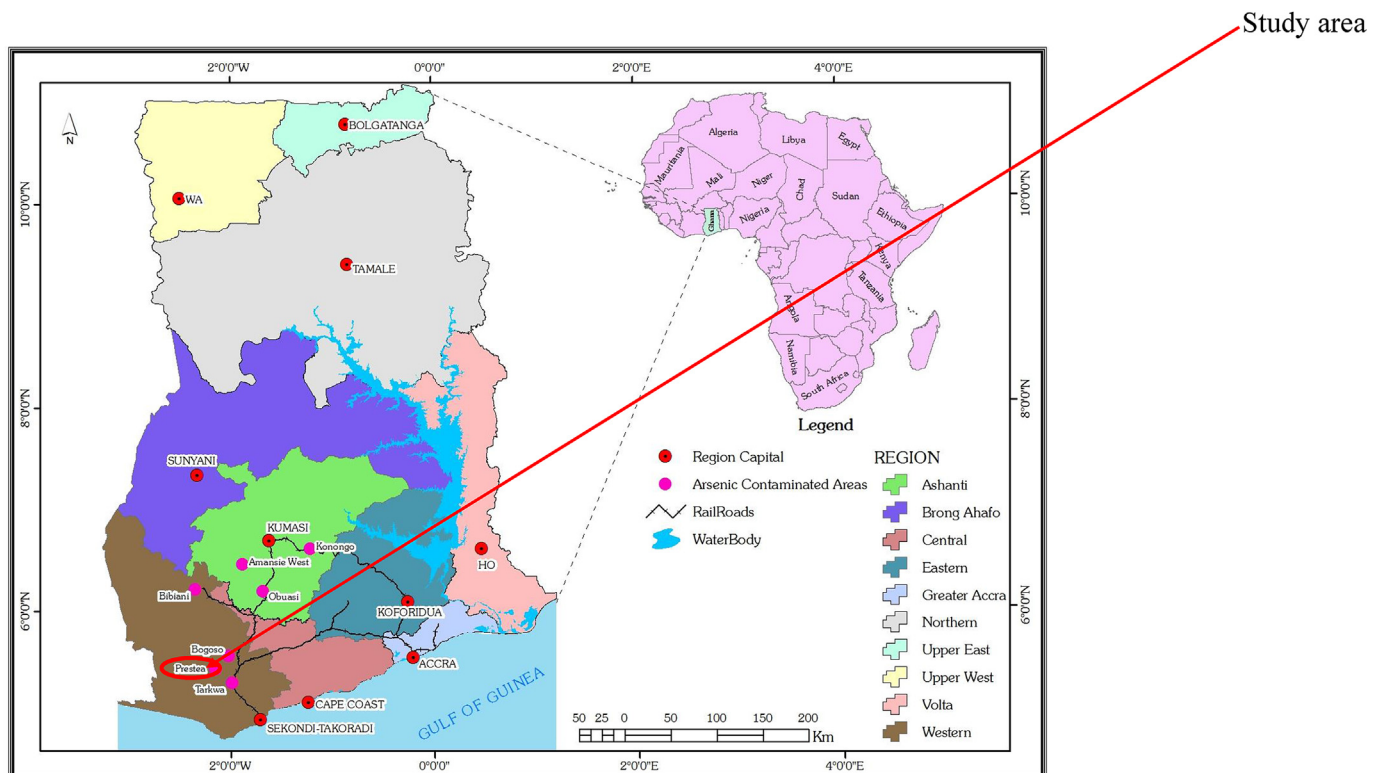


Fig. 1. Map of Ghana showing the study area and other arsenic contaminated areas.

Two gold mining fields were chosen for the study. The first site is an abandoned gold mine tailing deposited as a slurry into an impoundment between 1912 and 2002. The area (05°23'38"N, 02°09'58"W; Fig. 1) covers a total land space of approximately 126,000 m² and is completely bare of vegetation. Here, a composite sample was collected in early 2017 by sampling ten spots from 0 to 20 cm distributed randomly across the whole site. During a second campaign in early 2018, thirty-one samples were collected individually from different random sampling spots from a depth of 0–20 cm. In addition, two soil profiles were excavated and core samplers were inserted to collect samples at every 20-cm depth increment from 20 to 100 cm; therefore, ten samples have been collected from the two profiles.

The second site is an active mine tailing (05°26'03"N, 02°09'37"W; Fig. 1), which has been in operation since 1997. The area covers a total land space of approximately 121,000 m². Here, ten top soil samples were collected from different random sampling spots from a depth of 0–20 cm.

The soil samples were air-dried, crushed, homogenised, passed through a 2-mm sieve, and characterized for their basic properties and oxides content according to the standard methods of Sparks et al. (1996). Soil pH was determined in a soil: 0.01 M CaCl₂ solution ratio of 1:5 using the pH meter (Sentix 41, Wissenschaftlich-Technische Werkstätten (WTW) GmbH, Weilheim, Germany) according to Thomas (1996). The contents of total carbon and nitrogen were measured by an elemental analyser (Vario max cube, Elementar Analyse systeme GmbH, Hanau, Germany) (Wright and Bailey, 2001). The particle size distribution of the samples was then determined using the laser scattering method (Analysette 22; Fritsch GmbH, Idar-Oberstein, Germany) (Zobeck, 2004). The poorly and well crystalline iron oxide contents were determined according to Loepfert and Inskeep (1996). Dithionite-extractable iron (well crystalline iron) in soils was extracted with 3M sodium citrate + 1 M sodium bicarbonate + 1 g sodium dithionite in a water bath heated at 85 °C as described by Mehra and Jackson (1960). The poorly crystalline (Amorphous) Fe oxides were extracted with 0.175 M ammonium oxalate+0.1 M oxalic acid adjusted to pH 3.0 according to Loepfert and Inskeep (1996).

