Arsenic contamination from gold mining and remediation of active and abandoned mine spoils in Ghana

Dissertation

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by

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DEDICATION

This thesis is dedicated to my late grandmother, Ms. Mary Kwofie (was affectionately called by her grandchildren as, ‘auntie’). As a little boy, auntie sent me to the farm, protected me from harm, bought food for me and gave me money to start a kerosene selling business. I was only a child and did not understand the impacts of these actions. I grew up to understand how much selflessness she taught me and the deep love she showed me!

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Ich versichere an Eides statt, dass ich die eingereichte Dissertation selbstständig und ohne unzulässige fremde Hilfe verfasst, andere als die in ihr angegebene Literatur nicht benutzt und dass ich alle ganz oder annähernd übernommenen Textstellen sowie verwendete Grafiken, Tabellen und Auswertungsprogramme kenntlich gemacht habe. Außerdem versichere ich, dass die vorgelegte elektronische mit der schriftlichen Version der Dissertation übereinstimmt und die Abhandlung in dieser oder ähnlicher Form noch nicht anderweitig als Promotionsleistung vorgelegt und bewertet wurde. Weiterhin versichere ich, dass in Abbildungen nur die originalen Daten enthalten sind und keine inhaltliche Veränderungen oder Bildbearbeitungen unternommen wurden. Ebenso versichere ich, dass keine kommerzielle Vermittlung oder Beratung in Anspruch genommen wurde.

Albert Kobina Mensah
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PREFACE AND DECLARATION

This thesis was prepared based on the project, “Arsenic contamination and remediation of active and abandoned gold mining spoils in Ghana”. The PhD project was sponsored by the German Academic Exchange Service (DAAD) under the German Academic Exchange Service – Government of Ghana Scholarship for PhD training in Germany (Personal reference number: 91560903). The whole project cost, laboratory analyses and fieldwork were funded by the Ruhr University Bochum, Germany. The thesis was compiled from four research papers, two are already published, one revised manuscript is resubmitted for publication and the last one is yet to be submitted. The dissertation was submitted on the 23 September 2021, got accepted by the doctoral committee on the 15 December 2021 and the final oral disputation was held on the 21 December 2021 at 12:00 am in building IA 3/94, Ruhr University Bochum, Germany.

Chapter 2:

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ABSTRACT

Gold mining offers economic benefits to many countries including employment creation, boosting governments' revenues and foreign exchange earnings, and manufacture of ornaments such as jewelleries. In Ghana, gold mining exists in two major scales of production- large (industrial)- and small-scale; each contributes to the economy in diverse ways. Despite these benefits, gold mining has come with huge environmental costs including loss of arable fields, pollution of surface and groundwater, and accumulation of toxic elements in food crops, which causes skin diseases and deformities in new-born babies. This research was done to examine possible pollution with heavy metals and metalloids in gold mine sites, their dominant species, consequent mobilisation into watercourses, concomitant soil and human health implications, and possibilities for remediation of the mining sites. It was observed that the studied gold mining sites were heavily polluted with As, with maximum total content of 8,407 mg/kg. Arsenic pollution in the mine sites and their surroundings were strongly related to their Fe oxide and sulphide components, which predominantly control the mobility of As in the polluted sites. Additionally, the dominant As species in the spoils were mainly arsenopyrite- the primary mineral and scorodite- the secondary mineral. These elevated As pseudo-total concentrations, and main As species in the sites demonstrate their potential mobility. Consequently, there is the ability to increase availability to accumulate in food crops, in plants, in water, and pose consequent toxicity to the surrounding ecosystem. As verified by the high As total contents and high potential mobile fractions in the spoils' profiles, there is thus the potential of As to leach down the profile to pollute available groundwater, especially under ecological variations in soil redox potential and pH. Furthermore, the soil and human health hazard estimation demonstrated that the polluted sites presented extreme health danger to the inhabitants in the surroundings of the mine sites; and the hazards were higher in women and children. Therefore, soil remediation efforts need to be instituted to protect environmental and human health and as well to restore livelihoods of the populace. Some native plants (e.g., *Chromolaena odorata* and *Pityrogramma calomelanos*) that grow and survive in these polluted sites will be capable of cleaning As and thus, their commercial full-scale potential and applicability for green cleaning of the mine sites should be explored. Such plant remediation efforts can utilize C, P-rich and alkaline materials to boost the remediation effectiveness of the plants. Also, chemical remediation options such as the use of Fe-rich amendments can be used to lessen the bioavailability of As, to decrease migration into surface and groundwater and to mitigate the associated human health impacts. In conclusion, soil remediation measures should limit anaerobic conditions and encourage aerobic conditions at the site, which will thus reduce pH, increase the redox potential, and consequently restrict As mobilisation from the mine spoil.

KURZFASSUNG

Der Goldbergbau bietet vielen Ländern wirtschaftliche Vorteile, darunter die Schaffung von Arbeitsplätzen, die Erhöhung der Staatseinnahmen und Deviseneinnahmen sowie die Herstellung von Schmuck. In Ghana wird Gold in zwei großen Maßstäben abgebaut - in großem (industriellem) und kleinem Maßstab; beide tragen auf unterschiedliche Weise zur Wirtschaft bei. Trotz dieser Vorteile ist der Goldabbau mit enormen Umweltkosten verbunden, darunter der Verlust von Ackerflächen, die Verschmutzung von Oberflächen- und Grundwasser und die Anreicherung von toxischen Elementen in Nahrungsmitteln, die zu Hautkrankheiten und Missbildungen bei Neugeborenen führen. Im Rahmen dieser Studie wurden die mögliche Verschmutzung durch Schwermetalle und Metalloide in Goldminen, deren vorherrschende Arten, die daraus resultierende Mobilisierung in Wasserläufen, die damit verbundenen Auswirkungen auf den Boden und die menschliche Gesundheit sowie die Möglichkeiten zur Sanierung der Minen untersucht. Es wurde festgestellt, dass die untersuchten Goldminenstandorte mit einem maximalen Gesamtgehalt von 8.407 mg/kg stark mit As verschmutzt waren. Die Arsenverschmutzung in den Minenstandorten und ihrer Umgebung stand in engem Zusammenhang mit den Fe-Oxid- und Sulfid-Komponenten, die die Mobilität von As in den verschmutzten Standorten maßgeblich bestimmen. Darüber hinaus waren die vorherrschenden As-Spezies in den Abraumhalden hauptsächlich Arsenopyrit - das primäre Mineral - und Skorodit - das sekundäre Mineral. Diese erhöhten Pseudogesamtkonzentrationen von As und die wichtigsten As-Arten an den Standorten zeigen deren potenzielle Mobilität. Folglich besteht die Möglichkeit, dass es sich in Nahrungsmitteln, Pflanzen und im Wasser anreichert und folglich für das umgebende Ökosystem toxisch ist. Wie die hohen As-Gesamtgehalte und die hohen potenziell mobilen Fraktionen in den Profilen der Abraumhalden belegen, besteht somit die Möglichkeit, dass As im Profil nach unten sickert und das verfügbare Grundwasser verschmutzt, insbesondere bei ökologischen Schwankungen des Redoxpotenzials und des pH-Werts im Boden. Darüber hinaus hat die Abschätzung des Gesundheitsrisikos für den Boden und den Menschen gezeigt, dass die verschmutzten Standorte eine extreme Gesundheitsgefährdung für die Bewohner in der Umgebung der Grubenstandorte darstellen, wobei die Gefährdung für Frauen und Kinder höher ist. Daher müssen Bodensanierungsmaßnahmen eingeleitet werden, um die Umwelt und die menschliche Gesundheit zu schützen und die Lebensgrundlage der Bevölkerung wiederherzustellen. Einige einheimische Pflanzen (z. B. Chromolaena odorata und Pityrogramma calomelanos), die an diesen verschmutzten Standorten wachsen und überleben, sind in der Lage, die Böden zu reinigen, und daher sollte ihr kommerzielles Potenzial und ihre Anwendbarkeit für die umweltfreundliche Reinigung der Minenstandorte untersucht werden. Solche pflanzlichen Sanierungsmaßnahmen können C-, P-reiche und alkalische Materialien nutzen, um die Sanierungseffizienz der Pflanzen zu erhöhen. Auch chemische Sanierungsoptionen wie die Verwendung von Fe-reichen Zusätzen können eingesetzt werden, um die Bioverfügbarkeit von As zu verringern, die Migration in Oberflächen- und Grundwasser zu reduzieren und die damit verbundenen Auswirkungen auf die menschliche Gesundheit zu mindern. Zusammenfassend lässt sich sagen, dass die Maßnahmen zur Bodensanierung die anaeroben Bedingungen begrenzen und die aeroben Bedingungen am Standort fördern sollten, wodurch der pH-Wert gesenkt, das Redoxpotenzial erhöht und folglich die Mobilisierung von As aus dem Abraum der Mine eingeschränkt wird.

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LIST OF ACRONYMS

Al	Aluminium
ADD	Average Daily Dose
AMD	Acid Mine Drainage
ANOVA	Analyses of Variance
As	Arsenic
AsB	Arsenobetaine
AsC	Arsenochlorine
AsH_3	Arsine
As(III)	Arsenic three
As(V)	Arsenic five
Au	Gold
BAC	Bioaccumulation Concentration
BCF	Bioconcentration Factor
B.d.l	Below Detection Limit
BW	Body Weight
C	Carbon
Ca	Calcium
Cd	Cadmium
Cl	Chlorine
CF	Contamination Factor
CH_3	Methyl group
CO_3^{2-}	Carbonate
Cu	Copper
DAAD	German Academic Exchange Service
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
EC	Electrical Conductivity
ED	Exposure Duration
EF	Enrichment Factor
E_H	Redox potential
EXAFS	Extended X-Ray Absorption Fine Structure
FeII	Iron Two
FeIII	Iron Three
Fe	Iron
Fe_d	Dithionate iron oxide
FeO	Iron oxide
FeAsS	Arsenopyrite/Iron Arsenic Sulphide
FeS	Pyrite/Iron Sulphide
IARC	International Agency for Research on Cancer
ICP	Ion Chromatography Photometer
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
Igeo	Geo-accumulation index
IR	Soil Ingestion Rate
LCF	Linear combination fitting

Hg	Mercury
HI	Hazard Index
HSD	Honestly Significant Difference Test
HQ	Hazard Quotient
MC	Microcosm
MF	Mobile fraction
Mg	Magnesium
MMA	Monomethyl Arsenic
Mn	Manganese
Ni	Nickel
NSRRC	National Synchrotron Radiation Research Centre
P	Phosphorus
Pb	Lead
pH	Hydrogen ion concentration
PLI	Pollution load index
PMF	Potential mobile fraction
PTE	Potentially toxic element
R	Pearson’s r
R^2	Coefficient of Correlation
RFD	Oral Reference Dose
RSD	Relative Standard Deviation
RUB	Ruhr University Bochum
S	Sulphur
SD	Standard Deviation
SEP	Sequential Extraction Procedure
SHRA	Soil-to-human Health Risk Assessment
SO_4^{-2}	Sulphate
SUVA	Specific Ultraviolet Adsorption
TMA	Trimethyl Arsenic
TC	Total Carbon/Transfer Coefficient
TF	Translocation Factor
XANE	X-ray Absorption near edge structure spectroscopy

LIST OF SYMBOLS AND UNITS

cm	Centimetre
cm^3	Centimetre Cube
°C	Degree Celsius
dS/cm	Deci Siemens Per Centimetre
µS/cm	Micro Siemens Per Centimetre
dS/m	Deci Siemens Per Metre
g	Gram
g/kg	Gram Per Kilogram
kg	Kilogram
km	Kilometre
l	Litre
m	Metre
mg/m^3	Milligram Per Metre Cube
ml	Millilitre
mm	Millimetre
$m^{-1}\ mg^{-1}\ L$	Per Metre Per Milligram Litre
mg/l	Miligram Per Litre
mV	Millivolt
µl	Microliter
µg	Microgram
µg/kg	Microgram Per Kilogram
µg/g	Microgram Per Gram
µm	Micrometre
V	Volt

CHAPTER 1

1.0 Introduction

1.1 The problem and background

Soil pollution remains a global threat to human health, food security and environmental safety. It results from accumulation of toxic substances in the soil above recommended thresholds, especially when compared to the natural environment (Hou et al., 2020; Palansooriya et al., 2020; Wang et al., 2021). Presence of toxic substances may come from radioactive wastes (e.g. uranium and thorium) (Klubi et al., 2020; Singh et al. 2021), plastics (Walkinshaw et al., 2020; L. Yang et al., 2021), farming through the use of pesticides and organic fertilisers (Bundschuh et al., 2021), organic sources such as petroleum (Saha and Bauddh, 2021) and from inorganic sources including potential toxic elements (PTEs) from mining (Mensah et al., 2020, 2021; Shaheen et al., 2020). Accumulation of inorganic PTEs in the soil presents pressing problems to ecological and human well-being as they cannot undergo microbial degradation (Nwaichi et al., 2009). In such scenario, they remain in the soil for a prolonged period till efforts are taken to get rid of them or reduce their concentration in the soil and associated risks through sustainable remediation strategies (Bolan et al., 2014; Wang et al., 2021). Potentially toxic elements (e.g., As, Cd, Cu, Hg, Sb, V, etc.) when accumulated in the soil above permissible thresholds become public health threats to livestock, the food chain, water resources, the fauna, and the flora; and consequently, disrupt livelihoods and farmers' incomes. For instance, many fields (approximately three million) in Europe are negatively impacted by pollution, and great percentage (about 20%) of agricultural soils in China contain toxic substances above recommended thresholds (Hou et al., 2020).

In Ghana, gold mining is noted for environmental and social impacts in host communities (Mensah et al., 2015, 2021). These include, among others, the indiscriminate release of As, which in turn affects accurate performance of ecological functions as reported by Armah et al. (2014). Tailings dam is one of the waste lands resulting from surface mining of mineral and an estimated 5 to 7 billion tons are created annually at the global scale (Edraki et al., 2014; Lu and Wang, 2012). Surface gold mining affects surrounding areas through excavation of large quantity of earth materials and generation of mine wastes. Mine tailings comprise the residual fine (1 - 600 µm) material dumped after mineral extraction and processing, and it includes dissolved metals and other toxic elements (Edraki et al., 2014).

In many gold mining regions, As is associated with arsenopyrite (FeAsS) in gold mining spoils and tailings, making the spoils rich in As. Mobilisation of the mining ore (FeAsS) during mining and processing could significantly alter As biogeochemical cycle and consequently aid in its release into the surrounding ecosystem (Li et al., 2014). The released As can eventually get into rivers, get adsorbed unto its sediments, and the As-contaminated sediments can be carried over wide distances (Bundschuh et al., 2021). This can impact areas along river courses, the ocean, and the marine areas along coastlines. Consequently, these may pose potential health dangers to water, ecosystem, and humans in mining environs (Posada-Ayala et al., 2016; Bempah et al., 2013, Li et al., 2014; Mensah et al. 2020, 2021).

For instance, As contamination by mining at the upstream may cause pollution of irrigation water and may impact water quality of downstream users (Cagnin et al., 2017). At high concentrations, As is toxic to plants as reported by Shrivastava et al. (2015). Arsenate (AsV) is the principal form of As in soils and its chemical characteristics are like that of P; these properties enable As to compete with P in the plant system (Shrivastava et al., 2015). In addition, As hinders metabolic functions and impedes plant growth due to As-induced plant toxic effects. Also, microbial activity is inhibited significantly in As-contaminated soils as it reduces the activities and effectiveness of soil enzymes (Su et al., 2014; Gao et al., 2010). Furthermore, contact with As could cause many human health complications (Bortey-Sam et al., 2015; Chakraborti et al., 2013) as highlighted in the Fig. 1.3. These may include dermal, respiratory, cardiovascular, neurological problems, reproductive, immunological, genotoxic, liver cancer and cutaneous lesions (Acosta et al., 2015; Rehman et al., 2021). Early-life exposure to As may cause birth defects including shorter gestation period, low birth weight, and smaller new-borns were reported in Mexico by Laine et al. (2015). Further, Bundschuh et al. (2021) reported that accidental absorption of As-contaminated soil can harm the stomach, the kidney, the nervous system; and may cause in death in chronic cases.

In line with mine sector sustainability, it is thus imperative that As-contaminated mining spoils and tailings are progressively restored throughout the operational phase and during the decommissioning stage of the mine project life cycle. Additionally, sustainable approaches are required to repair the damage caused to the land during mineral exploration, to reduce release of As, to minimise runoff and spillage from the mining site, to reclaim the mine sites, to return the land to its pristine conditions and to ensure safe re-use of the land. Eventually, such measures are needed to safeguard the integrity of the environment and hence to protect the health of humans and animals in mining areas. In this respect, Wuana and Okieimen (2011) reported that soil remediation measures are thus taken to prevent impacts on humans, plants, or animals, and to restore the lost function of soil to allow its safe use.

Various techniques are proposed for cleaning As-contaminated soils, which are broadly categorised into mobilisation and immobilisation techniques (Bolan et al., 2014). Mobilisation technique here will mean As is released to enter the soil solution and is subsequently removed with the aid of plant species. Immobilisation techniques, involve complexing As from the soil solution through processes including adsorption, complexation, co-precipitation, and precipitation reactions. The benefits of using immobilisation options are that they lessen impacts caused to humans, animals, and plants in the surrounding environment; decrease their uptake into food crops; and they lessen leakage into surface and ground waters. Plant-based solutions, called phytoremediation, using green plants to clean up contaminated sites are also proposed in many studies (Antoniadis et al., 2017, 2021; Hou et al., 2020; Sheoran, 2011, 2010; Wang et al., 2021).

The time duration of soil remediation is a limiting factor as it may take many years to clean the soil and to restore its functions to the pristine conditions. The alternative could be to employ immobilisation techniques that will consequently reduce environmental impacts on plants, the ecosystem, food chain, groundwater and subsequently limit its bioavailability into humans. Examples of amendments for As immobilisation comprise clay, cement, zeolites, minerals, compost, manure, and microbes (Gul et al., 2015; Bolan et al., 2014). Manufacturing deposits (e.g., red mud) (Zou et al., 2018), iron oxides (Wang et al., 2021) and biochar (Beesley et al., 2013) are also reported as having potential for immobilising As in mine contaminated spoils. The As-immobilisation potential of biochar, for instance, may be caused by its relatively high carbon content and presence of positive ions such as Al, Fe and Mn on the surfaces (Beesley et al., 2013).

In Ghana, only limited studies have documented the sources and occurrence of As from gold mining spoils, making accurate appraisal of the scale of contamination problematic and inconclusive. Presently, As pollution is reported in few studies, principally focused on the Ashanti and Western gold mine-dominated regions of the country (Table 1.3). These studies are mostly outdated, employed the total content method in assessing the risk and extent of contamination, have not employed modern sophisticated methodology such as X-ray absorption near edge spectroscopy (XANE) to investigate the species responsible for the pollution. In addition, these studies have mostly ignored the various mechanisms and influences for instance the pH, dissolved organic carbon, phosphorus, oxides, sulphide, and redox potential that largely control mobilisation and the fate of transport of As. Likewise, these earlier scholarships have not conducted wide and deep studies on the human health implications of As and other PTEs of gold mining activities. Besides, no study has investigated the role flooding plays in mobilisation, controlling fate of transport, and migration of As from an abandoned mining spoil into surrounding surface and groundwater. Furthermore, studies on As remediation using biochar, compost, iron oxide, alone or in combination with green plants such as those of the native or introduced species such as ryegrass are noticeably absent in current scientific literature. Such technical studies and comprehensive examinations will be of paramount interest to the global scientific community and will contribute to sustainable development in Ghana. Thus, such scientific studies are essential to advise sustainable solution to As pollution and accompanying ecological and human health threats, and to eventually boost sustainable mineral mining. In this study, mining spoil refers to the wasteland that remains after extraction of the gold mine ore. Mine tailings are the processed material left after extraction of the mine ore. These two will be used interchangeably and they mean same thing in the thesis.

1.2 Arsenic chemistry, characteristics and forms in soils and sediments

Arsenic has atomic number of 33 and a mass number of 75 atomic mass unit. It has chemical characteristics of metals and non-metals (metalloidic element); and it belongs to group 5A in the periodic table (Bissel and Frimmel, 2003; Escobar et al., 2006). It consists of three allotropes: grey, yellow, and black. Natural As has one stable isotope, ^{75}As (Audi, 2003), but other isotopes have been synthesized according to Shrivastava et al. (2015). Chemical characteristics of As are like that of P, as the two are in the same group in the periodic table, and they form compounds through covalent bonding (e.g. Escobar et al., 2006; Hussain et al., 2019; Pigna et al., 2009; Shrivastava et al., 2015). Arsenic occurs in two major oxidation states: arsenite with valency of three (AsIII); and arsenate with valency of five (AsV) (Bundschuh et al., 2021; Shrivastava et al., 2015); it is present in other oxidation states such as -3 in arsenides (arsine), and 0 in elemental As (Shrivastava et al., 2015). In a neutral pH, arsenite is present in solution principally as H_3AsO_3 and arsenate dominates as $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Goldberg, 2011). Arsenic exists in two kinds: inorganic and organic (Bundschuh et al., 2021; Escobar et al., 2006; Mandal et al., 2019). Inorganic As are reported to be more prevalent and of more interest than the organic ones due to its key role in the biogeochemical cycle (Mandal et al., 2019). Inorganic As principally consists of the mineral kinds in deposits, whereas organic As is dominant in plants and animals due to As absorption (Shrivastava et al., 2015). Content of As in non-contaminated soils range from 0.1 - 40 mg/kg (Kabata-Pendias, 2011); total content threshold was earlier recommended to be less than 10 mg/kg (Fitz and Wenzel., 2002).

1.2.1 Inorganic arsenic

Arsenic is mainly found in the soil in inorganic forms in more than 300 As-containing minerals (Bissen and Frimmel, 2003; Kabata-Pendias, 2011). Arsenic is greatly associated with deposits of many metals, often recognised as good indicator in geochemical prospecting and hence it is mostly referred to as “pathfinder” (Kabata-Pendias, 2011). Arsenate is the predominant inorganic As in the soil with 60% proportion; sulphides and sulphosalts, 20%; oxides, 10%; and arsenites, arsenides, elemental and metal alloys at 10% (Bowell and Parshley, 2001; Drahota and Filippi, 2009). They are mostly found in close relationships with cations such as Fe, Cu, Co, S, Ni, Cd, Pb, Ag, Sb and Au (Drewniak and Sklodowska, 2013) and with other anions such as oxygen and chlorine (Bundschuh et al., 2021). Arsenopyrite (FeAsS) is the highest abundant As mineral, then pigment gold (As_2S_3), realgar (As_4S_4), and loellingite ($FeAs_2$) (Bundschuh et al., 2021). In acid mine drainage (AMD), arsenate and arsenite dominate ecosystems containing oxidized sulphur species (Cheng et al., 2009). Basic characteristic trait of mineral As is its unique strength when exposed to forces of weathering. The stability of sulphide As minerals is dependent on the following (Drewniak and Sklodowska, 2013):

i) covalent bonding between As and S,

ii) coordination bonding between Fe and As or S, and

iii) van der Waals forces existing between molecules.

Weathering, exposure to atmospheric oxygen, surface and groundwaters and alteration of primary minerals yield secondary As minerals called the arsenites, which are mostly the oxides of As(III); and arsenates, principally consist of oxides of As(V) (Table 1.2). Arsenites such as arsenolite and claudetite are weathering products of AsS, nonetheless they can be produced as well through roasting of As-containing minerals.

Scorodite is the most found As secondary mineral and are dominant in mining waste stockpiles and industrial deposits including mine tailings (Bempah et al., 2013; Mensah et al., 2020). Secondary As aggregates exhibit differences in water solubility and thus As availability. For instance, Ca-arsenates are water soluble, whereas Fe-arsenates are relatively insoluble (Drahota and Filipi, 2009; Drewniak and Sklodowska, 2013). The less soluble As-species are thus capable of precipitating and immobilizing As in contaminated mine spoils and consequently reducing their associated pollution of the environment.

1.2.1.1 Arsenic-sulphides in gold mining ores in Ghana

Gold is principally mined in two regions in Ghana: Ashanti (in areas such as Obuasi and Konongo) and western (in areas such as Prestea, Bogoso, Tarkwa and Nsuta). But all the 16 regions in Ghana, apart from the Greater Accra and the Volta region are hotspots of gold deposits. According to Oberthuer et al. (1997) and Hayford et al. (2009), arsenopyrite is the leading gold mining ore mineral in Ghana: Ashanti and Konongo mines are made up of 60 – 95% of the ore minerals; equal percentages of arsenopyrite and pyrite are found at the Prestea mine; and higher quantities of pyrite predominate at the Bogoso mine.