2.2. Extraction and determination of pseudo-total content and geochemical fractions of arsenic in the bulk soils and coarse and fine particles

For the analysis of pseudo-total arsenic contents and other main elements (Al, Fe, Mn, P, Ca, Mg), 0.25 g of finely ground bulk soil was digested in a microwave (CEM, Kamp-Lintford, Germany) at 120 °C for 15 min with 10 ml concentrated nitric acid; then, the digest was diluted with 10 ml de-ionized water, homogenised and filtered through a 0.45 µm membrane filter (USEPA, 2007).

The soil samples were further separated into coarse and fine particles. In this method, 30 g of the 2-mm sieved soil was weighed into a beaker and filled with water. The content was shaken on a Sonorex (Bandelin Sonorex Super RK 102 H) for 5 min and then poured through a sieve of 63-µm mesh size. The suspension containing the fine particles (silt and clay) was collected in a beaker, filtered, and air dried. The portion that remained in the sieve was taken as the coarse (sand) particles. The pH, total P, total carbon, total nitrogen, Fe oxides and As concentrations of the fine and coarse particles were determined and analysed using the methods described above.

We performed sequential extraction procedure (SEP) on selected samples of the abandoned mine spoil, the active mine spoils, and profile mine spoils to characterize As geochemical fractions both in the bulk soils as well as in the coarse and fine

particles. We used the procedure developed by Wenzel et al. (2001) to extract sequentially As for the operationally defined geochemical fractions (Water-soluble and un-specifically bound As (FI); specific-sorbed As/exchangeable fraction (FII); poorly (FIII)- and well-crystalline (IV) Fe oxide; and residual/sulphide fraction (FV)) as reported in the supporting materials (Appendix A; Table S1). Concentrations of As in the digests were measured with ICP-OES (Spectroblue, Ametek Materials Analysis Division). As a quality measure for the sequential extraction procedure, the extraction process was conducted in triplicates and the recovery rate was calculated:

$$\text{Recovery} = \frac{(\sum \text{FI} - \text{FV})}{\text{Total As}} \times 100$$

where ($\sum \text{FI} - \text{FV}$) is the sum of the element extracted in the five-step sequential extraction and "Total As" is the result obtained from the nitric acid microwave digestion.

2.3. Arsenic K-edge XANES spectroscopy analysis

Selected soil samples (two abandoned samples and one active) containing As concentrations of 4208.8, 6909.7 and 2450.0 mg kg⁻¹, respectively were selected for As K-edge X-ray absorption near edge structure (XANES) analysis. The XANES spectra was collected at the beamline TLS 07A in National Synchrotron Radiation Research Centre (NSRRC), Taiwan. The X-ray beam was monochromatized by a Si (111) double crystal monochromator with an energy resolution of $\Delta E/E \approx 2 \times 10^{-4}$. The fine soil powders were pressed into thin pellets with a diameter of 1-mm before analysis. The pellets were mounted on the Kapton tap, and fixed with a sample holder for the XANES spectra collection. Energy calibration was done using the first inflection point (i.e., 11867.0 eV) of the As K-edge absorption spectrum of As metal foil. The As K-edge XANES spectra were taken in the fluorescence mode by a Lytle detector in the energy range of 11,667–12,867 eV. The XANES data analysis is mainly based on Kelly et al. (2008). Arsenic speciation of the soil samples was determined using linear combination fitting (LCF) with a set of reference materials. We did LCF with six As standards, including scorodite, FeAsS, ferrihydrite-As(V), ferrihydrite-As(III), Goethite-As(V), and Goethite-As(III), by a function of fit all combinations in Athena, then the best fit was chosen based on the R-factor values. The scorodite and FeAsS were the best combinations for our samples; therefore, scorodite (FeAsSO₄) and arsenopyrite (FeAsS) were chosen for the linear combination fitting. Details of the methodology were reported in Liu et al. (2006).

2.4. Soil contamination and human health risk assessment

Soil contamination and health risks were calculated using the following risk assessment indices as employed by Rinklebe et al. (2019) and Antoniadis et al. (2017; 2019a, b).

2.4.1. Contamination factor (CF)

$$\text{CF} = \frac{C_s}{C_{\text{RefS}}}$$

Where, CF is contamination factor, C_s is the total As concentration (mg kg⁻¹) and C_{RefS} is the reference background value (6.83 mg kg⁻¹) in uncontaminated soils (world-wide average) reported by Kabata-Pendias (2011).

2.4.2. Human health risk assessment

Health risk assessment of persons exposed to the As-contaminated mine deposits were calculated for three groups: children, adult males and adult females. This was done by calculating the average daily dose (ADD, mg element kg⁻¹ bodyweight day⁻¹) using the formula:

$$ADD = Cs \frac{(IR \times EF \times ED \times 10^{-6})}{(BW \times AT)}$$

Where, Cs is the total As concentration in the mine spoils; IR is the soil ingestion rate (children = 200; adults = 100 mg dust day⁻¹); EF is the exposure frequency (children = 350; adults = 250 days year⁻¹); ED is the exposure duration (children = 6 years; adults = 25 years); BW is the body weight (children = 15 kg; adult males = 68 kg; adult females = 58 kg); AT is averaging time (children (6*365-days) = 2190 days; adults (25*365-days) = 9125 days); and 10⁻⁶ is for unit conversion as used and reported in Rinklebe et al. (2019).

Hazard quotient (HQ) was calculated as follows:

$$HQ = \frac{ADD}{RfD}$$

Where, RfD is As oral reference dose (0.0003). Values of HQ > 1 indicates higher probability of adverse health effects (Rinklebe et al., 2019).

2.5. Data and statistical analyses

We performed ANOVA in order to compare the variability of the means, and also employed multiple range test (Duncan's) at P < 0.05. Pearson moment correlations were conducted between As, its geochemical fractions and other relevant mine spoil soil parameters. The statistical analyses were carried out using IBM SPSS Statistics 23 (NY, USA). Boxplots in figures present the quantiles of the measured values along with the minimum and maximum values. OriginPro 9.1 b215 (OriginLab Corporation, Northampton, USA) was used to create the figures.

3. Results and discussion

3.1. Mine spoil soil characterisation

Soils of the mine spoils were predominantly sandy with mean proportions of 63, 41 and 57% for the abandoned topsoil, profiles, and active mine top soils, respectively (Table 1). The soil's pH

ranged from 6.6 to 7.6. Total carbon was low (0.64–2.2%), with higher values in the abandoned (1.1–2.2%) than the active mine soils (0.64–1.04%). High contents of total Fe were observed at both sites, particularly in the abandoned mine top soils (17.2–46.6 g kg⁻¹).

3.2. Pseudo-total content and contamination factor of arsenic in the mine spoils

3.2.1. Total contents

The range of As in the abandoned mine top spoil was high, with a minimum of 1807 mg kg⁻¹ and a maximum of 8401 mg kg⁻¹ resulting in a median of 4483 mg kg⁻¹ (Fig. 2). The pseudo-total contents of As in the abandoned profile samples varied only little with depth (range 3105–4142 mg kg⁻¹). There was little variation in As concentrations at the active gold mine spoil with a median value of 2456, minimum value of 2034, and maximum value 3801 mg kg⁻¹ (Fig. 2). Reasons for the differences between the two sites are not fully understood, but may be due to different ore mineralogy, differences in the historical extraction procedures or differences in age of the mine spoils.

Pseudo-total contents of As in the mine spoil soils

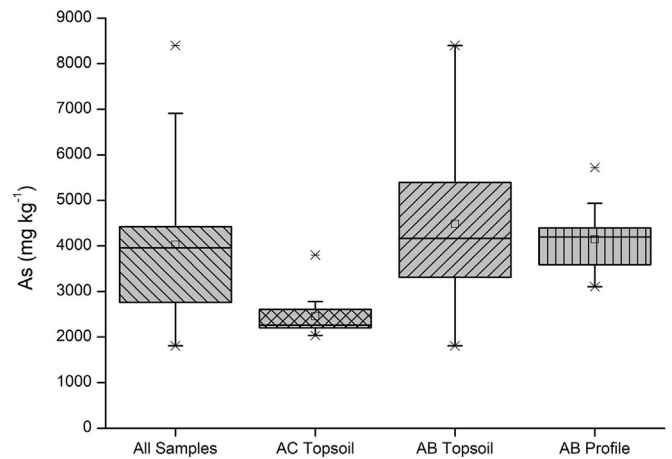


Fig. 2. Box plot showing distribution of As total content in all samples (n = 51), active (AC topsoil; n = 10), abandoned top spoil (AB topsoil; n = 31), and abandoned profile mine spoils (20–100 cm depth, AB profile n = 10). Asterisk marks (lower and upper) in the range represent 1% and 99% percentiles respectively. Asterisks outside the range represent outliers. Small rectangular boxes represent the mean.

Table 1 Mean, maximum, and minimum of selected basic properties and total metal content of the studied soils.

Parameter	Unit	Abandoned mining spoil						Active mining spoil								
		Top soil					n	Profiles				Top Soil				
		Min	Max	Mean	SD	Min		Max	Mean	SD	Min	Max	Mean	SD	n	
pH	–	6.8	7.7	7.1	0.3	31	6.6	8	7.6	0.5	10	6.8	7.5	7.1	0.2	10
TC	%	1.1	1.5	1.2	0.2	7	1.6	2.2	2	0.2	5	0.64	1.04	0.79	0.2	3
Sand		35	76	63	15	7	30	50	41	8	5	39	69	57	16	3
Silt		22	62	34	14	7	47	66	55	8	5	29	57	40	15	3
Clay		2	4	3	1	7	3	4	4	0.3	5	2	5	3	1	3
Al	g kg ⁻¹	1.69	6.97	3.16	1.09	31	4.48	10.88	7.17	2.02	10	2.70	4.12	3.56	0.48	10
Fe		17.22	46.60	23.48	5.28	31	21.24	26.18	23.29	2.10	10	19.34	24.93	22.69	1.67	10
Mn		0.20	0.49	0.39	0.06	31	0.42	0.58	0.50	0.05	10	0.20	0.37	0.28	0.05	10
P		0.20	0.37	0.29	0.03	31	0.30	0.47	0.38	0.05	10	0.19	0.30	0.23	0.03	10
Ca		8.65	23.94	11.58	2.85	31	15.25	19.90	18.05	1.61	10	2.58	13.60	5.19	3.12	10
Mg		4.65	12.40	6.18	1.38	31	6.70	9.88	8.23	0.98	10	1.89	6.15	2.88	1.28	10

SD: Standard deviation.

(1807–8401 mg kg⁻¹) far exceeded world soil average threshold of 6.83 mg kg⁻¹ for uncontaminated soils reported by Kabata-Pendias (2011); that of the German Soil Protection Law which considers soil concentrations of 25 mg As kg⁻¹ as a potential health hazard for playgrounds; and 140 mg kg⁻¹ for industrial sites (BBodSchV, 1999). It also far exceeds the total concentrations of 50 mg kg⁻¹ reported by Kabata-Pendias (2011) as phytotoxically excessive levels for plants. Even the minimum values far exceeded the trigger action value (65 mg kg⁻¹) and the maximum allowable concentrations (20 mg kg⁻¹) reported by Kabata-Pendias (2011). We assume that the extremely high As contents found in the mine stockpiles reflect the natural characteristics of the gold mineral (arsenopyrite) as will be discussed in section 3.3.

3.2.2. Soil contamination factor

According to the calculated soil contamination factor, the risk from As-soil contamination in the abandoned mine spoil was very high with a mean of 669 (Fig. 3). In the active mine spoil, the mean was 360 and for the profiles, 606 (Fig. 3). With CF values far above 6, the mine spoils displayed extremely high degrees of soil contamination according to the critical limits prescribed by Antoniadis et al. (2017). The contamination levels surpass the As contamination reported in other mine fields and regions in Ivory Coast (Kinimo et al., 2018), Ghana (Klubi et al., 2018), China (Shen et al., 2019) and Brazil (Teixeira et al., 2018).