Arsenopyrite occurs naturally in well-developed crystallised forms; free compounds are found spread in bearing-ores or assembled in groups and aggregates. The crystals vary in length from 50 - 200 µm, however might also gain lengths of numerous mm (Oberthuer et al., 1997) (Fig. 1.1). Electron microprobe evaluation of arsenopyrite by Oberthuer et al. (1994) indicated the following As-contents in arsenopyrite in mining hotspots: Ashanti mine = 39.4 - 45.9 wt.%, Prestea and Bogoso mine = 41.4 - 47.4 wt.%, Ni = 2.02 wt.%, Co (1.17 wt.%, Sb contents = < 0.2 wt.%. Synchrotron-based X-ray analysis by Mensah et al. (2020) also indicated that arsenopyrite accounted for 28 – 35% of total As in an abandoned mine tailing and 24% in an active mine tailing in Prestea. In the same study, scorodite accounted for 65 – 72% in the abandoned mining tailing, whilst it accounted for 76% in the active mine tailing. Details of these are further demonstrated and discussed in detail in chapters 2 and 4.

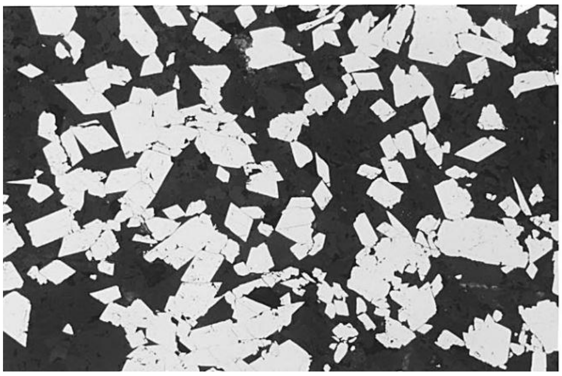


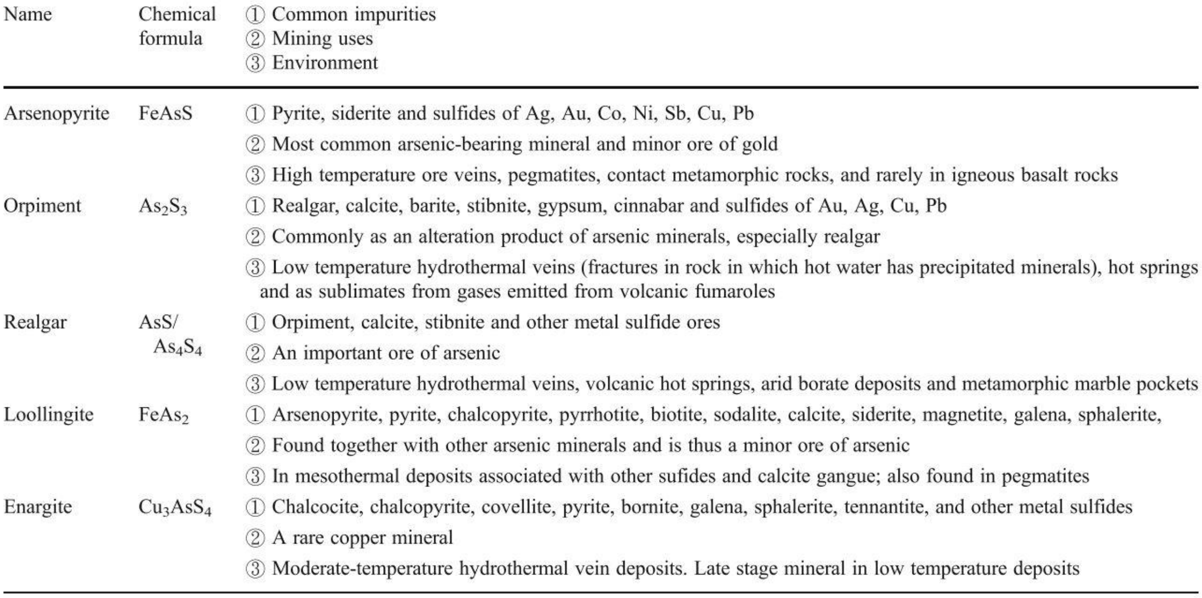
Fig. 1.1: Photomicrograph showing well-developed crystallised form of arsenopyrite sulfide ore (white) of the Prestea gold mine. Source: Oberthuer et al. (1997)

Pyrite (FeS_2), also known as ‘‘fool’s gold’’, is another inorganic As-bearing sulphide mineral found in gold mining ores and they are common in marine environments (Murphy and Strongin, 2009). Pyrite oxidation causes acid mine drainage (AMD). This process generates sulphuric acid and iron oxyhydroxides, and is responsible for contamination of streams, rivers, lakes, and reservoirs. Natural FeS_2 contains many other trace elements (e.g., Ag, As, Cd, Co, Cu, Hg, Pb, Sb, Se, and Zn), which are also of environmental concerns because they are released into neighbouring waterways during oxidative dissolution. These elements exist as substitutions in the pyrite lattice or as inclusions (Murphy and Strongin, 2009). According to Oberthuer et al. (1997), larger varieties of FeS_2 including auriferous arsenian pyrite exist at the Bogoso and Prestea mines (in some cases up to wt. 5.5% As).

Pyrrhotites exist as non-stoichiometric Fe–S points with constituents denoted as Fe_xS_{1-x} (Murphy and Strongin, 2009). Unlike pyrites, pyrrhotite is rarely found in marine environments. They occur as 10 – 30 µm spherical to egg-shaped inclusions rarely coupled with chalcopyrite in arsenopyrite, or overgrowing arsenopyrite in unusual forms. Oberthuer et al. (1997) reported that there is the possibility of limited to complete substitute of pyrrhotite by marcasite and/or pyrite.

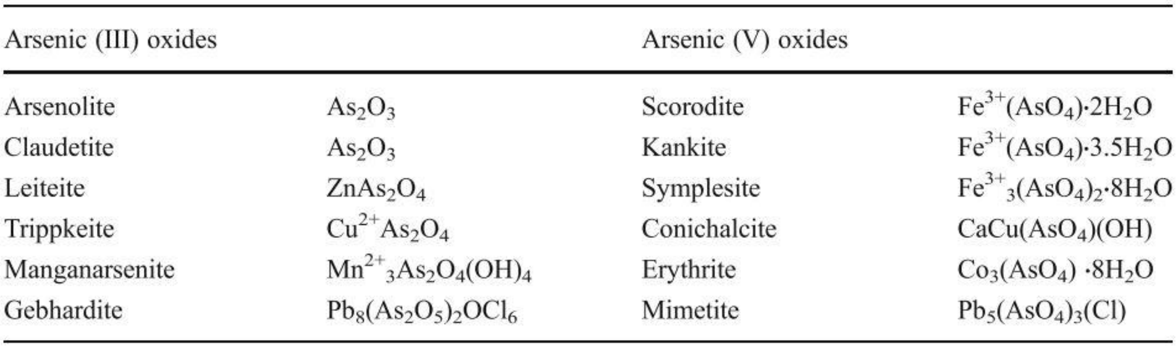
Marcasite has the capacity to replace pyrrhotite, less often intergrown with pyrite or pyrrhotite, or occurs as separate crystal aggregates. It occurs in two different forms of pyrite and has the S_2 pattern (Murphy and Strongin, 2009). Free-milling gold is rare in the sulphide ores. Most gold grains observed microscopically are below 20 µm in diameter, and they display irregular shapes.

Table 1.1: Common As bearing primary minerals (Smedley and Kinniburgh, 2002).



Name	Chemical formula	① Common impurities ② Mining uses ③ Environment
Arsenopyrite	FeAsS	① Pyrite, siderite and sulfides of Ag, Au, Co, Ni, Sb, Cu, Pb
		② Most common arsenic-bearing mineral and minor ore of gold
		③ High temperature ore veins, pegmatites, contact metamorphic rocks, and rarely in igneous basalt rocks
Orpiment	As_2S_3	① Realgar, calcite, barite, stibnite, gypsum, cinnabar and sulfides of Au, Ag, Cu, Pb
		② Commonly as an alteration product of arsenic minerals, especially realgar
		③ Low temperature hydrothermal veins (fractures in rock in which hot water has precipitated minerals), hot springs and as sublimates from gases emitted from volcanic fumaroles
Realgar	AsS/ As_4S_4	① Orpiment, calcite, stibnite and other metal sulfide ores
		② An important ore of arsenic
		③ Low temperature hydrothermal veins, volcanic hot springs, arid borate deposits and metamorphic marble pockets
Loollingite	$FeAs_2$	① Arsenopyrite, pyrite, chalcopyrite, pyrrhotite, biotite, sodalite, calcite, siderite, magnetite, galena, sphalerite,
		② Found together with other arsenic minerals and is thus a minor ore of arsenic
		③ In mesothermal deposits associated with other sufides and calcite gangue; also found in pegmatites
Enargite	Cu_3AsS_4	① Chalcocite, chalcopyrite, covellite, pyrite, bornite, galena, sphalerite, tennantite, and other metal sulfides
		② A rare copper mineral
		③ Moderate-temperature hydrothermal vein deposits. Late stage mineral in low temperature deposits

Table 1.2: Common As bearing secondary minerals (Smedley and Kinniburgh, 2002).



Arsenic (III) oxides		Arsenic (V) oxides	
Arsenolite	As_2O_3	Scorodite	$Fe^{3+}(AsO_4)\cdot 2H_2O$
Claudetite	As_2O_3	Kankite	$Fe^{3+}(AsO_4)\cdot 3.5H_2O$
Leiteite	$ZnAs_2O_4$	Symplesite	$Fe^{3+}{}_3(AsO_4)_2\cdot 8H_2O$
Trippkeite	$Cu^{2+}As_2O_4$	Conichalcite	$CaCu(AsO_4)(OH)$
Manganarsenite	$Mn^{2+}{}_3As_2O_4(OH)_4$	Erythrite	$Co_3(AsO_4)\cdot 8H_2O$
Gebhardite	$Pb_8(As_2O_5)_2OCl_6$	Mimetite	$Pb_5(AsO_4)_3(Cl)$

1.2.2 Organic arsenic

Inorganic As becomes methylated when it gets absorbed by the food chain and it is then converted into less toxic ones. Organic As are thus the less toxic kinds of As and they include monomethylarsine (MMA), dimethylarsine (DMA), and trimethylarsine (TMA) (Shrivastava et al., 2015; Bissel and Frimmel, 2003). Organic As, such as arsenobetaine or arsenocholine, are found in seafoods (Bissel and Frimmel, 2003). Methylation according to Goldberg (2011) is either the addition or substitution of methyl groups (CH_3) to a substrate. Thus, in this case, CH_3 group is added or substituted into an inorganic As mineral to become a methylated or organic As. As(III) methylated compound species exhibit greater toxicity than the As(V) ones. This is because As(III) methylated species are more responsive near tissue biological molecules than As(V) counterparts (Kalman et al., 2014). Consequently, As toxicity is dependent on its speciation as: As(III) > As(V) > organoarsenicals (Fergusson, 1990). Based on this, Bundschuh et al. (2021) then reiterated that mineral arsenite is sixty times extra toxic than arsenate, which is seventy times higher than the methylated As.

In soils, microbes such as bacteria, fungi, and algae can convert organic and inorganic As into a more volatile forms called arsines (AsH_3). Organic arsines (methyl arsines) are monomethylarsine (CH_3AsH_2), dimethylarsine ($(CH_3)_2AsH$) and trimethylarsine($(CH_3)_2As$) (Goldberg, 2011; Shrivastava et al., 2015). These arsine compounds are volatile, and they tend to escape into the atmosphere (Goldberg, 2011). Arsine is a very lethal gassy As species (Chauhan, 2008), produced in high anaerobic fields (Kossoff, 2012; Sharma, 2009). A decrease in pH favours AsH_3 formation (Shrivastava et al., 2015). In reducing conditions, As is released from wet soils and damp surfaces accompanied by CH_3AsH_2, $(CH_3)_2AsH$, and $(CH_3)_2As$ (Kossoff, 2012; Duker, 2005). Upon liberation into air through the action of microbes, these compounds may undergo oxidation in non-volatile forms and could be deposited back into the land (Bundschuh et al., 2021). The non-toxic forms of organic As are the arsenobetaine (AsB) and arsenocholine (AsC) (Kumaresan and Riyazuddin, 2001).

Thus, understanding As behaviour and speciation is key for designing empirical and appropriate remediation measures for mitigating As contamination problems in soils, sediments, and water and to eventually remove or reduce its human health-associated complications. Figure 1.2 summarises inorganic, organic, and biological forms of As including their empirical formulae and structure.

1.3 Natural and anthropogenic sources of As contamination

1.3.1 Natural sources

The prevalent forms of As present in the environment are the natural ones (Sailo, 2014; Smedley, 2002). They come from geological, hydrological and soil-forming biogeochemical processes (Escobar et al., 2006). Natural sources of As in soil and sediments are governed by the parent ore matter, volcanic activity, history of weathering, sorption ability, activity of soil microbes and precipitation ability (Kabata-Pendias, 2011). Arsenic concentration range between 1.7 and 400 mg/kg in alluvial rocks, and 1.3 - 3.0 mg/kg in igneous rocks (Escobar et al., 2006).

Additionally, natural sources may come from atmospheric emissions or when As-rich minerals are desorbed and dissolved (Bhattacharyya et al., 2003). According to Matschullat (2000), 17,150 tons of As are emitted to the atmosphere by volcanoes, 27 tons by the oceans, and 125 – 3,345 tons from burning of wood and oil as well as naturally occurring forest fires. Wind mobilization and deposition, and industrial releases also contribute to As in the environments. These suspended fragments fall on the land when fossil fuels are charred or during the use of smelters (a process termed as dry deposition) (Plant, 2007). Wet deposition, on the other hand, is the fraction of As from the atmosphere that gets dissolved in rainwater and subsequently falls back to earth (Kossoff, 2012). Other natural sources of As include those of arsines, discussed previously in section 1.2.2.

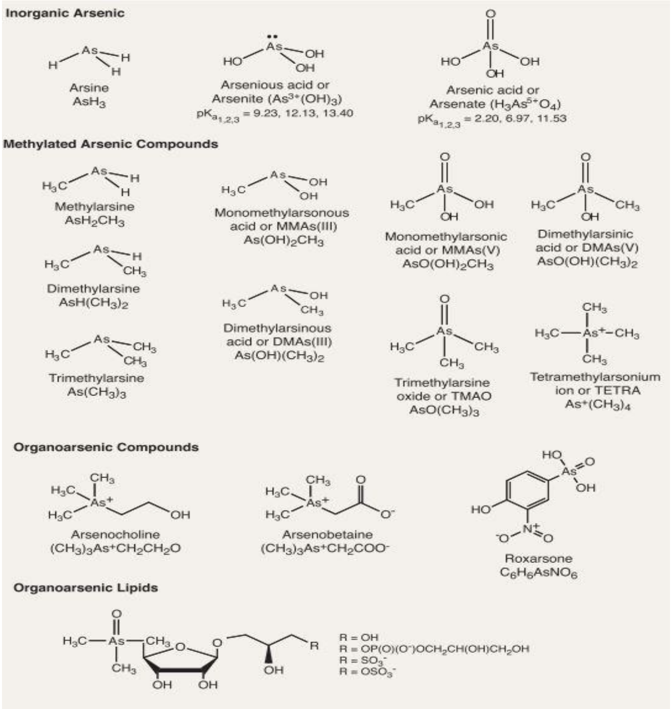


Fig. 1.2: Inorganic, organic, and biological forms of As in the environment. Source: O'Day (2006)

1.3.2 Anthropogenic sources

Areas that are less influenced by human activities contain As concentration of only a few nanograms per cubic metre (Bissel and Frimmel, 2003). Though soil As threshold contents may range from 0.01 - 100 mg/kg (Bissel and Frimmel, 2003), emissions from industrial companies, however, have increased dry and wet depositions into river sediments and agricultural lands (Kossoff, 2012). For instance, Williams (2001) found high As concentrations (range: 5 µg/L - 72 mg/L) in mining waters in seven countries of south-east Asia, Africa, and Latin America.

Burning of fossil fuels in households and power plants represents another anthropogenic source of As release (Bissel and Frimmel, 2003). For example, coal burning causes volatilisation of As_4O_6, leading to the discharge of As into the atmosphere (Matschullat et al., 2000). Fly ash from thermal power stations may also cause soil contamination (Bissel and Frimmel, 2003). Additionally, arsenical fungicides, herbicides, and insecticides may constitute anthropogenic sources as indicated by Goldberg (2011). Residues of As in soils with continuing application of arsenical pesticides, herbicides, and insecticides are found with maximum total content of 2 g/kg (e.g., Sadler et al., 1994; Yan-Chu et al., 1994). Arsenic is also employed in the manufacture of lead-acid batteries, other electronic products (Ning, 2002). These may constitute additional anthropogenic sources of As contamination to the soil, sediments, surface, and groundwater.

1.3.3 Arsenic contamination from gold mining

Gold mining and its activities constitute a major contributor to the release of high As content into the environment and mine surrounding areas (Drewniak and Sklodowska, 2013). Extraction of As-rich sulphide ores means creation of waste lands. These mine wastes are deposited as stockpiles and into tailing dams. Mine stockpiles and tailings can trigger discharge of As and other toxic elements into the environment. Concurrently, these can further be carried by running water or agents of erosion, and eventually pollute nearby ecosystem and various environmental media. Thus, As pollution from gold mining may either occur due to geogenic contamination (i.e., natural oxidation of parent material/the mine ore) or from anthropogenic sources (i.e., poor handling and/or management of mine wastes, etc.) (Bundschuh et al., 2021; Drewniak and Sklodowska, 2013; Hussain et al., 2019; Martiñá-Prieto et al., 2018; Mensah et al., 2020, 2021; Posada-Ayala et al., 2016; Study et al., 2014).

Fig. 1.3 illustrates natural and anthropogenic causes of As contamination due to gold mining, pathways of contamination and the associated-environment, social and human health impacts. As mentioned earlier, natural contamination mainly comes from the oxidation of the gold mining ore- the FeAsS. In other instances, mine tailings can also contain other sulphides (e.g., pyrite (FeS_2)) that are capable of generating acidity and releasing As when they undergo oxidation (DeSisto et al., 2016, 2017). As a result, Posada-Ayala et al. (2016) recounted that sulphide-dominated mine tailings are particularly rich source of As.

In other instances, As-rich tailing material may be carried by air or wind and may be deposited in the surrounding environment, posing threats to environmental and human health. Also, As may become mobilised during flooding (Mensah et al., 2021). Volcanic eruptions of such contaminated sites also have the capability of introducing and distributing As over a wide area. Besides, As can be generated through natural means from gold mining due to acid mine drainage. Acid mine drainage (AMD) is a spontaneous discharge of As when reactive sulphide minerals mainly pyrite and arsenopyrite are exposed to atmospheric oxygen, water and microbial action (Fosu et al., 2020).

In summary, AMD comes from the natural oxidation of the dominant gold mining sulphide minerals, FeAsS or the FeS in gold mining sites and spoils. Chemical, biological, and physical factors that influence AMD generation include air (oxygen), rain drop temperature and water saturation levels, microbial activity, and degree of metal sulphide exposure. Acid mine drainage or acid rock drainage (ARD) waters remain a major ecological challenge confronted by gold mining industries; demonstrated by the equations 1.1 and 1.2 (Drewniak and Sklodowska, 2013).

$$FeAsS(s) + 11/4O_2(aq) + 3/2H_2O(aq) \leftrightarrow Fe^{2+}(aq) + SO_4^{2-}(aq) + H_3AsO_3(aq) \quad (1.1)$$

$$H_3AsO_3 + 1/2O_2(aq) \leftrightarrow H_2AsO_4^- + H^+ \quad (1.2)$$

Anthropogenic sources of As contamination from gold mining may include abandonment of mining spoils, collapse of mine tailings, leaching of effluents from mine tailings, spillage from tailing dams, spillage from mine sites, surface runoff from mine sites, stockpiling of mine wastes, processing of mine wastes, poor/indiscriminate disposal of mine wastes and poor handling of mine hazardous materials as illustrated in Fig. 1.3.

1.4 Soil and biogeochemical factors influencing As contamination and mobilisation

1.4.1 Influence of soil pH

Soil pH is a major biogeochemical factor that affects sorption and desorption, oxidation state, solubility, mobility and thus toxicity of soil As species (Antoniadis et al., 2017; Bissen et al., 2003; Violante et al., 2010). In general, for cationic trace elements, lower pH results in higher mobility and availability, while higher pH results in increased mobility and availability for anionic species such as those of As (Antoniadis et al., 2017). For As, the explanation is that high pH reduces the electronegativity of silicate secondary compounds and hence facilitates their availability. Moreover, at high pH, positive charge on the surfaces of oxides diminishes, their activity and effectiveness for sorption decreases; and hence As retention reduces (Chen et al., 2012). These effects of pH on controlling As solubility and thus its availability are demonstrated in many previous studies.

For instance, Mamindy-Pajany et al. (2011) reported that studying the behaviour of As(V) onto mineral adsorbents containing Fe (e.g., hematite and goethite) as a function of pH aided to select the most suitable treatment for As stabilization in contaminated sediments. Moreover, Beiyuan et al. (2017) reported that pH is a key environmental factor that controls mobility of As in contaminated media; and that higher mobility of As occurs at lower redox potential and high pH. Further, batch leaching tests at different pH from Al Abed et al. (2007) showed a strong pH dependence on As and Fe leaching. This experiment focused on understanding the influence of pH on As availability and solubility; and to explain pH as a key factor of adsorption and mobility.

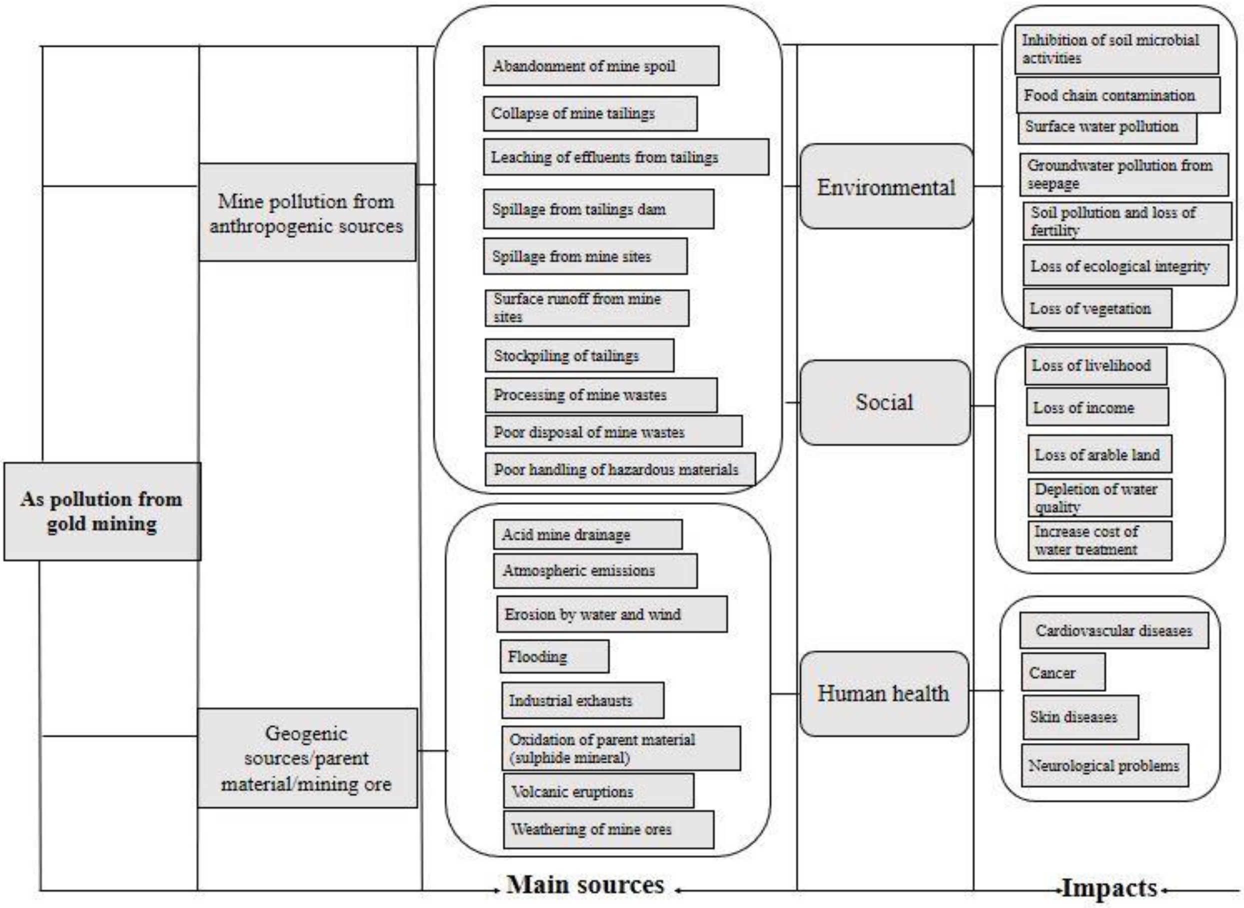


Fig. 1.3: Diagram depicting As contamination from gold mining, sources of contamination and environmental, social and human health impacts. Source: Author's construct

Violante et al. (2010) indicated that as the pH increases, the soil sorption capacity declines owing to a fall in positive charge of the inorganic material. Thus, increasing pH decreases sorption capacity of the soil for As species (Violante et al., 2010). Previous authors (e.g., Catalano et al., 2008; Martin et al., 2009; and Violante et al., 2008) explained the sorption capacity of anions using the "inner-sphere sorption and outer-sphere sorption" phenomena. They reported that specifically-sorbed ions or molecules have the potential to substitute OH^- found on the surfaces of variable charged-minerals. These reactions are encouraged at low pH, and they trigger OH^- groups to take protons. "Inner-sphere sorption" is also termed as specific sorption (Violante et al., 2008). Arsenates and arsenite form inner-sphere complexes (Violante et al., 2010). Depending on pH of the medium and surface coverage, As(V) may form different surface complexation onto inorganic soil constituents (O'Reilly et al., 2001). For instance, in wide pH ranges, As(V) sorption will rather be more encouraged than that of As(III). However, arsenite sorption onto ferrihydrite will be facilitated relative to arsenate in basic pH medium (Violante et al., 2010).