3.3. Mineralogical composition and As speciation in the mine spoils

The results of XANES analysis (Fig. 4) and the LCF results (Table S2) indicate that scorodite (FeAsSO₄) and arsenopyrite (FeAsS) are the two main As-dominated minerals in the mine spoils.

The scorodite and arsenopyrite accounted for 65–72% and 28–35%, respectively of total As in the selected abandoned samples and accounted for 76% and 24%, respectively in the active gold mine spoils (Appendix A; Table S2). The appearance of As primary mineral arsenopyrite could be sourced from the studied gold mine where arsenopyrite is associated with sulphide gold minerals, and co-exists in approximately equal proportions (50:50) with pyrite (Oberthuer et al., 1997; Hayford et al., 2009).

Scorodite is the dominant form of the As in the two studied soils,

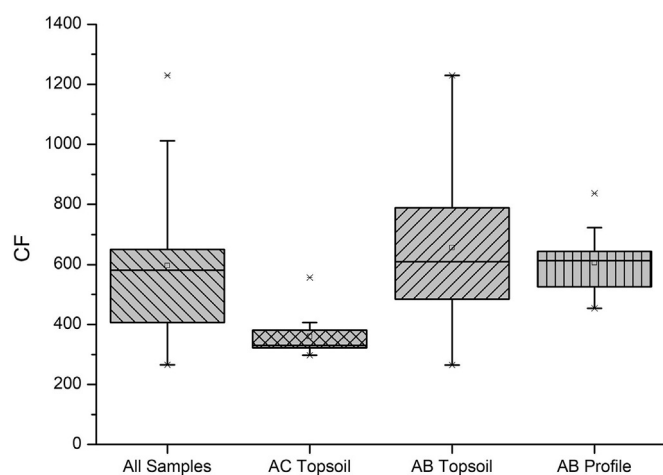


Fig. 3. Soil contamination factor (CF) of As contents in the mine spoils – all samples, active topsoil, abandoned topsoil and profiles. Asterisk marks (lower and upper) in the range represent 1% and 99% percentiles respectively. Asterisks outside the range represent outliers. Small rectangular boxes represent the mean.

and it is generally considered a secondary product of the natural oxidation and weathering of arsenopyrite (DeSisto et al., 2016; Murciego et al., 2010). These processes have obviously occurred in both the abandoned and active mine soils, producing scorodite. Similarly, Drewniak and Sklodowska (2013) showed that scorodite is the most dominant secondary As mineral in mine-waste heaps and industrial deposits. Arsenopyrite is one of the dominant sulphide ore minerals associated with the geology in this gold mine area (Hayford et al., 2009) and as indicated by the XANES spectroscopy analysis results. Therefore, both scorodite and arsenopyrite explain the high content of total As and Fe in the studied spoils.

3.4. Geochemical fractions and potential mobilisation of As in the bulk soils and in the coarse and fine particles of the studied spoils

3.4.1. Fractions of As in the bulk soils of the top abandoned and active mine spoils

In the abandoned mine spoil top soil, relatively dominant proportions of As in the bulk soil was prevalent in both the residual/sulphide (FV) (44% of total As) and in the amorphous Fe oxides fraction (FIII) (45%) (Fig. 5). For the active mine spoil soils, As in the bulk sample was most prevalent in fraction III (52% of total As), followed by the residual/sulphide fraction (FV = 36%). These indicate that As is primarily associated with poorly crystalline iron oxides and sulphides/mineral fraction. As shown earlier (section 3.3; Fig. 4), the mine spoils contain FeAsO₄ and FeAsS, which might be a reason for the dominance of As in the poorly crystalline iron oxides and sulphides/mineral. Therefore, we assume that the higher contents of As in FIII and FV in the bulk abandoned and active mine spoils may be due to higher proportions of FeAsS and FeAsO₄ in the samples (Fig. 4). Also, the total content of Fe was very high in both spoils, particularly in the abandoned ones (17–46 g kg⁻¹; Table 1). In this respect, Karak et al. (2011) and Giacomino et al. (2010) reported that the residual fraction of As is made up of greater proportions of arsenopyrite.

The relatively higher FV in the abandoned mine spoils than the active spoils and the relatively higher FIII in the active mining spoils than the abandoned bulk spoils (Fig. 5), might be related to age differences between both spoils. As mentioned in section 2.1, the abandoned bulk spoils are older than the active mining spoils, which may affect the activity of Fe oxides. As reported by Shaheen and Rinklebe (2014), Fe oxide contents in weakly developed and young soils, are dominated by the amorphous components. Consequently, increasing soil age and progressing pedogenesis may lead to increasing contents of crystalline Fe-oxides and hydroxides (Shaheen and Rinklebe, 2014). Additionally, the ratio of Fe_o to Fe_d (also referred to as activity ratio) may give indication of the age of soil and suggest progressive shift towards crystallinity of Fe oxides with age (Shaheen and Rinklebe, 2014; Maejima et al., 2002). The high Fe_o/Fe_d ratio (1.04) (calculated from the Fe_o and Fe_d values in Appendix A; Table S3) of the abandoned mine spoil might indicate its relatively older age than the active mining spoil. Thus, in the abandoned mine spoil top soil (older mine spoil), higher proportions of the total As could be structurally incorporated into the crystalline fraction and the soil minerals (the residual fraction) with time, making As unavailable (Shaheen and Rinklebe, 2014; Tack, 2010). In this respect, Antoniadis et al. (2017) reported that As over time may be held in an irreversible manner onto interlayer soil sites, and could be blocked by lattice-fixed cations such as K⁺ or occluded by evolved Al polymers.