The pH dependence of As species adsorption using the ionization capacities and surface charge phenomenon of adsorbates and adsorbents has been explained by Mamindy-Pajany et al. (2011). For instance, negatively charged arsenate species ($H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}) are reported to dominate higher pH media (i.e., 2 - 12). The surface charge of adsorbents is thus governed by reactions involving transfer of hydrogen ion among the mixture or suspension and the mineral surface. The surfaces of the adsorbate (i.e., the mineral) can be positive, negative or zero; and they are dependent on the pH of the media. For instance, FeO are described by their point of zero charge which matches with the pH of the solution (pH_{ZPC}: pH at zero charge). At this point, the surface charge of FeO is zero because it has same charge as the environmental media (the solution). In such scenario, Mamindy-Pajany et al. (2011) indicated that arsenate adsorption is promoted when surface charge of adsorbents is positive (e.g., when pH of FeO adsorbates is lower than pH_{ZPC} of adsorbents). In conclusion, such phenomenon immobilises As in the environment and reduces its mobility and consequent ecological toxicity.

1.4.2 Influence of soil redox potential

Water saturation in sediments and soils alters their chemical and biological properties, controls microbial populations, and regulates soil processes. In such scenarios, soils undergo a sequence of reducing and oxidising reactions, as soil’s stage shifts from oxidising to reducing environments under flooding (Du Laing et al., 2009). Thus, concentration of As during flooding conditions is governed by the redox potential (E_H). This occurs either through direct changes in the soil E_H due to created dynamics during wetting and drying regimes or via indirect E_H-induced changes in pH, DOC, and the chemical behaviour of Al, Fe, Mn, and S (Antoniadis et al., 2017; El-Naggar et al., 2019; Rinklebe et al., 2016; Shaheen et al., 2014a,b).

Table 1.3: Some studies reporting As contamination in environmental media from different gold mining regions in Ghana

Number	Place/region	Environmental media affected	Arsenic concentration reported	Reference
1	Obuasi/Ashanti Region	Soils from gold mine tailings	542 – 1800 mg kg^{-1}	Bempah et al. (2013)
2	Tarkwa/Western Region	Surface and ground water sources	0.43 – 25.9 mg/l (surface water); 0.137 – 4.343 (ground water)	Armah et al. (2010)
3	Tarkwa/Western Region	River samples	< 1.0 - 73 µg/L	Asante et al. (2005)
4	Obuasi/Ashanti Region	Soils around mine tailings	581 - 1711 mg/kg	Antwi-Agyei et al. (2009)
5	Obuasi/Ashanti Region	Shallow wells and boreholes	2 - 175µgl^{-1}.	Smedley (1996)
6	Obuasi and Kumasi/Ashanti Region	Vegetation, food crops from farms and markets, cooked foods from homes, local fish and meats, soil, and water samples	0.07 – 7.20 mg/kg for samples in Kumasi (non-gold mining town) and 0.12 – 70.50 mg/kg for samples in Obuasi (gold mining town)	Amonoo-Neizer and Amekor (1995)
7	Amansie West/Ashanti Region	Streams, natural drainage systems, catchment basins, and farmlands	> 15 ppm	Duker et al. (2004); Gyasi et al. (2012)
8	Konongo/Ashanti Region	Water sources, untreated ore and tailing samples	0.04 and 12.2 mg/L for water samples; 2,978 - 4,628 ppm for ore samples; and 1,776 to 1,787 ppm was found for samples collected from tailing heaps	Boadu et al. (2001)
9	Tarkwa/Western Region	Gizzard, liver, kidney and muscle samples from chicken, goats, and sheep	Gizzard: 100% As Liver: 83% As Kidney: 80% As Muscles: 52% As	Bortey-Sam et al. (2015)
10	Prestea/Western Region	Soil samples collected from active and abandoned gold mine tailings	2000 - 8400 mg/kg	Mensah et al. (2020)
11	Amansie West, Obuasi, Bibiani, Dunkwa-on-Offin, Tarkwa, and Birim North	River, lake, and stream sediments	0.26-5.35 (Amansie West), 2.5 - 19.96 (Bibiani), 33.34-1010.83 (Dunkwa), 0.89-43.29 (Tarkwa), 250-1490 µgkg^{-1} (Birim North).	Armah and Gyeabour (2013)
12	Prestea/western region	Water and sediments	Water samples: 0.90 – 8.25 ppm. Sediment: 942 – 10,200 ppm	Serfor-Armah et al. (2006)

13	Prestea/Western Region	Water and sediments	15 - 325 µg/L	Obiri et al. (2016)
14	Jimi River Basin/Ashanti Region	Sediments, water and fruits	1746.5 mg/kg	Akabzaa et al. (2005)
15	Rural Ghana	Ghana's rural hand-dug wells and boreholes	> 10 µg/L	Norman et al. (2006)
16	Prestea/western region	Soil and farms around a mine tailing	3,144 mg/kg	Mensah et al. (2021)
17	Gambaga, Nalerigu, Nawchugu/southeastern- northern Ghana	Soil and basin sediment samples	22.68 mg/kg	Arhin et al. (2020)
18	Mining districts in southwestern Ghana including Obuasi	Soil samples in mining areas	246 mg/kg	Kazapoe et al. (2021)
19	Mining towns in southwestern Ghana	Soil samples from gold mining areas	246 mg/kg	Arhin et al. (2019)
20	Tarkwa/southwestern Ghana	Water (rivers and groundwater) and human urine samples	Groundwater: 0.1 – 4.0 µg/L Rivers/streams: 0.5 – 8.0 µg/L Urine samples: 34 – 700 µg/L	Asante et al. (2007)

For instance, decrease in E_H during flooding and rainfall regimes could increase the pH, which in turn enhances As mobility and vice versa (Niazi et al., 2018; Rinklebe et al., 2016). Also, redox potential could cause metal reduction during reducing periods (e.g., from Al^{3+} to Al^{2+}, Fe^{3+} to Fe^{2+}, and Mn^{3+} to Mn^{2+}), and consequently cause desorption and dissolution of As bound to Al/Fe/Mn oxides. The opposite occurs in oxidizing environments from longstanding dry periods (Shaheen et al., 2014a,b).

Redox also influences As mobilisation through its indirect induced changes on the soil organic matter. Soil carbon is an effective carrier for As. This is because the surface of carbon is made up of many positive ions, which provide fertile sorption grounds for As and consequently reduce its mobility. Under redox conditions, organic matter influences As mobility in many ways. The following hypotheses are proposed: i) organic matter dissolution, which causes the liberation of the bound-As; ii) pH change associated with reduction reactions concerning organic matter desorption- causes desorption of held-As; iii) creation of soluble organic matter from the presence and decay of microbial biomass; iv) reductive dissolution of organic matter leading to release of Mn- and Fe-oxyhydroxides bound to organic matter and consequent release of bound-As (e.g., Grybos et al., 2007, 2009).

Redox potential regulates environmental toxicity of As through its influence on the availability of potentially mobile As fractions. Potentially mobile fractions of As consist of the un-specifically bound As, As specifically-sorbed on mineral surfaces, those bound to the amorphous and low crystalline iron oxides, and As bound to crystalline iron oxides (Dybowska et al., 2005; Wenzel et al., 2001). These components may be available due to biogeochemical changes including for example, the soil pH and redox settings. For instance, during reducing conditions, As bound to the Fe oxide fractions could be released (Lemonte et al., 2017) and become available for environmental pollution and accumulation in the food chain contamination. Thus, flooding and its related activities as well as and the existing E_H could influence the safety of food crops grown in As-contaminated mining areas.

Moreover, the effect of redox conditions equally plays a very critical role in controlling the fate of As transport by altering the oxidation states. This consequently affects their mobility and toxicity in aquatic environments and waterlogged soils (Rinklebe and Du Laing, 2011). As earlier stated, As(III), for instance, is more mobile than that of As(V). This could be facilitated by the presence of reducing agents in soil, which can reduce As(V) to As(III). Thus, addition of organic matter or waterlogging fields could accelerate this reduction and consequently increase As availability (Rinklebe, Shaheen, & Yu, 2016; Shaheen et al., 2018). Since As(V) is strongly retained by inorganic soil components, microbial oxidation results in the immobilization of As. Arsenic in well drained conditions is present as As(V), and as As(III) in reduced soil conditions, together with elemental form As (As-0) and as arsine (H_2As) (Bolan et al., 2014).

1.4.3 Influence of metal oxyhydroxides (Al/Fe/Mn)

Metal oxides (Al/Fe/Mn) perform critical functions regarding As pollution in soils and water systems (Bolan et al., 2014; Komárek et al., 2013; Wang et al., 2021). Oxides have significant, energetic surface areas and amphoteric nature, characteristics which provide suitable sites for remediation of As in contaminated spoils. Soil remediation with oxides is made possible because of their high capacity to adsorb and immobilise As through processes such as specific sorption, coprecipitation, and by forming inner-and outer-sphere complexes (Bolan et al., 2014; Komárek et al., 2013). Thus, surfaces of FeO(OH) may perform a key task in retaining As. Positive charged surface, for instance, leads to binding of As, and vice versa.

Metal oxides (e.g., ferric oxides, manganese oxides, aluminium oxides, titanium oxides, magnesium oxides, and cerium oxides) are considered promising adsorbents for treatment of As because they have large surface areas (Hua et al., 2012; Koo, 2012). Mench et al. (1998) reported decline in water extractable-As content, and lower uptake in plant tissues, when iron oxides were applied to As-contaminated garden soils. Similarly, Hartley and Lepp (2012) assessed the effectiveness of four Fe-bearing additives for reduction of As in three contaminated soils and found that goethite stood out as the most promising candidate for reducing uptake of As into the plant shoot As.

1.4.4 Influence of soil organic matter

Soil carbon is basically carrier of As and influences As (im)mobilisation via many means. For instance, there could be the formation of carbonates and carbon-As complexes; presence of surface functional groups; occurrence of positive and negative surface ions; indirect effects on the soil pH; and activation of microbes required for redox-controlled As solubility. For instance, a lower pH reduces the many negative charges on the surfaces of carbon and consequently increases its adsorption capacity for As and vice versa.

In calcareous soils and sediments, for instance, the presence of carbonates creates a valuable shield against a decline in their pH (Du Laing et al., 2009). Thus, carbonate production from soluble organic carbon, e.g., during liming of the soil, could concomitantly increase the presence of negative charges and may facilitate solubility and mobilisation of As.

Organic matter indirectly affects fate of As transport and migration by providing a food source for microorganisms. Additionally, provision of C can arouse microbial population and activities. This may catalyse a sequence of redox reactions in the presence of electron acceptors (e.g., oxygen and iron) (Du Laing et al., 2009). These reactions largely affect solubility of As in contaminated mining spoils. For instance, addition of wastewater to soils could raise sources of C supply and nutrient contents. Consequently, populated microbes may enhance reduction of As into more reduced forms (Kunhikrishnan et al., 2017). More on redox impacts on As mobilisation is elaborated earlier in section 1.4.2.

Other factors of interest that might influence As mobilisation increase its concomitant health threat include cation exchange capacity, soil particle distribution (e.g., presence of clay minerals), sulphide contents, anions presence (e.g., sulphates, chlorides, carbonates, fluoride, etc.), salinity and age of the mining spoil.

1.5 Toxicity of arsenic

Arsine gas (AsH_3) is reported as the most toxic compound (Kossoff, 2012; Sharma, 2009), and the fatal dose is 250 mg/m^3 at an exposure time of 30 minutes (Shrivastava et al., 2015). As earlier explained, As toxicity rests on their oxidation states and compound formulae (Nakamura, 2011). Soil inorganic As, for instance, are accumulated in the food chain, they become toxic, and in turn tend to affect various life forms (Shrivastava et al., 2015). As discussed earlier, As(V) is relatively less toxic than that of As(III). Additionally, As(V) is commonly immobile and found in mineral forms, whilst As(III) easily becomes mobilised into aquatic and living organisms. Thus, the fatal dose (LD_{50}) of As(III) is lesser (15 – 42 mg/kg) than that of As(V), with 20 – 800 mg/kg (Kaise et al., 1992). Also, As(III) binds with sulfhydryl groups (also called the ‘thiol’ groups- RSH) of proteins, and consequently results in clinical manifestations (Shrivastava et al., 2015). In the organic groups, fatal dosages for MMA (1.8 g/kg) and DMA (1.2 g/kg) are much lesser than TMA (10 g/kg)’s (Nakamura et al., 2011).

1.5.1 Plant health impacts

Plants growing in uncontaminated soil contains As < 3.6 mg/kg (Gebel et al., 1997), whilst Kabata-Pendias (2011) reported relatively specific value range (0 - 1.5 mg/kg). Plants can generally absorb As from the soil either through root uptake or dry deposition on its leaves (Shrivastava et al., 2015; Su et al., 2014). Plants can show signs of As phyto-toxicity through impeding germination of seed, decreasing the height of the plant and causing stunted growth, reducing growth of root, exhibiting necrosis in the leaves and reducing concentration of chlorophyll, lowering the yield of plants and they may be causing death of crops (e.g., Shrivastava et al., 2015; Su et al., 2014).

1.5.2 Soil microbial activities

Arsenic contaminated soils have reduced and impeded activities of soil microbes and their activities (Su et al., 2014). For instance, Kandeler et al. (1997) found that there was reduced microbial biomass in an As-contaminated soil closer to a mine site compared to those located farer away from the mine site. Additionally, Fliebbach et al. (1994) stated that high As content above the threshold could decrease soil microbial biomass significantly. Further, soil enzymes have a key function to play in the decay of organic matter and in cycling of nutrients. Arsenic in the soil thus lessens the effectiveness of soil enzymes (e.g., Su et al., 2014; Gao et al., 2010). Consequently, Chander et al. (1995), found that enzyme activities in As-contaminated soils declined by ten to fifty times.

Gao et al. (2010) studied pollution effects of toxic elements on soil enzyme activities and their microbial community. They found that microbial populations were significantly lower under polluted sites than under control treatment, with soil bacteria decreasing most in population size than the other soil microbes such as fungi and actinomycetes. Further, elevated heavy metal concentrations and toxicant levels differently impacted on soil enzyme activities, with inhibition of phosphatase, urease, and dehydrogenase activity.

Furthermore, Koo (2012) found that enzyme activities were negatively impacted due to high As contents in mine tailings. More particularly, the abundance and activities of soil enzymes were inversely proportional to the water-soluble fraction of As in the mining spoil. Thus, the soil enzymes activities were mainly affected by the As water-soluble fraction than by the other fractions. In same study, the treatments that decreased the As water-soluble fraction enhanced the soil enzyme activities.

1.5.3 Human health

Arsenic is categorised as a Class-I human carcinogen (IARC, 2012) and can cause many health complications (Ahoulé et al., 2015; Bortey-Sam et al., 2015). Some of these As-associated health complications are earlier highlighted in Fig. 1.3, and will be later discussed in chapters 3 and 4. Elevated As contents are observed in food crops in gold mining areas in Ghana, which can subsequently impact the health of residents (e.g., Obiri et al. 2006, 2010). Chronic exposure to As also causes skin lesions (Su et al., 2014). Skin problems such as melanosis (hyperpigmentation), keratosis, and leukomelanosis (hypopigmentation) are reported in As-contaminated areas in India (e.g., Shrivastava et al., 2015; Su et al., 2014). Arsenic is further reported as a famous carcinogenic element and can cause cancer (e.g., that of the skin, the lung, the bladder, the liver, and the kidney) (IARC, 2012; Khan et al., 2020). In Bangladesh, As poisoning in cattle resulted in difficulty in walking, diarrhoea, and death (Eisler, 1988).

Mycobacterium ulcerans, the bacterium responsible for Buruli ulcer, thrives in As-contaminated areas (Duker et al., 2004). Interestingly, As has been found to pose a health threat to women and children in gold mining areas, with median As hazard index values ranging from 3,000 to over 65,000 (Mensah et al., 2020). The oxidation of As-dominated minerals, which usually happens in mine spoils, provides a medium for this ulcer causing bacterium, and more than 2,000 cases of this ulcer have occurred in mining districts in Ghana (Duker et al., 2004). In Burkina Faso, skin lesions, ulcer necrotic tumour and deaths found predominant among village patients were later linked to As-poisoning from drinking of As-contaminated-groundwater (Ouedraogo, 2006; Smedley et al., 2007).

The health implications of As in animal foods of livestock (e.g., gizzard, liver, kidney, and muscle) in mining contaminated regions in Ghana are provided in Bortey-Sam et al. (2015). The study detected As contents ranging from 52% - 100% in the animal foods consumed by people in the mining areas. The pollution was attributed to the oxidation of the gold bearing ores; processing of the ore, which produces arsenic trioxide (As_2O_3) into the environment; migration of As into topsoil and in watercourses; and As absorption into food crops.

1.6 Remediation of As contaminated sites

From the afore-discussed environmental and human health threats posed by mining spoils on residents in mining communities, it is thus imperative that gold mining is carried out in a sustainable manner. This includes remediation and restoration of mine contaminated and degraded sites. In this section, I present and discuss briefly various green and sustainable remediation options available for cleaning As and reducing its contamination in mine lands. Recent and detailed reviews of these green technologies and sustainable options are provided in Hou et al. (2020), Palansooriya et al. (2020), and Wang et al. (2021). Bolan et al. (2014) reviewed literature on remediation of metal and metalloid contaminated soils and categorised the techniques of remediation broadly into mobilization and immobilization methods; explained earlier in section 1.1.

1.6.1 Mobilisation strategies for As remediation

1.6.1.1 Use of organic amendments

Application of organic materials generally modifies the soil physico-chemical and biological properties. They thus improve the structure of the soil, improve the water retention ability of soils, control soil temperature and pH, improve nutrients and organic matter of the soil as well encourage microbial population and activities. Consequently, organic amendments enhance soil quality, boost plant growth, and increase crop yield. In other instances, organic soil amendments are added with the purpose of cleaning the soil and ameliorating presence of toxic elements in contaminated soil and water.

For instance, amendments like sewage sludge (biosolids), manure, biochar, compost can be added to As-contaminated soils to increase mobility for subsequent uptake by plants. In this regard, there were increases in leachable As in compost-amended soils (e.g., Redman et al., 2002). This was attributable to DOC competition with As for sorption sites. Shaheen et al. (2017) observed that soil irrigation with sewage effluent concomitantly increased their total As contents by 3.3 folds as compared to irrigation with clean water.

Furthermore, under flooding condition, Yang et al. (2022) found that pig prepared biochar enhanced solubility of As and subsequently increased its mobilisation and release. They gave two main reasons to explain this observation: i. ‘anion exclusion’ resulting from the electrostatic repulsive force between negatively charged pig biochar and the leading negative As species (e.g., H_2AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}); and ii. production of soluble phosphate by the pig biochar which competed with As (an anion) for binding sites on soil minerals.

1.6.1.2 Application of inorganic P fertilisers and liming materials

Application of P fertilisers to As-contaminated soils can increase As availability and consequent environmental health threats. The role of P in As fate of transport and release has been extensively explained in previous sections. Thus, P fertilisers may be used to enhance the phytoextraction efficiency of hyperaccumulating plants for As.

Liming can also be done to increase and enhance mobilisation strategies for As removal. Generally, liming is carried out to correct the soil pH, by decreasing the presence of protons and increasing the presence of hydroxyl ions on the soil colloids. Liming materials, e.g., carbonates, oxides, and hydroxides of alkali and alkali-earth metals (e.g., Ca, Mg and Na) could be used to increase the soil pH and lessen soil acidity. Also, eggshells, mussel shells, and oyster shells, biochar, red mud, and clay minerals have soil liming abilities (Palansooriya et al., 2020).

Applying higher amounts of MgO can cause mobilisation of metalloid PTEs including As, and restriction of trace elements (e.g., Fe, Mn, and Zn) (Holland et al., 2018); which may be beneficial either to support plant growth or aid remediation of toxic substances in the soil. Thus, deciding on the appropriate soil properties and forecasting anticipated soil pH are key things to consider prior to addition of lime (Palansooriya et al., 2020). Even so, combining liming materials with other amendments can amplify liming effectiveness and reduce the associated-ecological impacts. Higher pH, reduction in acidity, production of more negative ions and charges, and increased formation of total CO_3^{2-} associated with liming are key reasons underpinning their influence on As mobility.

1.6.2 Immobilisation strategies for As remediation

Immobilisation of As could also be accomplished chiefly through adsorption, precipitation, and complexation reactions. These mechanisms cause redistribution of elements from solution state to solid state, and consequently reduce the solubility and bioavailability of the toxic materials. Examples include clay, cement, zeolites, minerals, phosphates, organic composts, and microbes (Bolan et al., 2014). Some studies (e.g., Hartley and Lepp, 2008; Lebrun et al., 2020) have shown the remediation ability of residues (e.g., red mud and iron oxides) for treating As-contaminated sites and reducing their bioavailability. Others have used combination of treatments or modified red mud or iron-oxide with biochar in reducing the bioavailability and release of As into the surrounding (Zou et al., 2018). Immobilisation technologies may be carried out off-site (*ex situ*) or on-site (*in situ*). On-site strategies are favoured because of lesser labour and energy needs, but their implementation will be contingent on peculiar site situations (Wuana and Okieimen, 2011). The strategy for solidification/stabilization treatment methods involves joining or inoculating agents for treatment into the polluted soil (Wuana and Okieimen, 2011).

1.6.3 Plant techniques for As remediation

This method of soil remediation uses green plants to facilitate removal of contaminants from the soil (Mensah et al. 2021; Reeves et al. 2017; Sheoran et al., 2010). According to Jiang et al. (2015), “phytoremediation, a green approach using plants to remediate toxic compounds, is a cost-effective, socially acceptable, and environmentally friendly technology for soil, and groundwater clean-up”. Reeves et al. (2017) suggested that hyperaccumulator plants can be assisted with application of conventional fertilizers to enhance their removal of high amount of toxic elements from the soil. Additionally, high biomass production capacity and high concentration of the desired element that can be extracted by the plants are two critical factors to be considered when selecting species for phytoremediation (Reeves et al., 2017). Other factors to consider in selecting suitable species for mine land remediation are provided in previous studies (e.g., Antoniadis et al., 2021; Mensah, 2015, 2021). It is thus recommended that hyperaccumulation plants are those plant species that are capable of accumulating 1000 mg As/kg in the dry matter of the plant tissue (e.g., Baker et al., 2000; Mahar et al., 2016). Recently, Mensah et al. (2021) observed that *Chromolaena odorata*, an indigenous plant growing closer to a derelict mining tailing in Ghana could offer potential for cleaning As from mining sites. In that study, *Chromolaena odorata* had As translocation factor of 4.7, further implying its ability to accumulate As from the mining soils. Translocation factor, bioconcentration factor and bioaccumulation factors are other indices used to appraise the phytoremediation potential of plant species; details are discussed in chapter 3.