The obviously lower percentage (0.5–1.3%) of As in F (IV) than F(III) in both spoils (Fig. 5) may indicate that adsorption of As by soils depends on the content of amorphous iron oxides, and that the fixation of As is highly influenced by the specific surface and crystallinity of the Fe oxides as indicated by Bissen and Frimmel

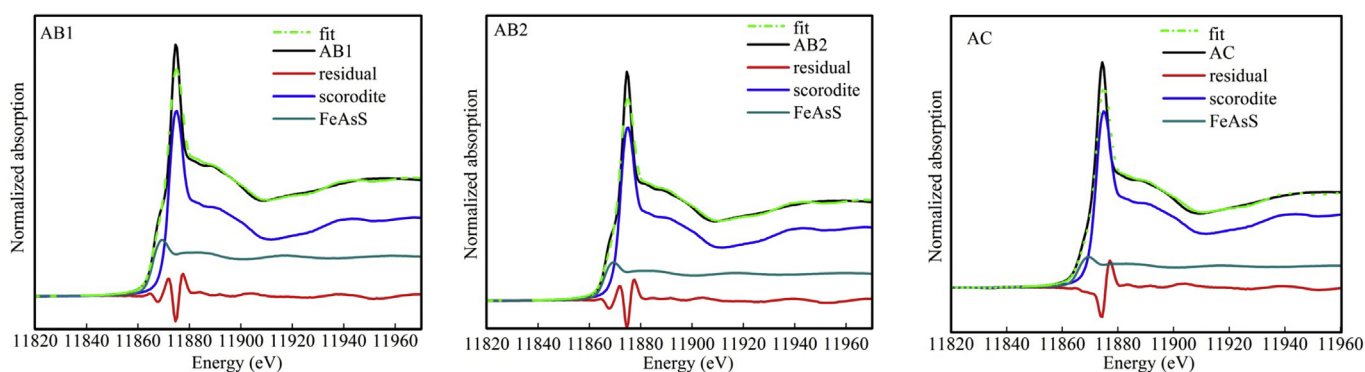


Fig. 4. Arsenic K-edge XANES spectra of selected abandoned (AB) and active (AC) mine spoils and their linear combination fitting results.

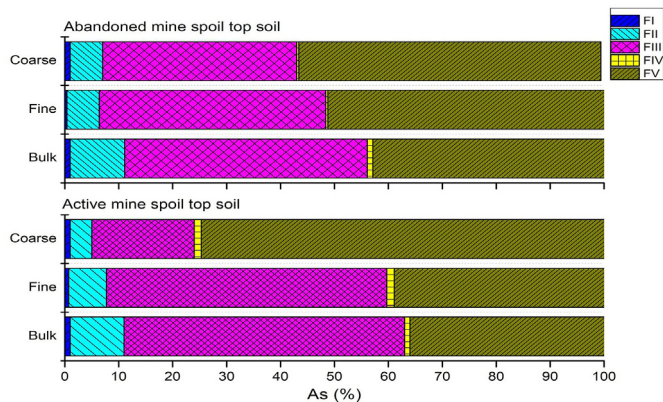


Fig. 5. Geochemical fractions of As (%) in the fine and coarse particles and the bulk soil of the active and the abandoned mine spoil top soils.

(2003). Bissen and Frimmel (2003) added that in contrast to crystalline structures, As does not only adsorb to the outer surface of amorphous iron oxides but also enters the loose and highly hydrated structures. This may explain why greater quantities of As was bound to the FIII than FIV (crystalline Fe oxides). This observation also agrees with that of Hartley et al. (2010), who found greater proportion of the total As associated with the amorphous iron oxide fraction of an untreated contaminated soil.

The bulk soil of both the abandoned and active mine spoils contained relatively equal proportions of As in fraction II (10%). This may indicate availability and potential mobilisation of As in fraction II (specifically-sorbed As/exchangeable fraction) from the active mine top soil coarse fraction upon changes in pH or the soil phosphate contents (Bolan et al., 2014).

The As in fraction I represents the water-soluble and unspecifically bound As. The fraction ranged between 0.4 and 1% in the mine spoil top soils (Fig. 4). This fraction (22.2–23.4 mg kg⁻¹), although very low, represents the most important fraction related to environmental risks and has been shown to correlate positively with As concentrations related to food chain and groundwater pollution (Violante et al., 2010). This fraction also forms the most mobile and toxic portion of As in soil/water systems as indicated by Karak et al. (2011). Mobile As easily forms outer-sphere complexes onto mineral surfaces (Violante et al., 2010). Karak et al. (2011) found a very small percentage (0.42%–2.55%) of As extracted by deionized water in As-contaminated garden soils in India, and attributed it to leaching loss of this labile fraction over years by the action of rain water.

3.4.2. Fractions of As in the fine and coarse particles of the top abandoned and active mine spoils

Both fine (52%) and coarse particles (56%) of the abandoned mine spoil top soils contained greater proportions of the sequentially extracted As in fraction V (Fig. 5). For the coarse particles of the active mining spoil, relatively larger amount of the As was found in the residual/sulphide fraction (FV = 75%) (Fig. 5). We hypothesize that the arsenopyrite geologic mineral present in the coarse particles, particularly in the active mine spoil, was resistant to weathering changes, hence making them retain larger As contents in the residual fraction.

The correlation results further indicated a highly significant positive relationship between total As and As in the FV in both the fine particles ($r = +0.96$; $P < 0.01$) and the coarse particles ($r = +0.82$; $P < 0.01$) (Appendix A; Tables S5 and S6). Results from the correlation analysis (Table S5) also indicated a highly positive significant relationship between total As and Fe ($r = +0.98$; $P < 0.01$) in the fine particles. This implies that greater proportion of the extracted As (composed of the residual fraction) are concentrated in the fine soil size particles. Further, the fine particles contained higher As contents in FIII (42–52%) than the coarse particles (36%) in both spoils, particularly in the active mining spoil (Fig. 5), which can be explained by the higher contents of amorphous Fe oxides (Fe_o) in the fine particles (13.4 g kg⁻¹) than in the coarse particles (1.8 g kg⁻¹) (Table S3). These may increase the positive charges on the surfaces of the fine particles (principally made up of about 37% clay + silt) compared to the coarse particles (made up of about 63% sand). The positive charges can adsorb As and increase their contents in the As fraction III (Reddy and DeLaune, 2008). Antoniadis et al. (2017) reported that soils with high clay content retain higher contents of As. The effects of Fe_o on influencing sorption of As is well reiterated by Antoniadis et al. (2017); Shrivastava et al. (2015); Bolan et al. (2014); and Komárek et al. (2013).

The fine particles also contained 6% and 7% contents of As in FII, respectively for abandoned and active top soils. In the coarse particles, FII As contents in the active was almost three times higher than the abandoned mine top soil (Fig. 5). However, a strong significant positive relationship between pH and %As in FII ($r = +0.6$; $P < 0.05$) in the coarse particles was noticed (Appendix A; Tables S5 and S6). For the fine particles, there was a strong significant negative correlation ($r = -0.7$; $P < 0.05$) between pH and specifically sorbed %As, which might indicate release and bioavailability for soil and plant under increasing pH. In this regard, Tack (2010) indicated that sorption capacity decreases with higher pH, due to the carbonates acquiring a negative charge at high pH. This phenomenon can make exchangeable As become available.

Potentially mobile As fraction (PMF) and the mobility factor

(MF) (Appendix A; Table S3) are used to explain the ease with which As is released into the surrounding ecosystem to contaminate environmental resources such as the water, groundwater, soil, and crops. Both indices are used to indicate mobilisation of the element and they indicate pollution that is largely affected by anthropogenic sources (El-Naggar et al., 2018; Karak et al., 2011). Low MF means lower mobility and biological availability of As in soils, and therefore an indication of relatively higher stability (Lee et al., 2011). In several studies (e.g., Shaheen and Rinklebe, 2014; Shaheen et al., 2017), fractions I+II are considered as the mobile fraction (MF) and FI+FII+FIII+FIV are considered the potential mobile fraction (PMF) (or non-residual fraction).

In the bulk sample of the abandoned and active mine spoil top soils, MF accounted for 10–11% of the total fractions. The PMF of the bulk samples of the active and the abandoned mine spoils were 64% and 56%, respectively (Fig. 5; Appendix A Table S3). The high potential mobility of As in the bulk samples indicates that As can become easily available under changing environmental conditions such as the pH, dissolved organic matter content and the redox potential changes as reported by Shaheen et al. (2018). Results from the correlation analyses (Table S5), for instance, indicated an inverse relationship between pH and percent PMF ($r = -0.88$; $P < 0.01$); and pH and percent MF ($r = -0.67$; $P < 0.01$), which mean that the mobility and potential mobility of As may increase with decreasing pH. However, under such tropical climate at the mine sites, long-term acidification may be more likely than alkalinisation, which may also reduce As mobilisation with time. The effects of redox potential and soil pH on the mobilisation of As is reported in other studies (e.g. Shaheen et al., 2017, 2018).

In the soil-size particles, percent PMF was lower in the coarse fraction (25% in the active mine spoils; and 44% in abandoned mine spoils) than the fine fraction (61% in the active mine spoils; and 48% in the abandoned mine spoils). This means that potential mobilisation of As from the coarse sandy particles was reduced because part of the As content was retained in the residual fraction. The percent residual fraction in the coarse particles was higher than that in the fine particles in both the active and abandoned mine spoils (Fig. 5). In the abandoned mine spoils, percent MF in the

coarse particles (7%) was similar to that in the fine particles (6%).

The MF and PMF in the soil sized fractions decreased as compared to the bulk top soils in both the abandoned and the active mine spoils. We hypothesize that the decrease of MF and PMF in the fine particles can be explained by the higher content of clay minerals, oxides, and the As-bearing secondary mineral scorodite and/or goethite in the fine particles than the bulk soils, which may increase sorption of As on soil surfaces, and thus reduce its potential mobilisation, release and consequent environmental effects. In this regard, Kumpiene et al. (2006) reported that retention of As by clay and Fe oxides reduces its mobile fraction and availability, with consequent reduction in groundwater and food chain contamination. Shrivastava et al. (2015) found that clayey soils contain more Fe oxides/hydroxides when compared to sandy soil, making clay soil to retain As. Additionally, Petelka et al. (2019) reported that metalloid retention capacity is higher in fine-grain soil particles (e.g. clay minerals) due to their larger surface area in comparison with coarse-grained particles (e.g. sand).

The portion of residual As (% of the total content) in the coarse particles was obviously higher than the bulk and fine particles in both spoils, and particularly in the active mine spoil (Fig. 5). We assume that the high portion of the residual As in the coarse particles might be due to the presence of the As bearing primary mineral arsenopyrite in the coarse particles, especially in the active spoil because it's younger than the abandoned and thus the effect of weathering is not enough to transfer it to the secondary As-bearing minerals (Murciego et al., 2010).

3.4.3. Fractionation of As in the fine and coarse particles of the abandoned mine soil profile

In the fine particles, a relatively higher portion of As was distributed in the residual/sulphide fraction (FV) and increased with depth from 20 cm to 100 cm, whilst at the same time, As in FIII decreased from 31% to 6–10% (Fig. 6 and Table S4). We assume here that higher percentage of the sulphide arsenopyrite and scorodite mineral could be more associated with the fine particles in the deep-layers than the 0–20 cm layer. We may attribute this observation to effect of soil weathering and leaching. Weathering