1.7 Research hypotheses and objectives

1.7.1 Hypotheses

This study was premised on the following assumptions, that:

i. Bulk and soil particle distribution differently affect the geochemical fractions, species, and mobility of As in the topsoil and profiles of abandoned and active mining spoils.

ii. Sites near abandoned gold mine spoil are contaminated with potentially toxic elements, may pose health risks to persons in gold mining region and native plant species near abandoned contaminated mine spoil may provide potential for remediation.

iii. Various reducing and oxidizing conditions will affect the mobilization and species of As from an As-contaminated gold mine spoils; and mobilization will be affected through redox-induced impacts on soil pH, dissolved organic matter content, and soil chemistry of Al, Fe, Mn, and S.

iv. Biochar, compost, iron oxides, inorganic fertilisers and manure provide potential measure to remediate the bioavailable As and the specific-sorbed As fractions in the gold mine spoil and restore the soil quality.

1.7.2 Objectives

The overall objective of this study was to study the extent and distribution of potentially toxic elements contamination, particularly As, from gold mining spoils and to propose sustainable soil remediation alternatives to repair the damage caused to the land during and after mineral exploration, to reduce release of As, and spillage from the mining site, to reclaim the mine sites and to ensure safe re-use of the land. Specifically, the study addressed the following objectives:

i. To quantify the spatial distribution of As, their dominant species, their geochemical fractions, potential mobilisation in the bulk, coarse and fine fractioned-soils, as well as soil and human health risks of children and adults exposed to As in contaminated active and abandoned gold mine spoils.

ii. To assess soil contamination and human health risk of potentially toxic elements via soil ingestion in sites near abandoned gold mine spoil and explore the potential of indigenous plant species for remediation.

iii. To quantify the impacts of different reducing and oxidizing conditions and redox-induced changes in soil pH, dissolved organic matter content, and chemistry of Al, Fe, Mn, and S on the mobilization and speciation of As from the As-contaminated gold mine spoils.

iv. To determine if *in situ* treatment of a mine spoil with biochar, compost, iron oxide, manure and inorganic NPK fertiliser may provide potential measure for remediation of bioavailability of As and improve soil quality of abandoned As-contaminated gold mine spoil.

1.8 Summary of methods (materials and methods)

1.8.1 Determination of total element contents and risk assessment

Before any full-scale remediation strategy could be planned on any soil or environmental media, initial characterisation of the media under investigation is a pre-requisite requirement. Thus, determination of total pseudo-trace element contents is a very important initial step and key to identifying a potential risk associated with toxicity of an element. Soil characterisation, determination of soil physico-chemical properties as well as determination of the total element contents in the contaminated gold mine spoil soils were carried out in each of the experiments using various laboratory methods and protocols. These were done using the nitric acid digestion method. The results generated enabled me to further do a calculation and carried out a risk assessment in terms of soil contamination and human health impacts of the mining spoils on the people living in the mining areas. Risk assessment in terms of soil contamination and human health threats is published in *Environmental Pollution* and *Science of the Total Environment* and discussed in detail in chapters 2 and 3. Details of the extraction are described in each of the published manuscript in the chapters.

1.8.2 Sequential extraction experiments

Total contents are not good indicators of bioavailability and do not reflect true toxic effects of potentially toxic elements (PTEs) (Wenzel et al., 2001). It is for this reason that the sequential extraction procedures (SEP) are employed. This procedure separates As into different binding forms or geochemical fractions. These fractions are defined as fraction I (non-specific sorbed-As/water soluble); fraction II (exchangeable and surface/specifically adsorbed); fraction III (crystalline iron oxide fraction); fraction IV (amorphous iron oxide fraction); and fraction V (residual fraction). Fractions I and II are classified as the soluble fractions and they are most toxic in terms of ecosystem and environmental pollution and toxicity. Greater percentages indicate greater environmental risks to water, groundwater, and translocation into the food chain. Details of these experiments are described in chapters 2, 4 and 5. Fig. 1.4 gives a summary of the sequential extraction procedure in a flowchart diagram and Fig. 1.5 shows a sequentially extracted As samples ready for analyses.

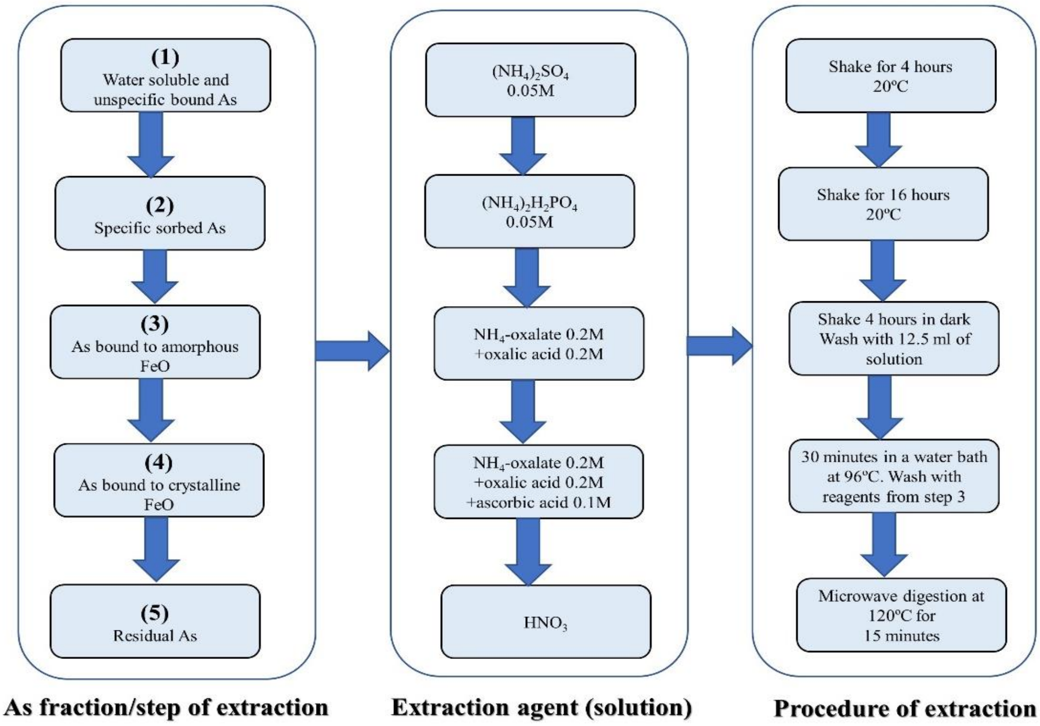


Fig. 1.4: Flow chart diagram of the sequential extraction procedure used in the study. Source: Author's own construct.

1.8.3 Size fractionation experiments

Research indicates that soils with higher clay content contain greater proportions of As than sandy soils (Antoniadis et al., 2017; Mensah et al., 2020). For a more detailed analysis of As geochemical fractions, the composite sample from the abandoned, active and profiles mining spoils collected in Ghana was further separated into a coarse and a fine fraction. Coarse fraction consisted of sand, whilst the fine fraction consisted of silt and clay. Details of this experiments are described in the published article in chapter 2.

Fig. 1.5: Soil filtrates ready for analysis and determination of As geochemical fractions with the inductive couple plasma-optical emission spectrometry (ICP-OES). Picture taken at Ruhr University Bochum Geography Institute Laboratory on the 14th of June 2019.

1.8.4 Remediation incubation experiments

Using a 28-day laboratory incubation study, I tested eight different soil amendments for remediation of the As-contaminated mining spoils and tailings. These amendments included composts, rice husk biochar, corn cob biochar, NPK fertiliser, manure, sewage sludge, iron oxide and red mud. These amendments were applied at different rates- 0.5%, 2% and 5% (w/w) to 300 g of the contaminated soil in an incubation jar. The NPK fertiliser was also applied at the rates of 5, 0.2 and 0.1 g/kg. Fig. 1.6 shows soil samples mixed with different rates of soil amendments and ready for incubation. Details of the experiments are described in the published article in chapter 5.

1.8.5 Redox experiments using the automated biogeochemical microcosm experiments

As indicated earlier, solubility and mobilisation of As under flooding or waterlogged conditions in a watershed is controlled by the soil redox chemistry (Shaheen et al., 2016; Rinklebe and Shaheen, 2017). These flooding conditions and redox potential concomitantly influence mobilisation of As into surface and groundwater, and affect uptake and translocation by plants (Zimmer et al., 2011; Ye et al., 2012). Studying the mobilisation of As due to varied redox settings can aid in risk assessment and in designing appropriate remediation techniques for As contaminated fields. Fig. 1.7 shows an As-contaminated abandoned mine spoil under waterlogged condition in Ghana.

Fig. 1.6: Arsenic-contaminated mine spoil soil mixed with different rates of soil amendments, ready for incubation. Picture taken at the Ruhr University Bochum Geography Institute Laboratory on the 20th of August 2019.

Experiments on redox effects on mobilisation of As was carried out using the automated biogeochemical microcosm (MC) in a simulated laboratory conditions to mimic conditions on the field. Briefly, in this method, the redox potential levels of the soil suspension are reduced and oxidised by alternate flushing the MCs with N_2 and synthetic air/O_2. The values of redox potentials (E_H) and pH as well temperature were recorded into a data logger connected via a computer to the system. Pre-set E_H windows were set and automatically maintained with the flushing of N_2 (to lower E_H) and synthetic air/O_2 (to raise the E_H). E_H and pH of samples taken 6 hours before the pre-defined E_H windows were recorded. Fig. 1.8 shows a typical soil microcosm in operation. Samples (herein, referred to as suspension or soil slurry) were collected at regular intervals using syringes (Fig. 1.9). The whole filtration process took place in a glove box at O_2 concentration at 0% (Fig. 1.10). Fig. 1.11 shows prepared samples ready for analysis. Details of this experiment are described in the published article in chapter 4.

Fig. 1.7: An abandoned As-contaminated mine spoil in Ghana. Source: Field campaign, March 2018.

Fig. 1.8: A typical soil microcosm in operation. Picture taken during experiments at the laboratory of soil and groundwater management, Bergische University in Wuppertal, September 2018.

Fig. 1.9: Samples (soil slurry/suspensions) collected in syringes for centrifugation and filtration. Source: Experiments at the laboratory of soil and groundwater management, Bergische University in Wuppertal, September 2018.

Figure 1.10: Glove box for sample filtration and subsampling under anaerobic conditions. Source: Picture taken during laboratory experiments at the Bergische University in Wuppertal, September 2018.

Fig. 1.11: Samples prepared for analysis. Source: Self-captured picture during laboratory experiments in Bergische University in Wuppertal, September 2018.

1.8.6 Arsenic speciation experiments using K-edge X-ray absorption near edge structure (XANES)

The bioavailable portion of As is also dependent to an extent on the speciation of the contaminant (Cancès et al., 2008). Thus, my objective here was to determine and quantify the dominant species of As and Fe in: i) the bulk soils of active and abandoned gold mine spoils collected from gold mine fields; ii) samples collected at various soil reducing and oxidising potentials. These experiments were carried out at the National Synchrotron Radiation Research Centre in Taiwan at Beamlines 07A and 17C1. Details of the experiments are described in the published article in chapter 4.

1.8.7 Pot experiments

Tripathi et al. (2007) suggested two strategies to help counter As pollution: removal of As from the environment, and growth and tolerance of safe crops that can be grown in the presence of As contamination. Thus, I employed a pot experiment using iron oxides, manure and compost applied solely or combination with rye grass for ameliorating the abandoned As-contaminated mining spoils. The amendments were carefully mixed with 3 kg of air-dry soil (< 2 mm) and kept in plastic pots of 3000 cm^3. Amendments were added solely or in combination at the rates of 5 % weight by weight amendment: soil basis. Treatments included control soil (without addition of soil amendments); compost only; manure only; iron oxides only; compost and manure; compost and iron oxides; and manure and iron oxides. Where amendments are applied together, each amendment were added at equal proportions. NPK fertiliser were also applied at the rates of 5 g/kg (0.5%) to all treatments to stimulate plant germination and growth. Each treatment will be replicated three times and gave a total of 21 pots (7 treatments x 3 replications). The experiments lasted more than 60 days and soil and plant analyses were done after this period.

1.9 Structure of the thesis

This thesis is organized into six chapters. The thesis is cumulative and is made up of four separate experimental studies in addition to general introduction, discussions, conclusions and recommendations for policy action and further studies.

Chapter one: introduces the problem and provides background to the study. Many concepts related to As chemistry, pollution and factors affecting mobilization as well as toxicity of As on environmental resources and human health are also reviewed. The chapter also briefly introduces the methods used to achieve the study objectives.

Chapters two: is a published manuscript on As contamination in abandoned and active gold mine spoils in Ghana, their geochemical fractionation, speciation, and assessment of the potential human health risk. This chapter is published in Elsevier *Environmental Pollution* (Mensah et al. 2020).

Chapter three: is a published paper on human health risk via intentional and accidental soil ingestion of potentially toxic elements and remediation potential of native plants near the abandoned mine spoil. This chapter is published in Elsevier journal *Science of the Total Environment* (Mensah et al., 2021).

Chapter four: this goes a step further and investigates the mobilization and speciation of As in the abandoned spoil under reducing and oxidizing conditions. This experiment was carried out at Bergische University in Wuppertal and National Synchrotron Radiation Research Centre in Hsinchu City in Taiwan. The chapter is a prepared manuscript ready for submission in the *Journal of Hazardous Materials*.

Chapter five: the chapter is based on the manuscript that reports findings from an experiment that investigated the impacts of biochar, compost, iron oxides and inorganic fertilizer on As bioavailability and soil quality restoration of the abandoned mine field. The chapter is submitted for publication in Elsevier journal *Ecotoxicology and Environmental Safety*.

Chapter six: provides general discussions of the study, provides summary, and proposes recommendations for a sustainable gold mining sites remediation and areas for further studies.

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CHAPTER 2

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

This chapter is based on the manuscript of the published article: **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. *Environmental Pollution*, 261, 114116. https://doi.org/10.1016/j.envpol.2020.114116

Abstract

This work aims at studying the total content, geochemical fractions, and species of arsenic (As) in the bulk soil and in the coarse and fine particles of topsoil and soil profiles collected from active and abandoned gold mine spoils in Ghana. We also assessed the human health risk for adults (male and female) and children. 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). Total As contents varied from 1,807 to 8,400 mg kg^{-1}, with the extremes occurring at the abandoned mine spoil. Arsenic was higher in the fine fraction (< 0.63 µm) than in the coarse fraction. 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 ($FeAsSO_4$ = 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 topsoil was higher (48 - 61%) than in the coarse fraction (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.

Keywords: Arsenic mobilisation, geochemical fractionation, gold mine spoils, soil contamination, human health risks.

2.1 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 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 source due to human activities including mining ones (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 mobilization 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 topsoil 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 fractioned-contaminated mine spoils, and iv) to assess soil and human health risks of children and adults exposed to As in contaminated gold mine spoils.

2.2 Materials and methods

2.2.1 Study area, soil sampling and characterization

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 meters; Fig. 2.1). 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. The mean annual temperature is 26.6 °C. The soils in the area are developed from weathering and natural oxidation of the auriferous Birimian sedimentary rocks, which are made up of quartz veins and sulphide ores (Hayford et al., 2009).

Gold mining, both large and small scale, form the major source of occupation and had resulted in extensive land degradation, water pollution, depletion of arable lands, loss of soil fertility and pollution with toxic elements in the area (Mensah et al., 2015). The major type of gold ore found in this area is the sulphide mineral. Gold in these ores is fine-grained and often locked in arsenopyrite crystals (Oberthuer et al., 1997; Hayford et al., 2009). Both underground and surface are the common types of mining practiced at the area.

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, which is currently being re-exploited by a local mining company and by illegal small-scale gold miners. The area (05°23′38″N, 02°09′58″W; Fig. 2.1) covers a total land space of approximately 126,000 m^2 and is completely bare of vegetation. Here, a composite sample was collected in early 2017 by sampling ten spots from 0 - 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 – 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. 2.1), which has been in operation since 1997. The area covers a total land space of approximately 121,000 m^2. Here, ten top soil samples were collected from different random sampling spots from a depth of 0 – 20 cm.

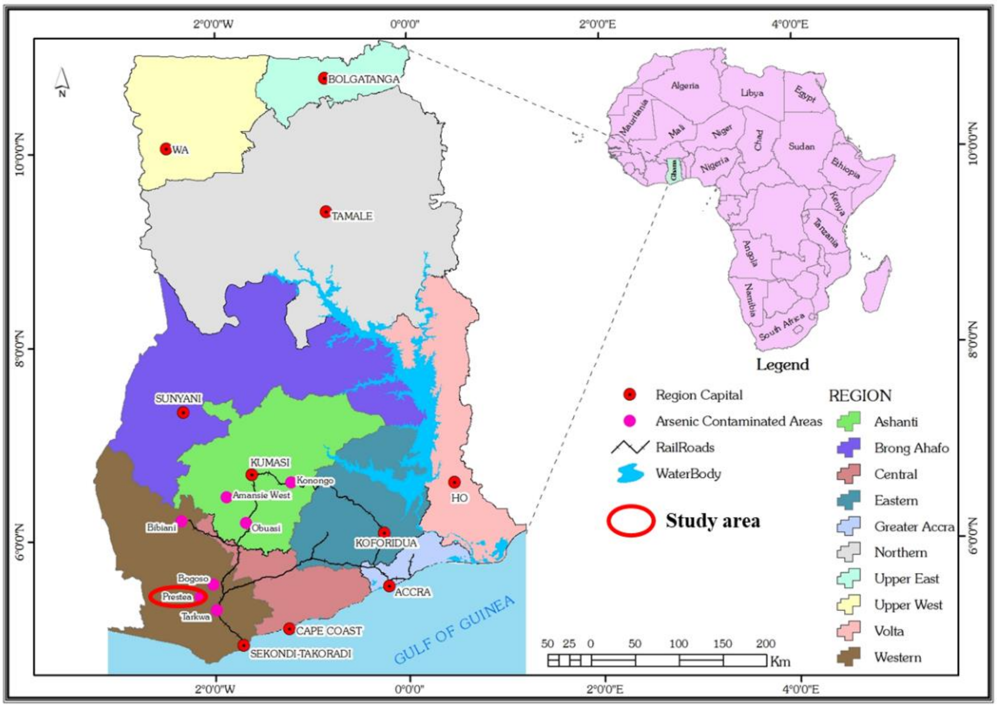

Figure 2.1: Map of Ghana showing the study area and other arsenic contaminated areas

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 $CaCl_2$ solution ratio of 1:5 using the pH meter (Sentix 41, Wissenschaftlich-Technische Werkstatten (WTW) GmbH, Weilheim, Germany). 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 Loeppert and Inskeep (1996).

2.2.2 Extraction and determination of total content and geochemical fractions of arsenic in the bulk soils and coarse and fine particles

For the analysis of 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 minutes with 10 ml concentrated nitric acid; then, the digested was diluted with 10 ml de-ionized water, homogenized, and filtered through a 0.45 ml membrane filter (USEPA, 2007).

The soil samples were further separated into a coarse and a fine fraction. 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 minutes and then poured through a sieve of 63-µm mesh size. The suspension containing the fine fraction (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) fraction. The pH, total P, total carbon, total nitrogen, Fe oxides and As concentrations of the fine and coarse fractions 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 Divison). As a quality measure for the sequential extraction procedure, the extraction process was conducted in triplicates and the recovery rate was calculated:

$$Recovery = \frac{(\sum \mathrm{FI} - \mathrm{FV})}{Total\ As}\ x\ 100 \qquad (2.1)$$

where (∑ FI – 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.

2.2.3 Arsenic K-edge XANES spectroscopy analysis

Selected soil samples (two abandoned samples and one active) containing As concentrations of 4,208.8, 6,909.7 and 2,450.0 mg/kg, respectively were selected for As *K*-edge X-ray absorption near edge structure (XANES) analysis. The XANES spectra was collected at 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(V)-As, ferrihydrite(III)-As, Goethite (V)-As, and Goethite (III)-As, by a function of fit all combinations in Athena, then the best fit was chosen based on R-factor values. The scorodite and FeAsS were the best combinations for our samples; therefore, scorodite ($FeAsSO_4$) and arsenopyrite (FeAsS) were chosen for the linear combination fitting. Details of the methodology were reported in Liu et al. (2006).

2.2.4 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).

2.2.4.1 Contamination factor (CF)

$$\mathrm{CF} = \frac{\mathrm{C_s}}{\mathrm{C_{RefS}}} \tag{2.2}$$

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

2.2.4.2 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:

$$\mathrm{ADD} = \mathrm{Cs}\frac{(\mathrm{IR} \times \mathrm{EF} \times \mathrm{ED} \times 10^{-6})}{(\mathrm{BW} \times \mathrm{AT})} \tag{2.3}$$

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:

$$\mathrm{HQ} = \frac{\mathrm{ADD}}{\mathrm{RfD}} \tag{2.4}$$

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

2.2.5 Data and statistical analyses

We performed ANOVA to compare the variability of the means, and 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.

Table 2.1: Mean, maximum, and minimum of selected basic properties and total metal content of the studied soils

Parameter	Unit	Abandoned mining spoil										Active mining spoil				
		Topsoil					Profiles					Topsoil				
		Min	Max	Mean	SD	n	Min	Max	Mean	SD	n	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

2.3 Results and discussions

2.3.1 Mine spoil soil characterisation

Characterisation of the abandoned and active mine spoil soils is shown in Table 2.1. Soils of the mine spoils were predominantly sandy with mean proportions of 63, 41 and 57% for the abandoned topsoil, profiles, and active mine topsoils, respectively. The soils had weakly acidic and mildly alkaline pH with values ranged from 6.6 to 7.6. The soils had low total carbon (0.64 - 2.2%), with higher values in the abandoned (1.1 - 2.2%) than the active mine soils (0.64 - 1.04%). Both the abandoned and the active mine soils contained higher concentrations of total Fe and Ca than Al and Mg. Higher contents of total Fe were observed at both sites, particularly in the abandoned mine topsoils (17.2 - 46.6 g kg^{-1}).

2.3.2 Total content and contamination factor of arsenic in the mine spoils

2.3.2.1 Total contents

Total As contents and distribution from different sampling spots on the abandoned (top and profiles) and the active mine top spoils, are shown in Fig. 2.2. The range of As in the abandoned mine top spoil was highest with a minimum of 1,807.0 mg kg^{-1} and a maximum of 8,401.0 mg kg^{-1} resulting in a median of 4,483.0 mg kg^{-1}. The total contents of As in the abandoned profile samples had variations within depth (range 3,105 – 4,142) with median value of 4,192.0 mg kg^{-1}. There was little variation in As concentrations at the active gold mine spoil with a median value of 2,456.0, minimum value of 2,034.0, and maximum value 3,801.0 mg kg^{-1}.

We assume that differences in the age of the mine spoils might account for the relatively higher total As contents in the abandoned mine spoil topsoils than the active mine top soils. The abandoned mine spoil had been in existence since 1912 and abandoned in the 2002 when operation by the mining company ceased. The active mine spoil had been in operation since 1997. Aging plays a major role in assessing the extent of contamination from mining operations and construction works where As has been recently added compared to areas where As has been deposited over many decades (Antoniadis et al., 2017). We also hypothesise that many years of accumulation of the mine wastes through anthropogenic means might have accumulated higher As contents at the top soil than in the profiles. High contents of toxic elements including As in gold mine spoils have been reported in other studies (e.g., Petelka et al., 2019; Posada-Ayala et al., 2016).

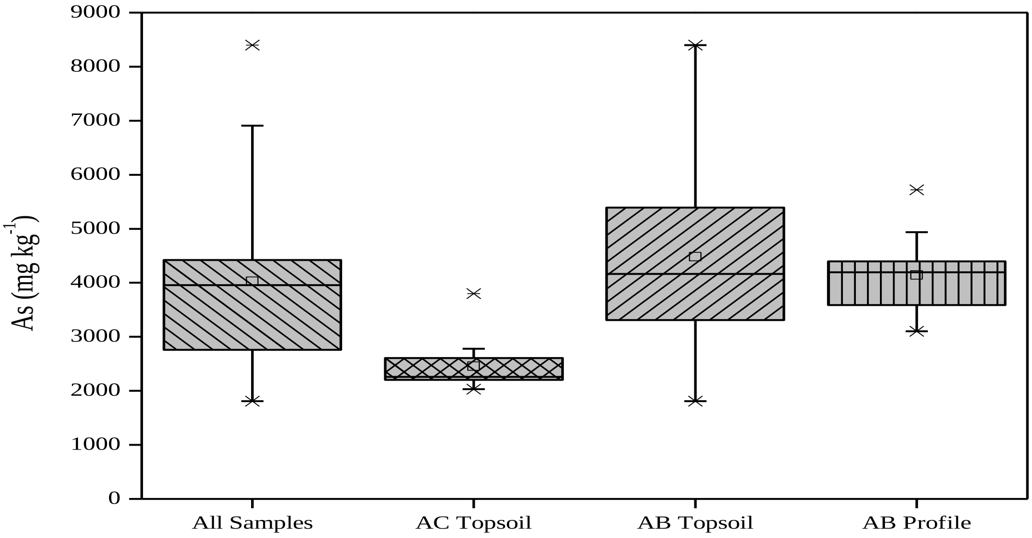

Fig. 2.2: Box plot showing distribution of As total content in all samples (n = 51), active (AC topsoil; n = 10), abandoned top spoil (AB topsoil; n = 31), and abandoned profile mine spoils (20 - 100 cm depth, AB profile n = 10). Asterisk marks (lower and upper) in the range represent 1% and 99% percentiles respectively. Asterisks outside the range represent outliers. Small rectangular boxes represent the mean.