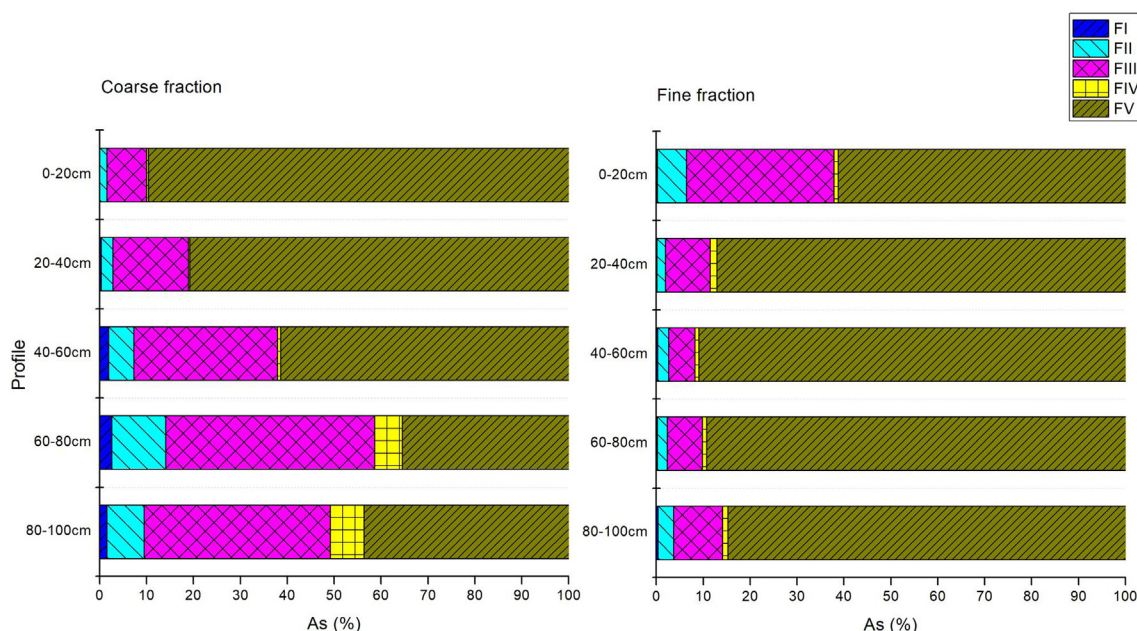


Fig. 6. Geochemical fractions of As (%) in the studied fine and coarse particles of the abandoned mine spoil soil profiles.

processes are reported to be more intense in top soil layers than the sub-layers (Li et al., 2016).

Many years of abandonment of the mine spoil may have subjected the FeAsS mineral in the surface layers to the effect of weathering and various oxidation and reduction processes. For instance, oxidation of FeAsS may lead to liberation and loss of As from the surface layers (DeSisto et al., 2016, 2017). This is further confirmed by the higher As potential mobile fractions (PMF) and mobile fractions (MF) in the 0–20 cm depth profile fine particles than the deeper layers (40–100 cm). In a similar study, Li et al. (2016) found higher As contents in the residual fraction of the sub-soil samples than their corresponding surface layers in an As-contaminated mine fields in China. The high accumulation of As in the FV (non-mobile fraction or residual fraction) is an indication of greater tendency of As to become unavailable. In this regard, Shaheen et al. (2017) reported that the As residues bounded to the soil matrix is not phytoavailable, and unavailable for leaching to contaminate the groundwater.

In the coarse particles, As showed a different distribution as compared to the fine particles, where the residual/sulphide As (FV) decreased clearly with depth. At the same time, the associated As with amorphous Fe oxide (FIII) increased with depth, reaching maximum values of about 40% in the deepest layers (Fig. 6). Therefore, the potential mobility (PMF = $\sum FI-FIV$) of As increased with depth in the coarse particles while it decreased with depth in the fine particles (Fig. 6). This may be due to lower concentration of the FeAsS minerals in soil depths of the coarse particles compared to the fine particles. Again, the process of weathering on the surfaces of the soil coarse particles may lead to oxidation and reduction of the amorphous iron oxide contents, leading to release and leaching of loosely-bound As from the top soils. This may account

for the lower FIII As contents at the topsoil and higher FIII at the sub-layers. For instance, As in the fraction III (amorphous iron oxide fraction) could be leached during reductive dissolution of the Fe-bearing mineral (Rinklebe et al., 2016). The released As may be lost from the soil surface or leach downwards to the soil sub-layers. These observations agree with those found in other studies (e.g. Shaheen and Rinklebe, 2014; Shaheen et al., 2017). In the 80–100 cm depth, As contents in the FIII decreased again and may be related to the geology of the mine spoil.

3.5. Human health risk of the mine spoils

Fig. 7 shows health risks associated with exposure to As-contaminated mine deposits and spoils for children, adult males and females, respectively. For children, median values of 6,5471–65,213 were observed. For adult males, median values of 4863–5158 were observed. And for adult females, median values ranged from 3244 to 6047.

The human health risks assessment indicated that children are at most health risk disadvantage with regards to exposure such as direct dust inhalation. The exposure risks were far above the critical limit of 1 (Antoniadis et al., 2019b; Rinklebe et al., 2019) and were in the decreasing order, children > adult females > adult males. The abandoned mine spoil posed greater health risks than the active, and profile mine spoils. The risks were also higher in the surface topsoil than from the profiles. The unfenced abandoned mine spoil serves as a passing place and as a play-ground for children, who could inhale, ingest and eat higher concentrations of these contaminated mine wastes. As reported by Armah and Gyeabour (2013), sediment ingestion by children is a primary exposure route of concern for contaminated sediments. Similarly, hazard