Total contents of As in the mine spoil soils (1,807.0 – 8,401.0 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.

2.3.2.2 Soil contamination factor

Fig. 2.3 shows soil contamination factor for the abandoned, profile and active mine spoils. The risk from As-soil contamination in the abandoned mine spoil was very high with a mean of 669 (unitless). In the active mine spoil, the mean was 360 and for the profiles 606. The mine spoils indicated very high strong degree of soil contamination (CF ≥ 6) 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).

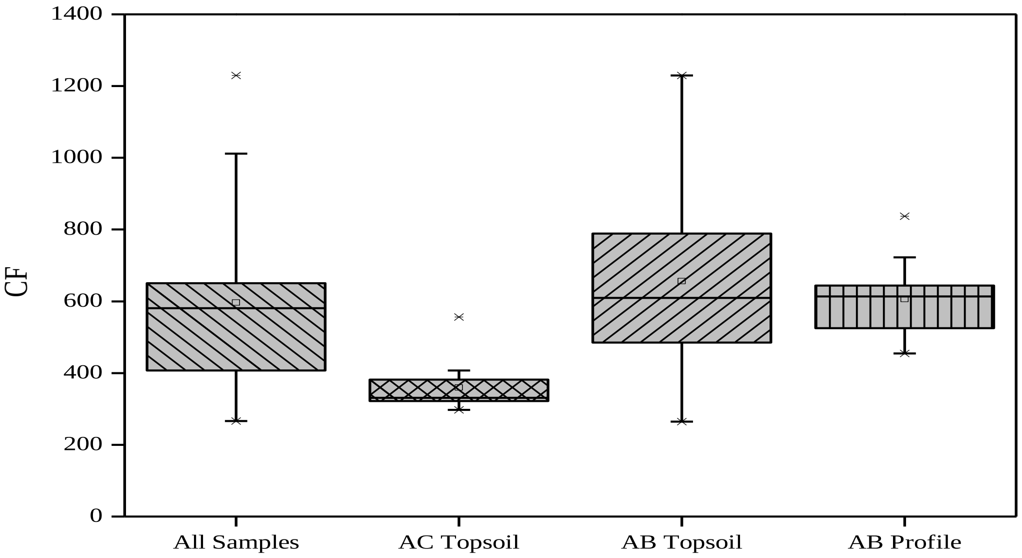

Fig. 2.3: Soil contamination factor (CF) of As contents in the mine spoils – all samples, active topsoil, abandoned topsoil and profiles. Asterisk marks (lower and upper) in the range represent 1% and 99% percentiles respectively. Asterisks outside the range represent outliers. Small rectangular boxes represent the mean.

2.3.3 Mineralogical composition and As speciation in the mine spoils

Results of XANES analysis to characterize the dominant As-bearing minerals in the mine spoil are shown in Fig. 2.4. The LCF results of the mine spoil are provided in supporting information (Appendix A; Table S2.2). It indicates the portion (%) of each mineralogical composition of As in the mine spoil. The results indicate that scorodite ($FeAsSO_4$) 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 S2.2). 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, and it is generally considered a secondary product of the natural oxidation and weathering of arsenopyrite (DeSisto et al., 2016; Murciego et al., 2010). The oxidation and weathering of arsenopyrite could happen in the studied area where the primary As minerals in the mining wastes were abandoned to the surroundings without any treatment. Those primary As minerals might be subjected to oxidation and weathering, producing scorodite. Also, results from 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. The dominance of both scorodite and arsenopyrite can be a reason for the high content of total As and Fe in the studied spoils.

2.3.4 Geochemical fractions and potential mobilization of As in the bulk soils and in the coarse and fine fraction of the studied spoils

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

In the abandoned mine spoil topsoil, 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. 2.5). 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 indicated earlier (section 3.3; Fig. 2.4), the mine spoils contain $FeAsSO_4$ 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 $FeAsSO_4$ in the samples (Fig 2.4). Also, the total content of Fe was very high in both spoils, particularly in the abandoned ones (17 - 46 g/kg; Table 2.1). 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.

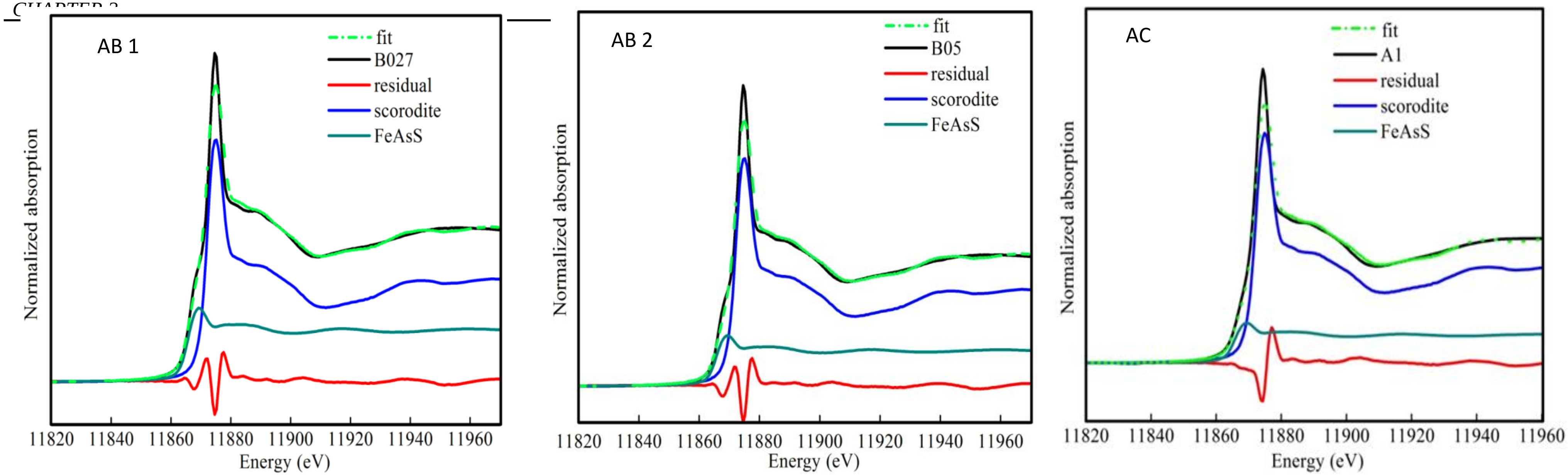

Fig. 2.4: Arsenic K-edge XANES spectra of selected abandoned (AB) and active (AC) mine spoils and their linear combination fitting results.

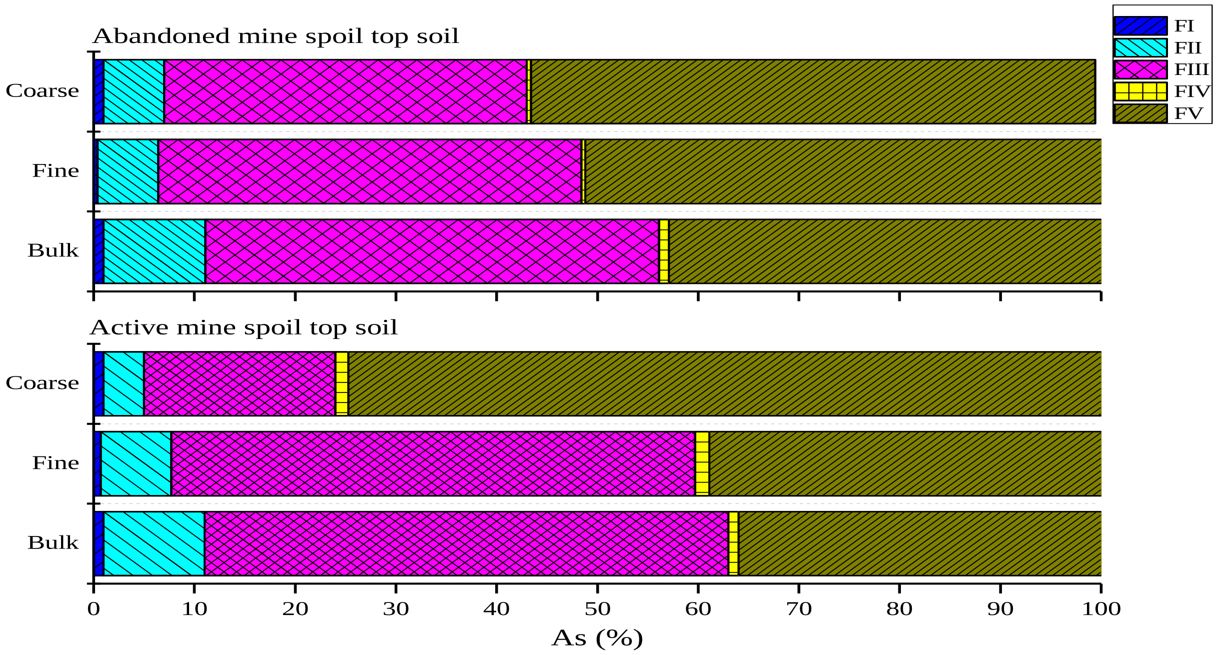

Fig. 2.5: Geochemical fractions of As (%) in the studied fine fraction, coarse fraction, and bulk soil of the active and the abandoned mine spoil top soils

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 2.5), 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 S2.3) 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. 2.5) 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 Bissel and Frimmel (2003). Bissel 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 un-specifically bound As. The fraction ranged between 0.4 and 1% in the mine spoil top soils (Fig. 2.4). This fraction (22.2 – 23.4 mg/kg), 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.

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

Both fine (52%) and coarse fractions (56%) of the abandoned mine spoil topsoils contained greater proportions of the sequentially extracted As in fraction V (Fig. 2.5). For the coarse fraction of the active mining spoil, relatively larger amount of the As was found in the residual/sulphide fraction (FV =75%) (Fig. 2.5). We hypothesize that the arsenopyrite geologic mineral present in the coarse fraction, 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 fraction (r = +0.96; $P < 0.01$) and the coarse fraction (r = +0.82; $P < 0.01$) (Appendix A; Table S2.5 and S2.6). Results from the correlation analysis (Table S2.5) also indicated a highly positive significant relationship between total As and Fe (r = +0.98; $P < 0.01$) in the fine fraction. This implies that greater proportion of the extracted As (composed of the residual fraction) are concentrated in the soil size fraction. Further, the fine fraction contained higher As contents in FIII (42 – 52%) than the coarse fraction (36%) in both spoils, particularly in the active mining spoil (Fig. 2.5), which can be explained by the higher contents of amorphous Fe oxides (Fe_o) in the fine fraction (13.4 g kg^{-1}) than in the coarse fraction (1.8 g kg^{-1}) (Table S2.3). 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 fraction (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 (2015); Bolan et al. (2014); and Komárek et al. (2013).

The fine fractions also contained 6% and 7% contents of As in FII, respectively for abandoned and active top soils. In the coarse fractions, FII As contents in the active was almost three times higher than the abandoned mine top soil (Fig. 2.5). However, a strong significant positive relationship between pH and %As in FII (r = +0.6; $P < 0.05$) in the coarse fraction was noticed (Appendix A; Table S2.5 and S2.6). For the fine fraction, 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 S2.3) 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, with consequence on human health. 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 (Figure 2.5; Appendix A Table S2.3). 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 S2.5), 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 alkalisation, 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 fractions, 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 fraction was reduced because part of the As content was retained in the residual fraction. The percent residual fraction in the coarse fraction was higher than that in the fine fraction in both the active and abandoned mine spoils (Figure 2.5). In the abandoned mine spoils, percent MF in the coarse fraction (7%) was like that in the fine fraction (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 fraction can be explained by the higher content of clay minerals, oxides, and the As-bearing secondary mineral scorodite and/or goethite in the fine fraction 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 (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 fraction was obviously higher than the bulk and fine fraction in both spoils, and particularly in the active mine spoil (Fig. 2.5). We assume that the high portion of the residual As in the coarse fraction might be due to the presence of the As bearing primary mineral arsenopyrite in the coarse fraction, 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., 2011).

2.3.4.3 Fractionation of As in the fine and coarse fraction of the abandoned mine soil profile

Distribution of As among its geochemical fractions in the fine and coarse particles is presented in Fig. 2.6 and Table S2.4. In the fine fraction, a relatively higher portion of As was distributed in the residual/sulphide fraction (FV) and increased with depth from 20cm to 100 cm, whilst at the same time, As in FIII decreased from 31% to 6-10%. We assume here that higher percentage of the sulphide arsenopyrite and scorodite mineral could be more associated with the fine fraction in the deep-layers than the 0-20 cm layer. We may attribute this observation to effect of soil weathering and leaching. Weathering 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 fraction 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 fraction, As showed a different distribution as compared to the fine fraction, 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. 2.6). Therefore, the potential mobility (PMF=∑FI-FIV) of As increased with depth in the coarse fraction while its 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 fraction compared to the fine fraction. Again, the process of weathering on the surfaces of the soil coarse fraction 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.

2.3.5 Human health risk of the mine spoils

Fig. 2.7 shows health risks associated with exposure to As-contaminated mine deposits and spoils for children, adult males, and females, respectively. In other words, direct As-contaminated dust inhalation by humans exposed to the abandoned, profile, active mine spoils as well as all samples. 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- 6047.

The human health risks assessment indicated that children are at most health risk disadvantage with regards to exposure to the As-contaminated mine spoils such as through direct dust inhalation. The exposure risks were 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.

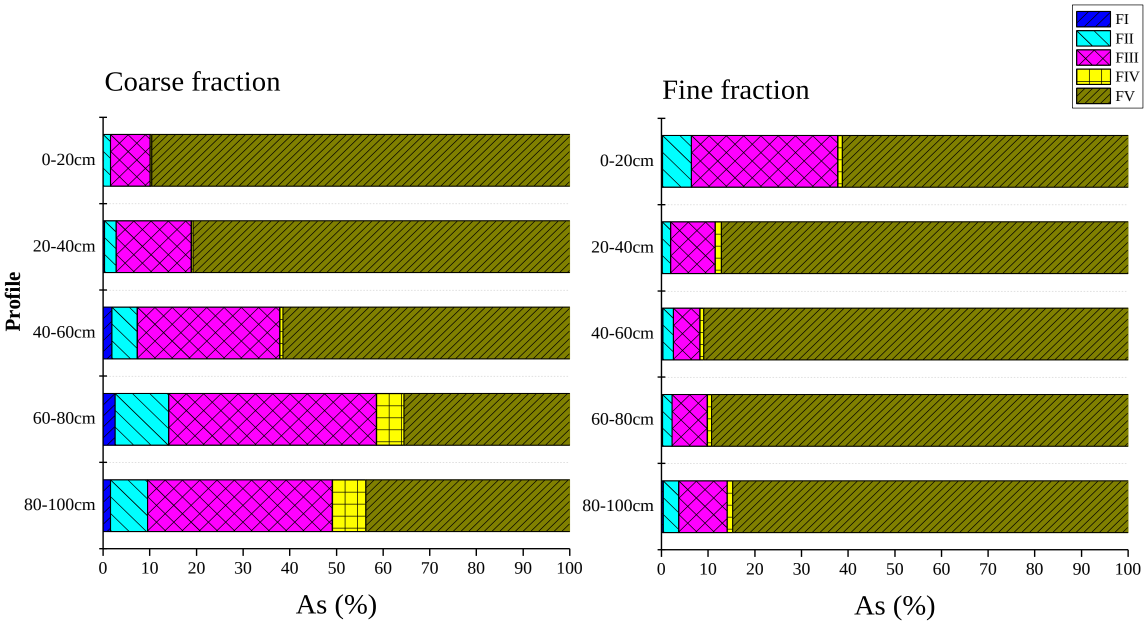

Figure 2.6: Geochemical fractions of As (%) in the studied fine and coarse fractions of the abandoned mine spoil soil profiles

The abandoned mine spoil posed greatest health risks to children, women, and men in the surrounding mining communities than the active, and profile mine spoils. The risks were also higher in the surface topsoil than from the profiles.

The abandoned mine spoil serves as passing place for women and men to their farms and villages and they could get exposed to higher risks of As contamination from this field. It also serves as a play-ground for kids and these children 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. Similar hazard quotient (index) of As had been found in other gold mining areas in Ghana (E.g., Armah and Gyeabour, 2013; Hadzi et al., 2018) but these works reported 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 (index) values lower than in our study.

2.4 Conclusions

We found that the studied gold mining spoils are severely contaminated with As, with a total content ranged between 1,807 and 8,400 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 fraction while its decreased with depth in the fine particles. The higher potential mobility of As in the fine fraction 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 fraction 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.

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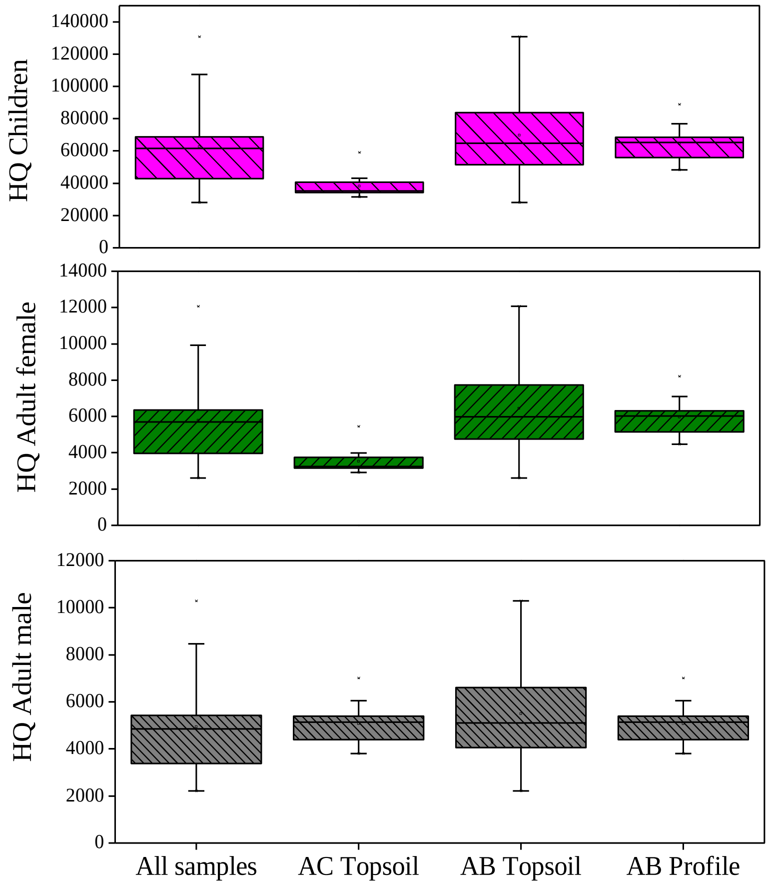

Fig. 2.7: Hazard quotient of children, adult males and females exposed to As contamination in all samples, active top soil, abandoned topsoil and profiles. Asterisk marks (lower and upper) in the range represent 1% and 99% percentiles respectively. Asterisks outside the range represent outliers. Small rectangular boxes represent the mean.

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Supplementary Materials (Appendix A) of the manuscript (chapter 2):

Arsenic contamination in abandoned and active gold mine spoils in Ghana: geochemical fractionation, speciation, and assessment of the potential human health risk.

Albert Kobina Mensah et al. (2020). Published in *Environmental Pollution*, 261, 114116. https://doi.org/10.1016/j.envpol.2020.114116

Table S2.1: Extraction scheme developed by Wenzel *et al.* (2001) used in the experiment.

As Fraction	Extracted fraction	Extracting Agent (Solution)	Procedure
I	Water-soluble and un-specifically bound arsenic	$(NH_4)_2SO_4$ 0.05 M	Shake at 20 °C for 4h
II	Specific-sorbed arsenic /exchangeable fraction	$(NH_4)H_2PO_4$ 0.05 M	Shake at 20 °C for 16h
III	Arsenic bound to amorphous oxides	NH_4-oxalate 0.2 M + oxalic acid 0.2 M; pH 3.25	Shake at 20 °C for 4h in the dark Wash with 12.5 ml of solution 3; pH 3.25
IV	Arsenic bound to crystalline iron oxides	NH_4-Oxalate 0.2 M + Oxalic acid 0.2 M + Ascorbic acid 0.1M; pH 3.25	Place for 30 min in a water bath (96 ° C) Wash with 12.5 ml of solution 3
V	Arsenic in sulphides and arsenides (Residual fraction)	Nitric acid conc. (HNO_3)	Digest in microwave

Table S2.2: Linear combination fitting results for As K-edge XANES spectra of soil samples. 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	Scorodite	FeAsS	R-factor
AB1	72%±1%	28%±1%	0.009
AB2	65%±0.8%	35%±1.3%	0.007
AC	76%±1%	24%±1%	0.021

AB 1 and AB 2 are selected samples from the abandoned mine spoils; AC is selected sample from the bulk active mine spoils.

Table S2.3: As geochemical fractions (mg/kg), potential mobile fraction (PMF), mobile fraction (MF), Al/Mn/Fed and Al/Mn/Feo in the bulk, fine and coarse fractions of the mine spoil top soil

Parameter	Unit	Abandoned mine spoil									Active mine spoil								
		Bulk			Fine			Coarse			Bulk			Fine			Coarse		
		Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n
FI	mg/kg	23.4	1.9	5	47.5	16.2	8	14.7	8.2	8	22.2	0.9	3	43.2	20.6	4	8.0	7.9	4
FII	mg/kg	248.6	84.7	5	776.4	351.3	8	84.1	24.1	8	260.7	5.7	3	416.5	83.0	4	24.2	25.4	4
FIII	mg/kg	1055.7	222.6	5	6736.2	4389.3	8	508.1	161.5	8	1423.9	190.9	3	3134.5	515.1	4	129.2	117.1	4
FIV	mg/kg	10.7	2.1	5	61.4	38.9	8	3.9	3.7	8	35.8	3.2	3	77.5	28.2	4	9.6	14.7	4
FV	mg/kg	1239.6	996.8	5	8750.8	6526.2	8	1330.7	1422.0	8	973.3	18.3	3	2610.1	1373.3	4	485.3	226.7	4
Total As	mg/kg	2425.9	1237.8	5	17927.8	11611.9	8	1968.0	1341.3	8	2455.7	0.0	3	5853.8	2004.1	4	954.2	481.6	4
∑ (FI-FV)	mg/kg	2578.0	1305.4	5	16372.3	11229.4	8	1941.5	1572.5	8	2715.9	176.0	3	6281.7	1924.5	4	656.1	246.8	4
Recovery	%	106.4	3.2	5	92.0	9.3	8	96.5	22.2	8	110.6	7.2	3	108.5	5.1	4	78.9	34.7	4
PMF	mg/kg	1338.4	310.4	5	7621.5	4783.3	8	610.8	184.1	8	1742.6	194.3	3	3671.6	570.3	4	170.9	162.0	4
PMF	%	56.1	11.1	5	48.3	6.1	8	43.7	20.5	8	64.0	3.0	3	60.8	11.0	4	25.1	17.6	4
MF	mg/kg	272.1	86.4	5	823.9	366.0	8	98.8	31.3	8	282.9	6.6	3	459.7	102.1	4	32.1	30.9	4
MF	%	11.1	1.5	5	6.0	1.8	8	7.1	3.4	8	10.4	0.4	3	7.6	2.1	4	4.5	3.3	4
Fed	mg/kg	4919.0		2	12715.0		2	1567.0		2	nd			nd			nd		
Feo	mg/kg	5110.0		2	13462.5		2	1851.8		2	nd			nd			nd		
Ald	mg/kg	232.8		2	315.1		2	157.5		2	nd			nd			nd		
Alo	mg/kg	150.4		2	172.0		2	<3.495		2	nd			nd			nd		
Mnd	mg/kg	72.8		2	147.4		2	37.3		2	nd			nd			nd		
Mno	mg/kg	105.1		2	219.8		2	54.3		2	nd			nd			nd		

Fe_d/Al_d/Mn_d = Fe/Al/Mn oxides with warm dithionite extraction (this is made up of both crystalline and amorphous iron oxides); Fe_o/Al_o/Mn_o = Fe/Al/Mn oxides extracted with oxalate (made up of only amorphous iron oxides).

nd: not determined

Table S2.4: As geochemical fractions (mg/kg), potential mobile fraction (PMF), mobile fraction (MF), pH, P, C, Mg, Ca, in fine and coarse fractions of the mine spoil soil profile

Fine fraction							Coarse fraction				
Parameter	Unit	0-20cm	20-40cm	40-60cm	60-80cm	80-100cm	0-20cm	20-40cm	40-60cm	60-80cm	80-100cm
FI	mg/kg	8.2	4.1	13.4	9.6	12.2	0.2	1.7	22.2	13.5	12.2
FII	mg/kg	214.1	66.3	99.3	86.3	107.1	8.5	14.5	64.3	59.8	61.9
FIII	mg/kg	1091.1	340.5	246.1	315.5	336.9	47.4	93.2	362.0	232.2	309.2
FIV	mg/kg	31.7	49.1	34.5	37.9	38.1	2.1	2.0	8.0	30.7	56.0
FV	mg/kg	2126.8	3110.1	3951.0	3739.2	2742.2	501.7	466.8	726.8	185.0	340.4
Total As	mg/kg	3567.6	3790.9	4542.5	4631.5	3944.8	484.2	351.3	615.5	472.0	406.5
∑ (FI-FV)	mg/kg	3471.9	3570.0	4344.3	4188.4	3236.5	559.9	578.2	1183.4	521.2	779.7
Recovery	%	97.3	94.2	95.6	90.4	82.0	115.6	164.6	192.3	110.4	191.8
PMF	mg/kg	1345.1	459.9	393.3	449.3	494.3	58.2	111.4	456.5	336.2	439.3
PMF	%	38.7	12.9	9.1	10.7	15.3	10.4	19.3	38.6	64.5	56.3
MF	mg/kg	222.2	70.3	112.7	95.8	119.3	8.7	16.2	86.5	73.3	74.1
MF	%	6.4	2.0	2.6	2.3	3.7	1.6	2.8	7.3	14.1	9.5
pH		7.5	7.5	7.7	7.7	7.7	6.8	7.0	7.0	7.0	7.0
Fe	mg/kg	26601.7	25815	25251.1	27193.3	22338	12582.7	9729.4	12806.3	9585.3	9093.7
Mg	mg/kg	7555.7	9390.8	7844	7576.1	7283.5	5052.7	4131.5	4679.7	4106.8	3626.7
Ca	mg/kg	12670.6	18262.6	16751.6	15467	14585.7	8156.5	6947.1	8581.9	7037.1	6065.3
P	mg/kg	398	376.7	345.3	344.8	342.8	207.2	171.3	173.7	172.3	158.1
TC	%	2.45	2.19	2.50	1.98	2.12	1.3	1.2	1.2	1.0	1.0

Table S2.5: Pearson moment correlation coefficients (r) between As fractions and other relevant parameters in the fine mine spoil soil.

Parameter	FI mg/kg	FII mg/kg	FIII mg/kg	FIV mg/kg	FV mg/kg	∑FI-FV mg/kg	PMF mg/kg	PMF %	MF mg/kg	MF %	FI %	FII %	FIII %	FIV %	FV %	Fetot mg/kg	N
silt	-0.73**	-0.7**	-0.7**	-0.6*	-0.58*	-0.67**	-0.7**	ns	-0.7**	ns	ns	ns	ns	ns	ns	-0.7**	14
sand	0.73**	0.7**	0.68**	0.6*	0.57*	0.66*	0.7**	ns	0.67**	ns	ns	Ns	ns	ns	ns	0.68**	14
Soil TC	-0.6*	ns	ns	-0.57*	ns	ns	ns	-0.81**	ns	-0.56*	-0.54*	-0.55*	-0.83**	ns	0.81**	ns	14
pH	-0.66*	ns	ns	ns	ns	ns	ns	-0.88**	ns	-0.67**	-0.61*	-0.66*	-0.9**	ns	0.88**	ns	14
Ast	0.78**	0.94**	0.97**	0.67**	0.96**	0.99**	0.97**	ns	0.93**	ns	ns	Ns	ns	-0.55*	ns	0.98**	14
Fet	0.8**	0.93**	0.98**	0.76**	0.96**	0.99**	0.98**	ns	0.93**	ns	ns	Ns	ns	ns	ns	1	14
Mgt	ns	ns	ns	ns	ns	ns	ns	-0.75**	ns	-0.71**	-0.65*	-0.7**	-0.73**	ns	0.75**	ns	14
Cat	ns	ns	ns	ns	ns	ns	ns	-0.8**	ns	-0.8**	-0.7**	-0.8**	-0.78**	ns	0.8**	ns	14
Pt	0.6*	0.7**	0.7**	ns	0.73**	0.73**	0.7**	ns	0.7**	ns	ns	Ns	ns	-0.75**	ns	0.72**	14

$\%\mathrm{PMF} = \frac{\sum(\mathrm{FI-FIV})}{\sum(\mathrm{FI-FV})} * 100$; $\%\mathrm{MF} = \frac{\mathrm{FI+FII}}{\sum(\mathrm{FI-FV})} * 100$; $\%\mathrm{FI, FII, FIII, FIV, FV} = \frac{\mathrm{FI,FII,FIII,FIV,FV}}{\sum(\mathrm{FI-FV})} * 100$

* correlation is significant at $P < 0.05$; ** correlation is significant at $P < 0.01$; ns: not significant relationship

TC = total carbon; Ast = total As; Fet = total Fe; Mgt = total magnesium; Cat= total calcium; Pt= total phosphorus.

Table S2.6: Pearson moment correlation coefficients (r) between As fractions (mg/kg) and other relevant parameters in the coarse mine spoil soil

	FI mg/kg	FII mg/kg	FIII mg/kg	FIV mg/kg	FV mg/kg	∑FI-FV mg/kg	PMF mg/kg	PMF%	MF mg/kg	MF%	FI%	FII%	FIII%	FIV%	FV%
pH	ns	ns	ns	ns	ns	ns	ns	ns	ns	0.61^{*}	0.7^{**}	0.57^{*}	ns	ns	ns
	13	14	14	12	14	13	13	13	13	13	13	13	13	13	13
Astot	ns	ns	0.6^{*}	ns	0.82^{**}	0.8^{**}	ns	ns	ns	ns	ns	ns	ns	ns	ns
	13	14	14	12	14	13	13	13	13	13	13	13	13	13	13
Fetot	ns	ns	ns	ns	0.82^{**}	0.75^{**}	ns	ns	ns	ns	ns	ns	ns	ns	ns
	13	14	14	12	14	13	13	13	13	13	13	13	13	13	13
Ptot	ns	ns	0.54^{*}	ns	0.63^{*}	0.62^{*}	ns	ns	ns	ns	ns	ns	ns	ns	ns

$\%\mathrm{PMF} = \frac{\sum(\mathrm{FI}-\mathrm{FIV})}{\sum(\mathrm{FI}-\mathrm{FV})} * 100$; $\%\mathrm{MF} = \frac{\mathrm{FI}+\mathrm{FII}}{\sum(\mathrm{FI}-\mathrm{FV})} * 100$; $\%\mathrm{FI}, \mathrm{FII}, \mathrm{FIII}, \mathrm{FIV}, \mathrm{FV} = \frac{\mathrm{FI,FII,FIII,FIV,FV}}{\sum(\mathrm{FI}-\mathrm{FV})} * 100$

* correlation is significant at $P < 0.05$; ** correlation is significant at $P < 0.01$; ns: not significant relationship

TC = total carbon; Ast = total As; Fet = total Fe; Mgt = total magnesium; Cat= total calcium; Pt= total phosphorus.

CHAPTER 3

Human health risk via soil ingestion of potentially toxic elements and remediation potential of native plants near an abandoned mine spoil in Ghana

This chapter is based on the manuscript of the published article: **Mensah, A. K.**, Marschner, B., Antoniadis, V., Stemn, 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. *Science of the Total Environment*, 798, 149272. https://doi.org/10.1016/j.scitotenv.2021.149272

Abstract

Integrated studies about potentially toxic elements (PTEs) in sites near gold mining spoils, their contamination and human health risk, as well as remediation potential of native plants are limited. Therefore, our aim was to assess the human health risk of PTEs (Al, As, Cd, Cr, Cu, Fe, Ni, Pb, Ti, V, and Zn) in sites near an abandoned gold mine spoil in Ghana. We collected 52 soil samples near the mine spoil and from a natural forest, determined their total element contents, and calculated the soil contamination factor (CF), enrichment factor (EF), geo-accumulation index (*Igeo*) and the pollution load index (PLI). In addition, we calculated the human health risk of soil ingestion for adult males, females, and children using the hazard quotient (HQ) and hazard index (HI). We also assessed the phytoremediation potential of five native plants (*Alchornea cordifolia, Chromolaena odorata*, *Lantana camara, Pityrogramma calomelanos*- fern, and *Pueraria montana*) growing near the mine spoil, and calculated their transfer coefficient (TC) and translocation factor (TF). Total content of As (maximum: 3,144.0 mg/kg) surpassed the trigger action value of 65 mg/kg. Total Zn content at 90th percentile in the Pueraria field (197 mg/kg) and maximum value at mine surrounding (76.7 mg/kg) were above the world soil average (70 mg/kg). Pollution load index and EF values indicated severe levels of soil contamination particularly with As and Ti. Hazard index (HI) values for all sites for children (0.7 – 134.56), adult males (0.05 – 10.6), and adult females (0.13 – 12.77) were above 1 and indicated high human health risk especially on children and women. Translocation factor shows that native plant species such as *Chromolaena odorata* and fern accumulated As, Cu, Ti, and Zn into their shoots and may thus have the potential to reduce the high soil contamination and its associated human health risk.

Keywords: Human health risk, Mining, Multi-element contamination, Phytoextraction, Potentially toxic elements.

3.1 Introduction

Mine spoils are major reservoirs and point-source pollution of soil potentially toxic elements (PTEs) such as Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, and Zn (Mensah et al., 2020; Ramírez et al., 2020). These may result in risks of transfer of PTEs into nearby plants, food crops, soil, surface and ground water. Metal contamination in soils/sediments may affect water quality, aquatic organisms, food safety and thus could cause potential long-term health impacts on humans and ecosystems. In other cases, there is the risk of metal oral intake through soil ingestion by children who most often use metal contaminated land or abandoned mine sites as play-grounds (Bansah et al., 2018; Shaheen et al., 2020b). Additionally, unfenced abandoned mine spoil sites could serve as a passing place for residents, who may inhale contaminated dust or ingest contaminated mine wastes as reported by Mensah et al. (2020). Oral ingestion of soil PTEs remains a major route of exposure affecting human health in gold mining regions (e.g., Armah and Gyeabour, 2013; Bansah et al., 2018; Mensah et al. 2020). This may be through unintended ingestion of dust, dirt, and soil; or intentionally, through geophagy - the practice of intentional eating earth or soil substances such as clay (Narh et al., 2021). Geophagy is a common practice among pregnant women in Africa and Latin America (Bundschuh, 2021; Narh et al., 2021). In gold mining areas, where As constitutes a known constituent in metal ores, tailing deposits, soil and dust, these present major human and animal health concerns (Bundschuh, 2021). For instance, acute and chronic exposure to As could cause human health problems such as skin damage, carcinogenic symptoms, and circulatory system defects (Bortey-Sam et al., 2015; Antoniadis et al., 2019b). Additionally, excessive accumulation of copper in the body through consumption of contaminated food and water causes Wilson disease, which affects function in multiple organ systems, including the liver and the brain (Mulligan and Bronstein, 2020). Further, exposure and accumulation of Cd, Cr, Pb, Ni, and V in vital body organs may be associated with health complications such as reproductive, development toxicity, hepatic, hematological and immunological health defects, abortions, infertility, birth defects, and malformations (Apostoli and Catalani, 2015).

The benefits associated with gold mining in Ghana (e.g., employment creation and generation of government revenues) are, however, often counterbalanced with negative environmental impacts on ecological integrity and human health resulting from poor management of mine wastes (Bempah et al., 2013), runoff from stockpiles (Mensah et al., 2015), and abandonment of mine spoils left untreated (Mensah et al., 2020). These actions further exacerbate anthropogenic release and migration of PTEs into the environment and consequently affect human health and livelihoods of the people. Efforts made to remediate metal contamination problems in gold mine spoils have mainly involved chemical stabilization with the use of oxides to reduce metal solubility (Komárek et al., 2013; Palansooriya et al., 2020; Wang et al., 2021), removal and replacement of contaminated soil with clean soil (Bansah and Addo, 2016), and soil washing and soil flushing (Bolan et al., 2014; Wang et al., 2021). In other instances, there has been employment of containment strategies involving the use of constructed barriers, caps and liners to reduce migration and transfer of toxic elements (Wuana and Okieimen, 2011). The major disadvantages of these methods are that they are quite challenging tasks and expensive to many mining companies. Moreover, unlike organic compounds, PTEs cannot degrade, and hence their cleanup usually requires removal (Nwaichi et al., 2009) or decreasing their uptake, surface runoff or leaching using immobilization and stabilization techniques (Bolan et al., 2014; Palansooriya et al., 2020).

Phytoremediation using native plants is proposed as a cost-effective alternative for environmental management, which could be used to mitigate heavy metal contamination problems in gold mine soils (Nwaichi et al., 2009; Puga et al., 2015). In such scenario, some authors (e.g., Antoniadis et al., 2021; Sheoran and Choudhary, 2021; Pathak and Shah, 2021; Petelka et al., 2019) have recently suggested that it may be wise to use well-adapted native species of the locality under investigation when choosing potential plants for contaminated site phytoremediation. Further, native and indigenous species are preferred over exotic species because they may fit fully and better into the functional local ecosystem and adapt better to local climate (Mensah, 2015). Phytoremediation is still an emerging science (Ashraf et al., 2013), which needs more in-depth investigation and study to upscale its applicability. For instance, the potential of native plants such as *Chromolaena odorata*, *Pityrogramma calomelanos*- fern, *Alchornea cordifolia*, *Lantana camara* and *Pueraria montana* for cleaning mine contaminated spoils has so far not been fully explored and works on them are rare or mostly found in scattered pieces (e.g., Bansah and Addo, 2016; Issaka and Ashraf, 2021; Liu et al., 2019; Petelka et al., 2019). For instance, Liu et al. (2019) tested *Lantana camara* for only Cd remediation and found that the plant showed high Cd tolerance with bioaccumulation and translocation factors greater than 1 in Cd-contaminated soils in China. Additionally, Ashraf et al. (2013) studied the potential of nine native plants for metal remediation of contaminated mine tailings in Malaysia and found that *Pteris vittata* L., among the plants had high phytoextraction potential for Pb. Consequently, phytoremediation reduces human health impacts associated with PTEs through reduction in food chain contamination, controlling their mobility, reduction in metal transfer into surface and groundwater and through ensuring a metal contaminated-free environment. Additionally, phytoremediation could control water and wind erosion, ensure water quality, reduce runoff from contaminated mining spoils, conserve soil moisture, maintain and increase soil fertility, contribute to carbon sequestration, and may aid in recreational purposes.

Our previous study (Mensah et al., 2020) investigated the soil and human health risk of soil ingestion in gold mine areas in Ghana but focused only on As contamination in mine tailings and not sites near the mine spoils. Likewise, Cai et al. (2017) investigated the sources, contamination, and mobility of As in rivers and stream sediments impacted by gold mining in China, but focused only on As pollution, and ignored other soil metal contamination of equal environmental concerns from the mining sites, their human health implications on the residents and remediation opportunities. Similarly, Rinklebe et al. (2019) studied the human health implications of soil potentially toxic elements on adults and children but focused on only riparian soils along the Central Elbe River in Germany, and ignored available options for remediation of the multi-element contaminated riparian soils. These previous works only focused on the impacts separately from possible gentle remediation options for metal clean up. Such consolidated scientific environmental and health implication assessment studies are limited in current scientific literature.

Thus, we holistically addressed the problem in this study using worldwide-recognised soil contamination and soil ingestion health risk indices as a methodology to assess the soil and human health risk of potentially toxic elements in sites near former gold mine spoil in Ghana. Additionally, we studied and proposed alternative options for remediation of these multi-element contaminated sites. The soil-to-human health risk assessment (SHRA) methodology, according to USEPA (2002), can be applied to conduct a detailed health risk assessment of any residential or commercial/industrial scenario and is recommended as a viable initial tool in planning remediation of contaminated sites. The reported limitations (e.g., Shaheen et al. 2020; Taylor et al., 2020) of SHRA are that it is based on rigid assumptions which are not unique for every exposed human, it does not consider pre-existing health problems, and it lacks certainty.

Recognizing these limitations, SHRA is the single most important approach to identifying possible health risks deriving from PTE exposure and it is the most adopted method in literature in assessing the human exposure to soil PTEs (Shaheen et al. 2020; USEPA, 2002). Eventually, SHRA indicates the possibility of health risk associated with exposure to PTE. Thus, such studies provide a necessary initial step of assessing health risk, aid in addressing problems concerning the risk of metal pollution and human health outcomes associated with mining and abet in proposing more sustainable approaches towards reclamation of multi-element contaminated mining spoils in gold mining-dominated regions. Ultimately, the study will contribute to ensuring responsible mineral extraction and sustainable development in the mining sector. Therefore, our objectives were to: i) assess soil contamination with potentially toxic elements due to gold mining, ii) quantify the human health risks of possible soil ingestion of potentially toxic elements by residents in mining environments, and iii) quantify the remediation potential of native plant species in gold mining region.

3.2 Materials and Methods

3.2.1 Study area

The study was conducted in a gold mining community in the western region of Ghana, with a population of about 35,760 (Mensah et al., 2015). The area is located at 5.43274 latitude and 2.14284 longitude; at an elevation of 59 m above sea level. It receives a mean annual rainfall of 1711 mm; annual temperature is 26.6 °C, and humidity typically ranges between 70 and 80%. The soil in the area is acidic and deficient in major essential nutrients. The greater part of the population is engaged in gold mining, petty trading, subsistence and cash crop farming (Mensah et al., 2015). Indeed, in such rural communities, about 100 percent of households (98%) are engaged in farming activities and depend on this sector for livelihood. Vegetables (such as okra, tomatoes, and pepper), cereals (such as maize), and root and stem tuber crops (such as cassava, cocoyam and *Colocasia*), as well as cash crops (mainly oil palm and cocoa) are grown by farmers in the area. Additional details about the study area are reported in Mensah et al. (2020).

3.2.2 Soil and plant sampling

We collected 52 soil samples from different sampling spots around an abandoned gold mine spoil in an area that measures 126,000 m^2 (Mensah et al., 2020). The soil samples were obtained from four sites around the mine spoil and from a natural forest. The sites around the mining spoil covers a total land space of 134,000 m^2, whilst the sampled natural forest area measures 961 m^2. The first site is an area surrounding the mine spoil (thereafter named mine surrounding). There, we collected twenty-four samples from individual random spots. We additionally collected six individual samples each from a second site, dominated by cassava (farm 1); also from a third site colonised and dominated by *Pueraria montana* (thereafter named Pueraria field); and from a fourth site, dominated by plantain, cocoyam and cocoa on a subsistence scale (farm 2). Moreover, ten samples were collected from individual sampling points from a natural forest (unmined area – control field). Apart from the natural forest, all other sites were in the vicinity of the abandoned mine spoil. 'Mine surrounding' was used for sampling locations where no major agricultural or land use activities are currently taking place. The distance between the sites around the mine spoil and the natural forest is about 3.5 km. All soil samples were collected within a depth of 0 – 20 cm and individual coordinates were recorded. Details of the sample collection from individual sample points at the various sites are shown in a map in the supplementary materials (Appendix A; Fig. S3.1).

Five different native naturally growing plant species in the surrounding of the abandoned mine spoil were harvested: *Chromolaena odorata*, *Pityrogramma calomelanos*- fern, *Alchornea cordifolia*, *Lantana camara* and *Pueraria montana*. The names of the plants were identified with the help of a botanist at the Department of Botany, University of Cape Coast, Ghana. The plant samples were each separated with sharp scissors into two main parts – aboveground biomass and below-ground biomass. Aboveground biomass consisted of stem and leaves; the below-ground biomass consisted of roots. These were later placed in labelled Ziploc bags and their weights determined. The harvested plant parts were thoroughly washed, rinsed in distilled water, and dried to constant weight at 65 °C in an oven. After determining their oven-dry weights, plant samples were milled to fine powder and stored in plastic bags until analysis. Details of the collected plant species are provided in Appendix A; Fig. S3.2.

3.2.3 Chemical analyses

The collected soil samples were air-dried for 48 hours, crushed, and all debris was removed. We then homogenised the samples, passed them through a 2-mm sieve, and characterized them for their basic physico-chemical properties using standard methods (Sparks et al., 1996). Soil pH was measured using a soil: 0.01 M $CaCl_2$ solution ratio of 1:5 with pH meter (Sentix 41, WTW GmbH, Weilheim, Germany). Electrical conductivity (EC) was determined using a soil: water ratio of 1:5 with EC meter (TetraCon 325, WTW GmbH, Weilheim, Germany). Total contents of carbon and nitrogen were measured by an elemental analyser (Vario max cube, Elementar Analyse systeme GmbH, Hanau, Germany). Soil texture was measured with the laser scattering method (Analysette 22; Fritsch GmbH, Idar-Oberstein, Germany) as prescribed by Zobeck (2004).

3.2.4 Extraction and determination of total PTE contents in soils and plants

We extracted the pseudo-total contents of Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, and Zn using the microwave digestion method as described in USEPA (2007). In this method, 0.25 g of finely ground soil sample was microwave digested (CEM, Kamp-Lintford, Germany) at 120 °C for 15 minutes with 10 mL concentrated nitric acid at 1600W. Then, the digest was diluted with 10 mL de-ionized water, homogenised, and filtered through a 0.45 mL membrane filter. For the plant samples, we used the same procedure as in the case of the soil but with 0.125 g of fine milled plant samples. Contents of PTEs in the soil and plant digests were measured with inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectroblue, Ametek Materials Analysis Divison). As a quality measure, standard solutions and blanks were used and all extraction processes were conducted in triplicates. Additionally, analyses of standard reference materials, SRM 2709a for baseline trace elements concentrations (National Institute of Standards and Technology, USA), and European Commission Community Bureau of References (reference material No. 679, cabbage powder batch number 345 and No. 414, trace elements in plankton) were used to check and verify concerns of data quality. The calibration range was between 0 and 2 mg/l and recovery rates ranged from 107 – 120%. Detection limits of elements for our ICP-OES measurements were as follow (in µg L^{-1}): As = 3.36, Cd = 0.25, Cr = 1.46, Cu = 0.53, Ni = 1.47, Pb = 8.30, Ti = 8.0, V = 0.46, and Zn = 0.77.

3.2.5 Soil contamination assessment

We assessed the degree of topsoil (0 – 20 cm) contamination with PTEs using four indices: contamination factor (CF), enrichment factor (EF), pollution load index (PLI) and geo-accumulation index (I_{geo}). Additionally, non-carcinogenic human health risk associated with possible soil ingestion of PTEs was calculated using Hazard Quotient (HQ) and Hazard Index (HI). These indices have successfully been employed in past studies for monitoring the extent of PTE contamination and assessing human health risk of soils along rivers in Germany

(Rinklebe et al., 2019), in garden vegetable soils (Antoniadis et al., 2017b), in children's playgrounds in Beijing (Jin et al., 2019), in temperate and arid regions in Germany and Egypt (Shaheen et al., 2020b), around lead/zinc smelter in southwestern China (Li et al., 2015), around industrial area in Greece (Antoniadis et al., 2017c; 2019a), around abandoned iron-ore mines in north central Nigeria (Isinkaye, 2018), and in mine tailings in Ghana (Mensah et al., 2020).

3.2.5.1 Soil contamination factor (CF)

$$\mathrm{CF} = {}^{\mathrm{Cs}}/_{\mathrm{Cref}} \qquad (3.1)$$

where CF = soil contamination factor, Cs = total element content in soil (mg/kg), Cref = reference/background value of the element in uncontaminated soil (world soil average values were obtained from Kabata-Pendias, 2011). The reference background values for the various PTEs in mg/kg, also reported in Fig. 1, were used as follows: As = 6.8; Al = 20,000; Cd = 0.2; Cr = 59.9; Cu = 38.5; Fe = 20,000; Ni = 29, Pb = 27; Ti = 0.57; V = 90; and Zn = 70. The reference value for Ti was obtained from Saha et al. (2015), that of V from Li et al. (2015), and those of Al and Fe were obtained from Shaheen et al. (2020b). This index further classifies the degree of soil contamination using the following categories: low contamination (when CF < 1), moderate contamination (CF = 1 – 3), considerable contamination (CF = 3 – 6), and very high contamination (CF ≥ 6) (Li et al., 2015; Mensah et al., 2020; Rinklebe et al., 2019; Shaheen et al., 2020b).