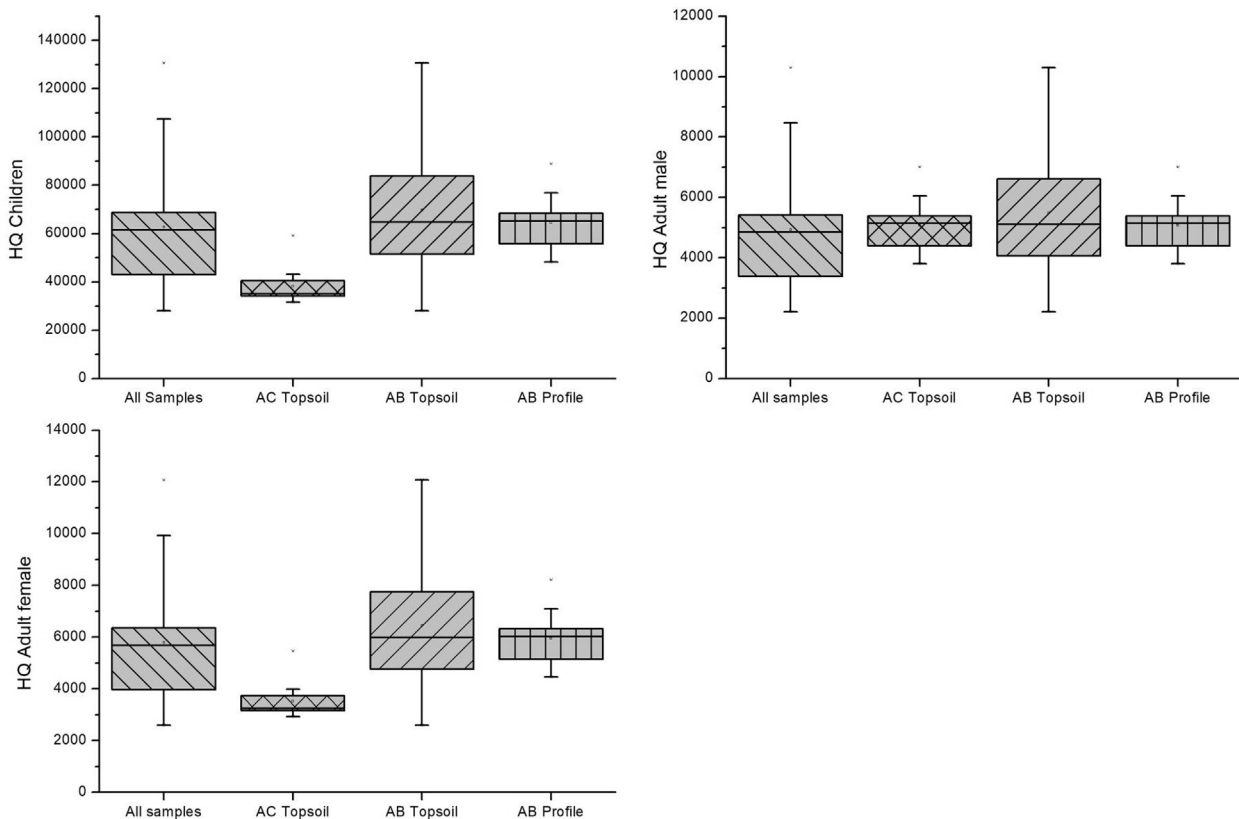


Fig. 7. Hazard quotient of children, adult males and females exposed to As contamination in the all samples, active top soil, abandoned topsoil and profiles. Asterisk marks (lower and upper) in the range represent 1% and 99% percentiles respectively. Asterisks outside the range represent outliers. Small rectangular boxes represent the mean.

quotients of As have been reported from other gold mining areas in Ghana (E.g. Armah and Gyeabour, 2013; Hadzi et al., 2018) but these works determined values far lower than those found in our study. Similarly, Li et al. (2015) found that higher As content in the topsoil posed a potential health risk to children in smelter mine area in southwestern China but reported hazard quotient values lower than in our study.

4. Conclusions

We found that the studied gold mining spoils are severely contaminated with As, with a total content ranged between 1807 and 8400 mg kg⁻¹, and the abandoned mine spoil was more contaminated than the active spoils. Association of As to the poorly crystalline Fe oxide (FIII); and the residual/sulphide fraction (FV) gives an indication that solubility of As in the mine spoil soils could be greatly governed by the contents of amorphous iron oxides and the dominant As bearing primary (arsenopyrite) and secondary (scorodite) minerals. The particle size distribution of the soils and the profile depth affected the distribution of As among the geochemical fractions. The potential mobility (non-residual fractions) of As was higher in the fine particles than the coarse particles and the bulk soil, particularly in the active spoils. Also, the potential mobility of As in the profiles increased with depth in the coarse particles while its decreased with depth in the fine particles. The higher potential mobility of As in the fine particles of the 0–20 cm layer may increase its potential availability and toxicity to plants, while the increase of As potential mobility in the coarse particles of the deep layers (40–100 cm) may increase its leaching to the groundwater particularly under the potential changes of soil redox potential.

The extremely high total As contents, and the high potential mobility demonstrate a high environmental risk. Furthermore, the human health risk assessment revealed that the abandoned mine spoil posed greatest elevated health risk especially to children and women. Therefore, remediation actions should be explored to reduce the risk of As into water sources, provide protective cover, improve soil fertility of the sites and protect human health. Further research could explore in detail how the various biogeochemical factors such as the pH, redox potential, organic matter content, Fe, and sulphides in the residual fraction could control the mobilisation of As from the mine spoils to adjacent waters and surroundings.

Authors statement

The paper is authored by Mr. Albert Kobina Mensah, Prof. Bernd Marschner, Prof. Sabry M. Shaheen, Dr. Jianxu Wang, Prof. Shan-Li Wang and Prof. Jörg Rinklebe.

All authors contributed to the paper and have approved the revisions. **Mr. Albert Kobina Mensah** conducted the research, did analyses of the data and wrote the first draft of the manuscript. **Prof. Bernd Marschner, Prof. Sabry M. Shaheen, and Prof. Jörg Rinklebe** proofread, reviewed, restructured the article and conceptualized and supervised the entire work. **Dr. Jianxu Wang and Prof. Shan-Li Wang** ran the experiments on arsenic speciation at the National Synchrotron Radiation Research Centre (NSRRC) in Taiwan and did the analyses of the data. All authors proofread the final manuscript and approved the final versions for submission.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2020.114116>.

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