3.2.5.2 Pollution Load Index (PLI)

PLI is the product of the individual CF values of all studied potentially toxic elements, as per Rinklebe et al. (2019) and Shaheen et al. (2020b):

$$\mathrm{PLI} = (\mathrm{CFs,1} \times \mathrm{CFs,2} \times \ldots \times \mathrm{CDs,n})^{1/n} \qquad (3.2)$$

where $\mathrm{CF}_{\mathrm{s,\,1}}$, $\mathrm{CF}_{\mathrm{s,\,2}}$, $\mathrm{CF}_{\mathrm{s,\,n}}$ are the contamination factors of elements 1, 2, …, n under consideration. PLI > 1 indicates substantial PTE soil contamination of the area under study.

3.2.5.3 Enrichment factor (EF)

EF helps to ascertain whether PTE pollution in the soil is geogenic or anthropogenic. EF assumes that the contents of elements such as Al and Fe occur in a natural medium and are mostly geogenic, and thus Al or Fe are used as normaliser element in calculating the enrichment (Li et al., 2015; Shaheen et al., 2020b). Therefore, enrichment of the soil with higher contents of PTEs (higher EF values) are an indication of pollution from anthropogenic origin. EF categorizes contamination as minor (if EF = 1.5 – 3), moderate (EF = 3 – 5), severe (EF = 5 – 10) and very severe (EF > 10) as per Antoniadis, et al. (2017a, b).

$$\mathrm{EF} = {}^{(\mathrm{Cs}/\mathrm{Als})}\big/_{(\mathrm{Cref}/\mathrm{Alref})} \tag{3.3}$$

where Als is the total content of Al in the contaminated soil, and Alref is the total content of Al in the uncontaminated/background reference soil (e.g. Li et al., 2015; Saha et al., 2015; Shaheen et al., 2020b).

3.2.5.4 Geo-accumulation index (*Igeo*)

Geo-accumulation index as per Klubi et al. (2018) is given as:

$$Igeo = \log 2\left(\frac{\mathrm{Cs}}{1.5\mathrm{Crefs}}\right) \tag{3.4}$$

3.2.6 Human health risks assessment

Non-carcinogenic health risk assessment of three groups of persons (children, adult males and females) exposed to possible soil ingestion of the contaminated soils in the mining environments were calculated for all studied PTEs. This involved three main steps: first, we calculated average daily dosage (ADD) of possible soil ingestion of the PTEs; this was followed by the calculation of hazard quotient (HQ); and then we calculated the hazard index (HI). HI is the summation of HQs of all the studied PTEs. It is assumed that an adverse health impact there exists when HQ and HI are above 1, whilst adverse health effects are unlikely at HQ and HI of less than, or equal to, 1 (e.g. Li et al., 2015; Rinklebe et al., 2019).

Average daily dose (ADD), calculated in mg kg^{-1} bodyweight day^{-1}:

$$\mathrm{ADD} = \mathrm{Cs}\frac{(\mathrm{IR}\times\mathrm{EF}\times\mathrm{ED}\times 10^{-6})}{(\mathrm{BW}\times\mathrm{AT})} \tag{3.5}$$

where IR is soil ingestion rate (children = 200; adults = 100 mg dust day^{-1}); EF is exposure frequency (children = 350; adults = 250 days year^{-1}); ED is exposure duration (children = 6 years; adults = 25 years); BW is body weight (children = 15 years; adult males = 68 kg; adult females = 58 kg); AT is average time (which is 6*365 days = 2190 days for children, and 25*365 days = 9125 days for adults); and 10^{-6} is for unit conversion. Values are as used and reported in previous studies (e.g. Armah & Gyeabour, 2013; Bortey-Sam et al., 2015; Mensah et al., 2020; Rinklebe et al., 2019; Shaheen et al., 2020b).

Calculation of Hazard quotient (HQ) was then done:

$$\mathrm{HQ} = \frac{\mathrm{ADD}}{\mathrm{RfD}} \tag{3.6}$$

where RfD is PTE oral reference dose as follows: As = 0.0003; Al = 1; Cd = 0.001; Cr = 1.5; Cu = 0.04; Fe = 0.7; Ni = 0.02, Pb = 0.0035; Ti = 0.0003; V = 0.28; and Zn = 0.3 (values in mg PTE per kg bodyweight per day, as obtained from N. Li et al., 2015; P. Li et al., 2015; Rinklebe et al., 2019; Shaheen et al., 2020b; Shen et al., 2019). RfD values for Ti was obtained from Saha et al. (2015); and that of V from Li et al. (2015).

3.2.7 Determination of plant element uptake and phytoremediation potential

3.2.7.1 Soil-to-plant transfer factors

Total PTE uptake in plants was determined as contents of the elements in plant. The phytoremediation potential of the tested plant species was determined using soil-to-plant transfer indices. The PTE accumulation by plant roots and shoots can be assessed using the bio-concentration factor (BCF) and bio-accumulation coefficient (BAC), respectively, as reported and used in previous studies (e.g., Ali et al., 2019; Antoniadis et al., 2017a,b; 2021; Fitz and Wenzel, 2002; Yoon et al., 2006; Wang et al., 2006; Azeem et al., 2021).

The soil-to-plant transfer factors measure the concentration of trace elements in plant to the concentration of the same element in soil. Therefore, these factors measure the capacity of a plant species to accumulate the element from the contaminated soil. The BCF is defined as the ratio of element concentration in the roots to the soil element total content, while the BAC is defined as the ratio of element concentration in the shoots to the soil element total content (Fitz and Wenzel, 2002; Yoon et al., 2006; Wang et al., 2006; Ali et al., 2019; Azeem et al., 2021). Plants that show BCF/BAC values less than 1 are reported to be unsuitable for phytoextraction (Fitz and Wenzel, 2002; Yoon et al., 2006; Shaheen and Rinklebe, 2015). The equations are as follow:

$$\mathrm{BAC} = \frac{\text{Metal content in shoot}}{\text{Total metal content in soil}} \tag{3.7}$$

$$\mathrm{BCF} = \frac{\text{Metal content in root}}{\text{Total metal content in soil}} \tag{3.8}$$

3.2.7.2 Root-to-shoot transfer factor

PTE translocation from root to shoot was assessed using the translocation factor (TF). The TF quantifies and estimates the upward mobility of elements from the roots (below-ground biomass) into aerial parts (aboveground biomass, which could include shoot, stem, or leaf). A TF of 1 is a recommended threshold for categorizing a plant species as being with phytoremediation potential (Antoniadis et al., 2021; Zine et al., 2020, 2021). Thus, TF describes the characteristic nature of hyper-accumulating species; and it is a decisive parameter for classifying plant species for phytoremediation (Marchiol et al., 2004). The following equation as described in Marchiol et al. (2004) and used by other researchers (e.g. Ali et al., 2019; Yoon et al., 2006; Fitz and Wenzel, 2002; Antoniadis et al., 2017a, b; Azeem et al., 2021) was employed:

$$\mathrm{TF} = {}^{\mathrm{Cshoot}}/_{\mathrm{Croot}} \qquad (3.9)$$

where Cshoot = content of element in the plant shoot in mg/kg, Croot = content of element in the plant root in mg/kg.

3.2.8 Data treatment and statistical analyses

We ran a one-way ANOVA between means of different parameters, including fields (natural forest, mine surrounding, Pueraria field, farm 1 and farm 2). We further performed multiple range tests using the Tukey’s Honestly Significant Difference (HSD) test among means of the different studied fields at $P < 0.05$. Additionally, we ran Pearson moment correlations between the total contents of PTEs and relevant soil physico-chemical parameters. The statistical analyses were performed using IBM SPSS Statistics 25 (NY, USA). Boxplots were created to display quantiles of measured values along with their minimum and maximum values, median, means and outliers. Figures were created with the OriginPro 9.1 b215 (OriginLab Corporation, Northampton, USA) software.

3.3 Results and Discussion

3.3.1 Soil physico-chemical properties

The physico-chemical properties of the various sites near the abandoned mine spoil and natural forest are shown in Table 3.1. The soil texture was dominantly silty with silt having a range between 50% and 85%; higher silt contents were found in farm 2 (71.7 – 84.8%) and the mine surrounding (70.0 – 74.4%). Soil pH from all fields were generally acidic (range: 3.8 – 5.9;

average value, 4.0), with the maximum pH being observed at the Pueraria field and the minimum at the mine surrounding. Total carbon contents were generally below 4% (range: 0.1% – 3.1%) in all fields, with relatively higher contents observed in the natural forest and farm 2. Additionally, total contents of nitrogen ranged between 0.1% and 0.3%. The fields were far from being salt-affected as demonstrated by their low electrical conductivities (22.5 – 124.6 µS cm^{-1}), with maximum values found in the Pueraria sites. Higher contents of total Mn were observed in farm 1 (196.8 – 1216 mg/kg) and in the Pueraria fields (67.1 – 161.6 mg/kg).

3.3.2 Total element contents in the sites

Total contents of PTEs in the various mining environments are presented in Fig. 3.1. Iron showed the highest total contents among the elements with a range between 6,208 mg/kg and 60,320 mg/kg, with minimum values observed in the natural forest and the maximum values in the Pueraria field. Higher total Fe contents were equally observed in farm 1 (22,000 – 56,720 mg/kg) and farm 2 (20,480 – 33,360 mg/kg). This was followed by the contents of Al (2,352 – 9,840 mg/kg in all fields), and greater contents were observed in the mine surrounding (3,768 – 7,952 mg/kg), farm 1 (4,176 – 9,840 mg/kg), farm 2 (4,880 – 8,640 mg/kg), and Pueraria field (4,936 – 6,488 mg/kg) than in the natural forest (2,350 – 3,232 mg/kg). Arsenic was the third most abundant element in all fields (10.8 – 3,144.0 mg/kg). As for the rest of the elements, they had relatively higher contents in the areas near the abandoned mine spoil (i.e. mine surrounding, farms 1 and 2, and the Pueraria field) than in the forest: Cd (0.2 – 1.6 mg/kg), Cr (6.6 – 281.6 mg/kg), Cu (3.4 – 34.8 mg/kg), Ni (0.6 – 19.7 mg/kg), Pb (3.1 – 28.9 mg/kg), Ti (4.5 – 170.4 mg/kg), V (8.6 – 175.2 mg/kg) and Zn (30.4 – 319.2 mg/kg).

Iron contents in all studied fields (except in the forest) exceeded the reference background concentration of 20,000 mg/kg (Shaheen et al., 2020b). The principal primary and secondary minerals contained in the abandoned mine spoil are FeAsS and $FeAsO_4$, which contain the greater proportions of Fe as found in our earlier work (Mensah et al., 2020) and reported by Hayford et al. (2009). Thus, we assume that high contents of total Fe in soils and farms near the abandoned mine spoil may be due to mobilisation and deposition from the unfenced contaminated mine spoil. This mobilisation or deposition might happen either through water or wind erosion, surface runoff, or rainfall, as explained in similar previous studies (e.g. Armah and Gyeabour, 2013; Rinklebe et al., 2020).

Table 3.1: Mean, minimum, and maximum values of selective soil properties of the studied soils

Field	Statistics	pH	EC	Clay	Sand	Silt	C	N	C/N
			(µS/cm)	(%)	(%)	(%)	(%)	(%)	
Natural Forest	Mean	4.1	54.6	3.2	43.6	53.2	2	0.2	10.0
	SD	0.1	11.2	0.3	3.0	2.9	0.5	0.0	0.8
	Min	4.0	38.9	2.8	39.5	50.0	1.3	0.1	9.6
	Max	4.3	70.9	3.7	47.2	57.2	2.7	0.3	12
	n	6	6	6	6	6	10	10	10
Mine Surrounding	Mean	4.3	48.9	7.1	21.4	71.5	1.8	0.2	9.5
	SD	0.5	17.3	0.8	1.5	2.1	0.6	0.1	1.3
	Min	3.8	22.5	6.1	19.2	69.9	1.1	0.1	7.6
	Max	5.6	82.7	8.3	22.8	74.4	3.1	0.3	12.6
	n	11	11	6	6	6	24	24	24
Pueraria Field	Mean	5.0	84.9	11.5	18.7	69.8	0.9	0.1	6.7
	SD	0.8	35.0	3.7	18.7	4.0	0.4	0.1	1.9
	Min	4.5	58.7	7.1	7.7	64.7	0.4	0.1	5.2
	Max	5.9	124.6	16	11	74.1	1.3	0.2	9.3
	n	3	3	6	6	6	6	6	6
Farm 1	Mean	4.7	43.6	9.3	28.5	62.3	0.8	0.1	6.8
	SD	0.3	14.7	0.7	3.6	4.2	0.3	0.0	1.5
	Min	4.4	26.6	8.5	24.7	56.5	0.5	0.1	5.0
	Max	5.0	52.5	10.6	33.0	66.0	1.1	0.2	8.4
	n	3	3	6	6	6	6	6	6
Farm 2	Mean	4.1	47.8	7.6	12.5	80.0	2.2	0.2	9.9
	SD	0.2	8.1	1.1	6.3	6.2	0.1	0.0	0.4
	Min	4.0	40.9	6.4	8.2	71.7	2.0	0.2	9.6
	Max	4.3	56.7	9.1	20.6	84.8	2.2	0.2	10.4
	n	3	3	6	6	6	6	6	6

Farm 1 = Peasant farm under cassava cultivation; Farm 2 = Subsistence farm consisting of cocoa, plantain and cocoyam; EC: electrical conductivity.

In mine spoil soils, higher contents of Fe have previously been reported (e.g. Armah and Gyeabour, 2013; Bansah and Addo, 2016; Mensah et al., 2020); but these works reported relatively lower contents than those found in our study.

Likewise, total contents of As in all fields (10.8 – 3144 mg/kg) exceeded the world soil average (6.8 mg/kg) as reported in Kabata-Pendias (2011). Particularly, higher contents were observed in the mine surrounding (69.4 – 3144.0 mg/kg). These were followed by As in the Pueraria field, and in farm 2. Lower total As contents (10.8 – 23.0 mg/kg) were observed in the forest, but contents similarly exceeded the world soil average, whilst its maximum value exceeded the maximum allowable content reported in Kabata-Pendias (2011). We assume that high contents of As even in the natural forest may be more of geogenic enrichment. Additionally, As contents in all fields near the abandoned mine spoil surpassed the trigger action value (65 mg As/kg) (Kabata-Pendias, 2011), and the German Trigger Value threshold for playgrounds (25 mg As/kg). The high content of As in the soils near the abandoned mine spoil may be due to transport, mobilisation and accumulation from the contaminated spoil as mentioned and explained in detail in Mensah et al. (2020). Similarly, heavily As-polluted sediments and soils in the vicinity of abandoned mine spoil are reported in Slovakia (with concentrations up to 5,166 mg As/kg) by Hiller et al. (2012) and in India (>2,000 mg As/kg) by Chakraborti et al. (2013): they reported values similar or higher than those found in our study. It is indeed reported that active and abandoned mine spoils with no reclamation may be responsible for pollution of surrounding soils and groundwater with toxic elements (e.g. Chakraborti et al., 2013; Tapia et al., 2019; Mensah et al., 2020).

As for Zn, their total content in all sites including the natural forest were below the background reference (Fig. 3.1), but the 90th percentile (197 mg/kg) in Pueraria field (Appendix A; Table S3.1), and the maximum values of the mine surrounding (76.7 mg/kg) were above the 70 mg/kg world soil average (Douay et al., 2013; Kabata-Pendias, 2011). Furthermore, the maximum (319.2 mg/kg) in the Pueraria field was above the maximum allowable content (i.e. 300 mg Zn/kg) reported for agricultural soils by Kabata-Pendias (2011), but fell below the trigger action value (i.e. 1500 mg Zn/kg; Kabata-Pendias, 2011).

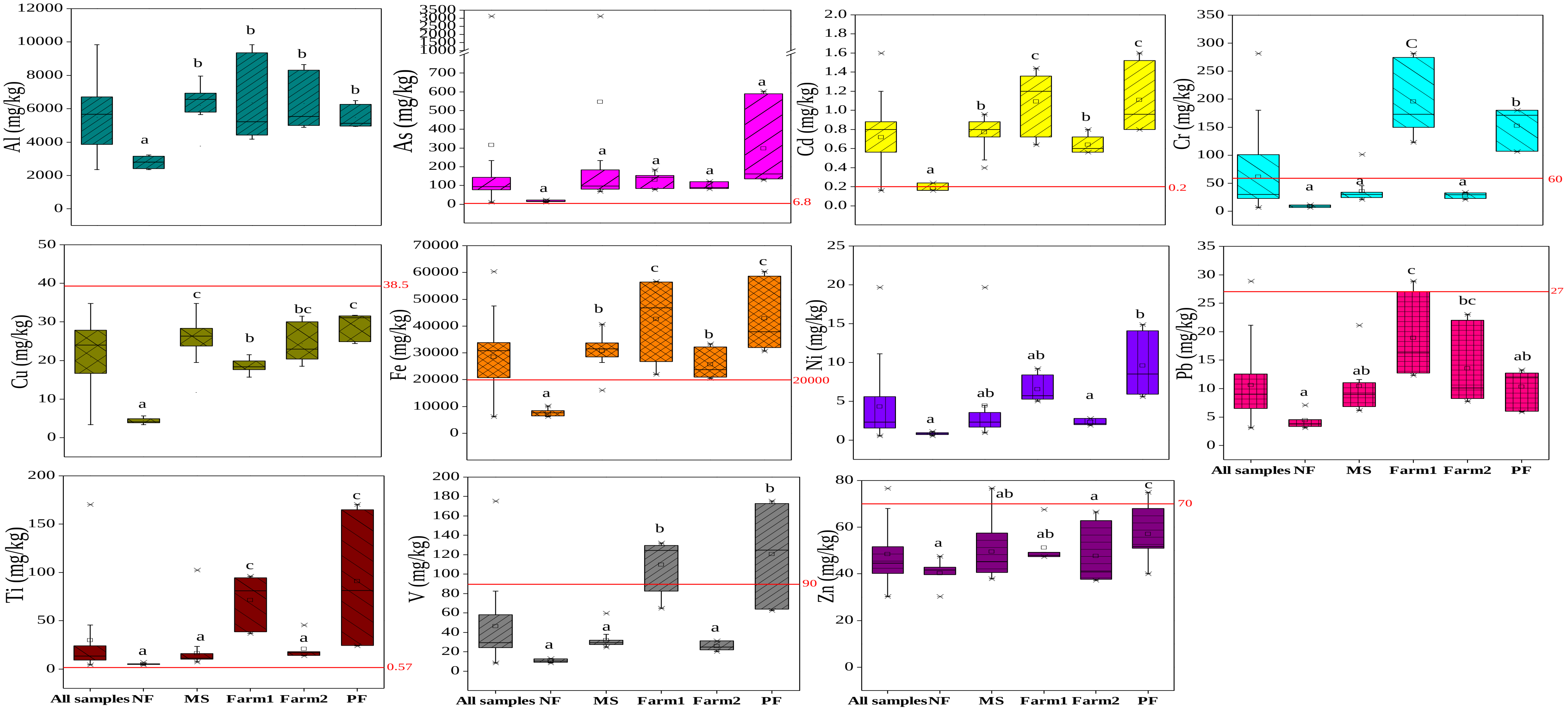

Fig. 3.1: Total contents of soil potentially toxic elements (mg/kg) in soils and farms near the mine spoil. NF = natural forest; MS = mine surrounding; PF = Pueraria field. Asterisk marks (lower and upper) in the range represent the 1% and 99% percentiles, respectively. Asterisks outside the range represent outliers. Small rectangular boxes represent mean values.

We assume that Zn accumulation near the mine spoil may be related to anthropogenic effluent release from the on-going artisanal gold mining activities in the surrounding (Armah and Gyeabour, 2013), or through dust emission generated from motor vehicles (Douay et al., 2013). High contents of Zn (average, 731.5 mg/kg) in soils of industrial mining areas have also been reported in Greece by Antoniadis et al. (2017c).

Total contents of Al, Cu, Ni, and Pb (except the maximum value, 28.9 mg/kg in farm 1) in all sites were below their respective world soil averages. Cadmium (except in the forest) and Ti, on the other hand, exceeded their world soil average thresholds. Cadmium and Ti in the soils correlated positively with Fe, Mn and negatively with C. This may mean that Cd and Ti accumulation in the mine soil may be influenced by the contents of Fe, Mn, and C. The negative correlation between C and Cd and Ti indicates that total Cd and Ti may be lower in soils which happen to have high carbon and higher in soils with low carbon content. Additionally, Cd correlated positively with Al, whilst Ti correlated negatively with P contents (Appendix A; Table S3.2). Thus, Cd and Ti may be held with Fe/Mn oxides in the mine spoil soil either through co-precipitation, adsorption, surface complexation, ion exchange or occlusion in the soil crystal lattice, as indicated by Liu et al. (2018). In this regard, the metals may be leached or released to contaminate the nearby food chain and available surface and groundwater during dissolution of the soil mineral (Gu et al., 2019). Positive correlation between Cd and Fe/Mn; as well as negative relationship with C, have been reported by Liu et al. (2018). High contents of Cd in agricultural soils were found to be above FAO/WHO permissible threshold in mining regions in China (Shen et al., 2019).

For Cr and V, average total contents in the natural forest, mine surrounding, and farm 2 were below reference values, whilst average contents in farm 1 and Pueraria field exceeded them. The maximum (175.2 mg/kg) (Fig. 3.1) and 90th percentile values of total V (174.0 mg/kg; Appendix A; Table S1) in the Pueraria field were above the maximum allowable concentrations (150 mg V/kg), as reported in Kabata-Pendias (2011).

In summary, average total contents in all fields were in the order: Fe > Al > As > Cr > Zn > V > Ti > Cu > Pb > Ni > Cd. Fe contents in the fields near the mine spoil exceeded the reference background value. Total As in all fields also surpassed their world soil average. Total Zn at 90th percentile in the Pueraria field, and maximum values in the mine surrounding were above the world soil average, whilst Zn maximum in the Pueraria field was above the maximum allowable content. Cadmium (except in the forest) and Ti exceeded their world soil average. On the other hand, total contents of Al, Cu, Ni, and Pb were below their world soil averages.

3.3 Soil contamination factor

Arsenic (1.6 – 460), Cd (0.8 – 8.0), Fe (0.3 – 3.0) and Ti (8.0 – 299) from all the mining environments exhibited average CFs greater than 1. On the other hand, mean CF values of Al (0.1 – 0.5), Cu (0.1 – 0.9) and Ni (0 – 0.7) were less than 1 (Fig. 3.2). In addition, maximum CF values of V (1.9) were > 1 in farm 1 and in the Pueraria field, whilst Zn CF (4.6) was > 1 in the mine surrounding and in the Pueraria field. Chromium exhibited average CF of 1, with CF in the natural forest, mine surrounding, and farm 2 being less than 1. Contamination factor values of Cu, Cr, Ni, Pb, V, Zn, Al, and Fe indicated that there is no contamination derived from these metals in the natural forest. A few possible explanations may account for the fact that there was no contamination in the natural forest compared to the sites near the mine spoil. These include absence of large-scale mining activities in the forest, the location which is away from the mine spoil (3.4 km away), or presence of mixed vegetation which buffers the soil against wind erosion and deposition of contaminated materials. In a similar study, Douay et al. (2007) reported higher metal (e.g. Cd and Pb) contamination in the topsoil near a former zinc smelter site than those found at some distance away from a former smelter site in France. The study further indicated that Cd found in the agricultural soils was negatively correlated and thus inversely proportional with the distance from the former smelter of point-source pollution (Douay et al., 2007). However, As (CF = 2.0 – 3.4) in the natural forest showed moderate to considerable degree of soil contamination. Additionally, the high CF of Ti (7.9 – 12.1) in the natural forest indicates very severe degree of soil pollution and contamination with Ti in the forest. These may be attributed to reported illegal small-scale gold mining activities in the forest or other activities as explained in section 3.2.

Contamination factor of Cr in farm 1 (2.1 – 4.7) and the Pueraria field (1.7 – 3.1) indicated moderate to considerable degrees of soil contamination. Cadmium CF in farm 1 (3.2 – 7.2) and the Pueraria field (4 – 7.6) indicated considerable to very severe soil contamination. Additionally, there was an indication of moderate to considerable degree of soil contamination in farm 2 and mine surrounding. Cd contamination in our study was comparable to that found by Shen et al. (2019). The authors in that work reported that soil Cd levels in the mining

Tongling city in China were above the Chinese Environmental Soil Quality Standards and indicated potential environmental and human health risk to the residents in the mining area. Also, Fe CF values observed near the abandoned mine spoil in the mine surrounding (1.3 – 2.0), farm 1 (1.1 – 2.8) and farm 2 (1.02 – 1.67), as well as in the Pueraria field (1.5 – 3.0), indicated moderate degree of soil contamination with Fe. Vanadium also showed moderate degree of contamination, particularly in farm 1 and in the Pueraria field.

Concerning the CF of As and Ti in the mine surrounding, Pueraria field, as well as in farms 1 and 2 (Fig. 3.2), they surpassed the threshold of 6, and indicated very severe degree of soil contamination with As and Ti. As is mostly found to be among the most abundant elements in multi-element contaminated soils and is known to be associated with industrial mine wastes, as reported previously in Greece (Antoniadis et al., 2019a), Ghana (Mensah et al., 2020), Germany (Rinklebe et al., 2019) and Egypt (Shaheen et al., 2020b). Furthermore, As contamination in our study was higher compared to other works (e.g. Kinimo et al., 2018; Klubi et al., 2018; Shen et al., 2019; Teixeira et al., 2018), but lower than the values found in Mensah et al. (2020). As for Ti, fewer studies have reported its enrichment in soils and associated it with health impacts; in fact, it is usually excluded by most current studies monitoring soil PTEs and their risk (e.g. Antoniadis et al., 2017b,c; Rinklebe et al., 2019; Shaheen et al., 2020b). This shows the novelty of our work in filling this gap in current scientific knowledge regarding Ti and its associated soil contamination and human health risk.

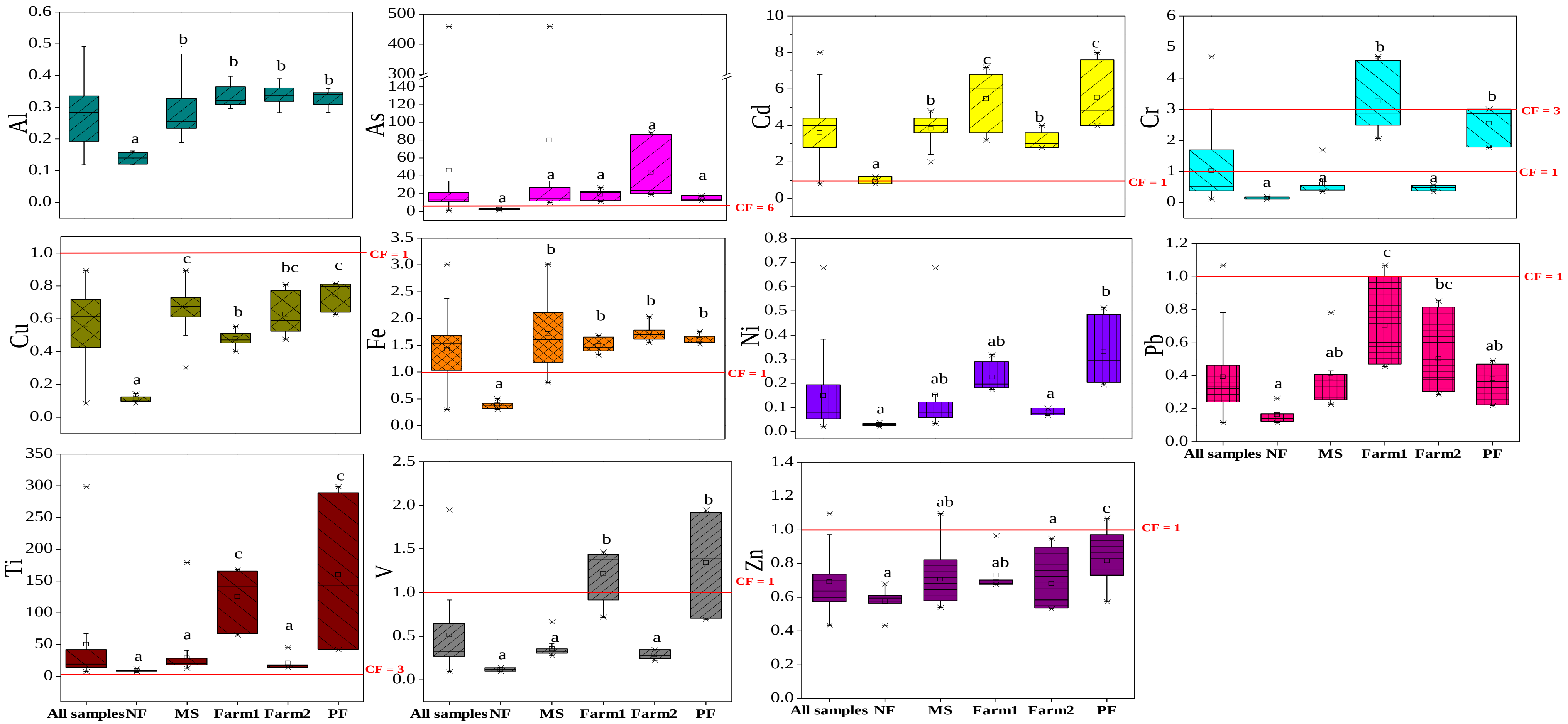

Fig. 3.2: Soil contamination factor of PTEs in the soils and farms near the mine spoil. NF = natural forest; MS = mine surrounding; PF = Pueraria field. Asterisk marks (lower and upper) in the range represent the 1% and 99% percentiles, respectively. Asterisks outside the range represent outliers. Small rectangular boxes represent mean values.

3.3.4 Pollution load index

Pollution load index (PLI) is an indication of multiple element contamination in an area. Thus, a higher PLI shows that an area is collectively contaminated with more than one source of PTEs. The PLI of the studied elements in our work is shown in Fig. 3.3. The PLI of the elements under consideration in all sites ranged between 0.3 and 2.4, with the lowest values observed in the natural forest and the highest in farm 1 and in the Pueraria field. Pollution load index values observed in the natural forest were all below 1, indicating no significant pollution. The possible reasons for the non-significant pollution of the natural forest soils were explained earlier in section 3.2. Pollution load index values in farm 1 (1.6 – 2.3) and in the Pueraria field (1.89 – 2.36) bear an indication of significant soil pollution of these sites. Antoniadis et al. (2019a) and Shaheen et al. (2020b) have previously reported high soil PLI in multi-element contaminated soils, higher than those found in our study. The level of soil pollution of the various sites based on their respective median PLI values were in the order: Pueraria field > farm 1 > mine surroundings > farm 2 > natural forest. Based on the CF findings discussed earlier, it is suggested that the reported PLI is mainly attributed to the high CF of As, Cd, Fe, Ti and to a lesser extent to Cr. Similarly, Shen et al. (2019) found that soil pollution of farmlands in a gold mining region in China was mainly caused by Cd and As, and to a lesser extent by Cu and Zn. Shaheen et al. (2020b), on the contrary, found that Se was the main contributor to soil pollution, followed by As, Mo, Cr, Cu, and Zn in a study concerning Germany and Egypt.

3.3.5 Enrichment factor and geo-accumulation index

The average EF values of the elements show that all sites were enriched with Ti, As, Cd, Fe, Cr, Zn, Pb, Cu, and Ni (in this decreasing order; Table 3.2). In the natural forest, high EF values of Ti (65.9), As (18.1), and Cd (6.6) indicated severe (EF = 5 – 10) to very severe (EF > 10) levels of enrichment and, hence, extreme soil contamination. As noted earlier, we assume that these levels of soil enrichment of the forest with As, Cd and Ti may be caused by both anthropogenic and geogenic sources. Likewise, in the mine surrounding, Pueraria field, farms 1 and 2, top soils were extremely to extremely severe contaminated with Ti, As, and Cd as demonstrated by their EF values. Enrichment factor values of Ti, for instance, exceeded 50, reaching all-time high average values of 292.3 and 621.7 in farm 1 and in the Pueraria field, respectively.

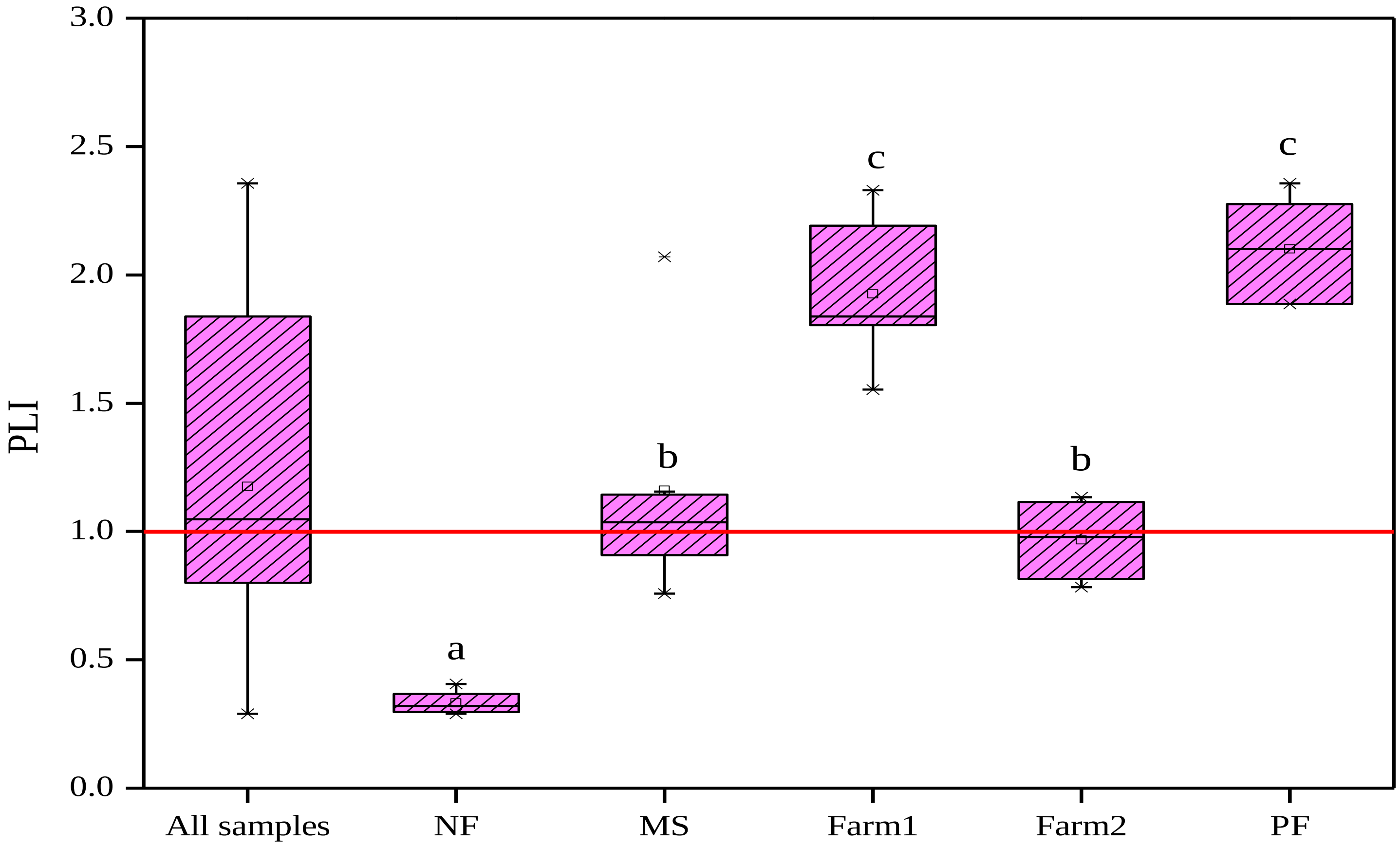

Fig. 3.3: Soil pollution load index (PLI) of PTEs in the soils and farms near the mine spoil. NF = natural forest; MS = mine surrounding; PF = Pueraria field. Asterisk marks (lower and upper) in the range represent the 1% and 99% percentiles, respectively. Asterisks outside the range represent outliers. Small rectangular boxes represent mean values.

Likewise, As EF values for the mine surrounding and Pueraria field reached a maximum of 2,435.4 and 277.2, respectively. These indicate extremely severe levels of soil contamination with As and Ti in the gold mining area. Based on EF, Kinimo et al. (2018) found that average As concentrations in sediments were significantly higher in industrial gold mining areas than in non-mining areas in Ivory Coast. Additionally, Cr showed very severe topsoil enrichments in the Pueraria field (EF = 9.6) and farm 1 (EF = 7.2). Zhang and Liu (2002) recommended that contamination is probably of anthropogenic origin where EF > 1.5. Thus, we may conclude that soil pollution with Ti, As, Cd in the soils near the mine spoil may be due to anthropogenic gold mining activities in the region. Gold mining activities such as crushing and amalgamation (Kinimo et al., 2018), abandonment of mine spoils and poor management of mine wastes (Mensah et al., 2020), as well as stockpiling of mine wastes in mounds (Mensah et al., 2015) may release toxic elements into the environment and nearby ecosystem. In this respect, Kinimo et al. (2018) reported that there is therefore a link between industrial gold mining and As contamination in nearby wetland sediments. As for I_{geo}, the values in all the mine sites were As (0.1 – 8.3), Ti (2.4 – 7.6), and Cd (-0.9 – 2.4) (Appendix A; Table S3.3). The rest of the elements had negative I_{geo} values indicating the absence of significant contamination.

3.3.6 Human health risk assessment

The hazard quotients (HQs) of soil ingestion of PTEs are shown in Fig. S3.3; Appendix A for children, adult females, and adult males. In all sites, relatively high HQ values were observed for children, followed by female adults and then male adults. Observed HQs of As were above unity for children in the mine surrounding, the Pueraria sites, and farms 1 and 2, whilst that of the natural forest were below unity. In adult males and females, the maximum HQ values of As were above unity in the mine surrounding and in the Pueraria sites. Higher As HQ values above unity for both children and adult males and females have been found in our previous study on abandoned and active mine tailings in Ghana (Mensah et al., 2020), a study that reported median HQ values multiple times higher than those found in this study. Similar to our findings, higher HQs of As for children than males and females are repeatedly reported in other studies (e.g. Mohammadi et al., 2020; Rinklebe et al., 2019; Shaheen et al., 2020b). For children, higher Ti HQs than unity were observed in farm 1 and in the Pueraria sites, whilst the maximum value of Ti was observed in the mine surrounding.

Table 3.2: Mean, minimum, and maximum values of topsoil (0 – 20 cm) enrichment (enrichment factor) with PTEs in the soils studied

Field	Statistics	As	Cd	Cr	Cu	Fe	Ni	Pb	Ti	V	Zn
Natural Forest	Mean	18.1a	6.6a	1.1a	0.8a	2.8a	0.2a	1.2a	65.9a	0.9a	4.2a
	SD	5.1	1.0	0.1	0.1	0.2	0.0	0.5	6.9	0.0	0.7
	Min	13.2	5.0	0.9	0.6	2.6	0.2	0.9	56.7	0.8	3.3
	Max	26.8	8.4	1.2	0.9	3.2	0.3	2.2	77.1	0.9	5.3
	n	10	10	10	10	10	10	10	10	10	10
Mine Surrounding	Mean	330.4a	12.9bc	2.2a	2.2bc	5.0bc	0.6ab	1.4ab	92.9a	1.2a	2.5a
	SD	701.3	3.5	2.1	0.8	0.9	1.0	0.9	83.1	0.5	1.2
	Min	26.8	7.0	1.0	1.3	3.3	0.1	0.6	39.2	0.8	1.4
	Max	2435.4	23.4	9.0	4.7	7.2	3.6	4.2	451.8	2.2	5.8
	n	24	24	24	24	24	24	24	24	24	24
Pueraria Field	Mean	149.3a	20.9d	9.6b	2.7c	8.1d	1.2c	1.4ab	621.7b	5.1b	5.4a
	SD	98.0	8.4	3.1	0.3	3.1	0.6	0.4	464.6	2.5	6.1
	Min	74.8	12.3	5.5	2.4	4.9	0.8	0.9	131.1	2.2	2.3
	Max	277.2	32.2	12.1	3.3	11.8	2.1	1.8	1203.5	7.8	17.8
	n	6	6	6	6	6	6	6	6	6	6
Farm 1	Mean	50.0a	13.5cd	7.2b	1.3ab	5.2cd	0.6ab	2.1b	292.3b	2.9b	2.8a
	SD	38.3	7.5	4.9	0.7	2.9	0.5	1.6	231.5	2.0	1.5
	Min	5.1	1.0	0.1	0.1	0.2	0.0	0.5	6.9	0.0	0.7
	Max	122.3	23.5	11.3	2.2	9.0	1.4	5.1	658.9	5.6	5.3
	n	6	6	6	6	6	6	6	6	6	6
Farm 2	Mean	49.7a	10.4a	1.5a	2.0bc	4.1ab	0.3ab	1.7ab	69.2a	0.9a	2.2a
	SD	19.6	1.2	0.2	0.2	0.2	0.0	1.1	41.7	0.1	0.6
	Min	28.6	8.7	1.3	1.9	3.9	0.2	0.9	40.0	0.8	1.4
	Max	72.8	11.5	1.9	2.3	4.5	0.3	3.3	151.7	1.0	3.2
	n	6	6	6	6	6	6	6	6	6	6

Farm 1 = Peasant farm under cassava cultivation; Farm 2 = Subsistence farm consisting of cocoa, plantain and cocoyam. Different letters within same lines indicate that means differ significantly from one another at $P < 0.05$ according to the Tukey's Honestly Significant Difference test.

The resultant hazard index (HI) values for all sites were 0.7 – 134.56 for children, 0.05 – 10.6 for adult males and 0.13 – 12.77 for adult females (Fig. 3.4). In all fields, HI was in the following decreasing order: children > adult females > adult males. The high HI values especially for children in the mine surrounding, the Pueraria sites, and farms 1 and 2 surpassed by far the critical threshold of 1, indicating very high health risk implications associated with PTEs for children in the mining communities. Similar results have also been found in other similar works (e.g. Antoniadis et al., 2019a; Mohammadi et al., 2020).

In terms of relative contributions to total HI in the natural forest, As accounted for the greatest average contribution (74%) of the total health risk of all person groups (children, adult females, and adult males) (Fig. S3.4; Appendix A). This was followed by Ti (23.6%), and Pb (1.8%), while all other PTEs, including Cd, Zn, Cu, and Ni, collectively contributed 0.6% of the total human health risk. In the mine surroundings, the highest average contribution to HI was by As (88.1%) and Ti (11.03%), whilst the other elements accounted for the 0.87% of the total human health risk. Similarly, in farm 1, the average contribution to the total HI was mainly by As (63.2%) and Ti (35.7%). In farm 2, the average contribution to human health risks was in the order: As (87.7%) > Ti (10.8%) > Pb (1.07%) > Cd (0.18%) > Cu (0.17%). Likewise, in the Pueraria field, the contribution was in the order: As (68.7%) > Ti (30.8%) > Pb (0.24%). Thus, it can be reiterated that As contents in the sites near the mining spoil may pose health risk to the residents, as explained earlier. In this regard, Bundschuh et al. (2021) reported that chronic exposure to high levels of As in soils and groundwater in Latin America caused consequent health impacts (such as cancer, Buruli ulcer, skin lesions, reproductive problems, cardiovascular diseases, and cognitive problems) on the residents. Our findings agree with those presented by other similar works. For instance, Mohammadi et al. (2020), assessing the health risks of trace elements (Ag, Al, As, Ba, Be, Co, Cr, Cu, Fe, Mn, Ni, Pb, Rb, Sr, Ti, V) in western Iran, found that As contributed the highest percentage of non-carcinogenic health risk. Additionally, Shen et al. (2019) found that As, Pb, and Cr had the highest contribution to the total health risk quotient in agricultural soils in a gold mining city in China, and As in particular posed major carcinogenic risk to the people in the region.

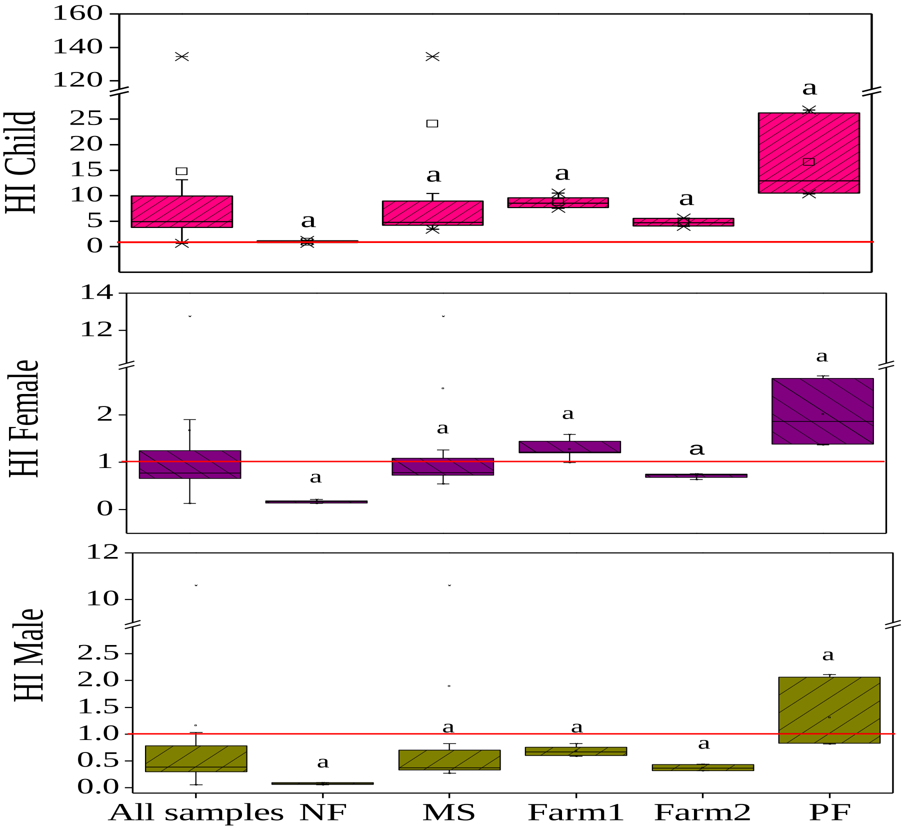

Fig. 3.4: Non-carcinogenic soil ingestion hazard index (HI) of the studied PTEs from the soils and farms near the mine spoil. NF = natural forest; MS = mine surrounding; PF = Pueraria field. Asterisk marks (lower and upper) in the range represent the 1% and 99% percentiles, respectively. Asterisks outside the range represent outliers. Small rectangular boxes represent mean values.

3.3.7 Plant element uptake and phytoremediation potential

3.3.7.1 Plant element uptake

The concentration of As, Cu, Ti, and Zn in the five native plant species is presented in Appendix A; Fig. S3.5. The other elements in this study (Al, Cd, Cr, Ni, Pb, and V) were not detected. Zinc had the highest concentration in the aboveground biomass of all five tested native plant species. Likewise, in the below-ground biomass, contents of Zn in plants surpassed 50 mg/kg in all the native plant species, with maximum content observed in *Pueraria montana* (84.6 mg/kg) and minimum in *Alchornea cordifolia* (60.0 mg/kg). The highest Zn concentration was found in *Lantana camara* (162.0 mg/kg), followed by *Chromolaena odorata* (157.0 mg/kg), *Pueraria montana* (147.41 mg/kg), *Alchornea cordifolia* (136.0 mg/kg), and fern (128.2 mg/kg). Zinc content in both the above- and below-ground biomass exceeded an expected plant content of usually not higher than 50 mg/kg for plants in uncontaminated soils (Antoniadis et al., 2021). Additionally, sensitive plant species are reported to be retarded in growth with Zn content range between 100 and 500 mg/kg (Kabata-Pendias, 2011). Our findings agree with Antoniadis et al. (2021), who found that Zn was the element with the highest concentration among As, Cd, Cr, Ni and Pb in twelve tested phytoremediation plant species in Germany. Further, Conesa et al. (2007) found that the highest Zn concentration was found in *Zygophyllum fabago* shoots (750 mg/kg) among Pb, Zn and Cu in a phytoremediation research in southeast Spain. Indeed, Zn is recognised as a highly mobile element and as reported by Kabata-Pendias (2011), it is bound to low molecular weight organic compounds in xylem fluids and in other plant tissues; this may explain its high mobility usually found in plants. In this respect, Sakakibara et al. (2011) found that Zn was the most highly accumulated element among As and Cd in *Eleocharis acicularis* growing in heavy metal-contaminated water and sediments in southwestern Japan.

Copper was the next most abundant element in most cases in plants' aboveground biomass. The highest Cu concentration was found in *Chromolaena odorata* (48 mg/kg) and the lowest in fern (13.7 mg/kg). *Pueraria montana*, *Lantana camara*, and *Alchornea cordifolia* had Cu concentrations of 27.6, 25.1 and 21.8 mg/kg, respectively. In terms of concentration in their roots, Cu ranged between 9.8 and 22.8 mg/kg, with the maximum value observed in *Pueraria montana* and the minimum in fern. Copper concentrations especially in the aboveground biomass exceeded 10 mg/kg usually expected for plants in non-contaminated soils and were comparable to those found by Antoniadis et al. (2021). Additionally, Cu concentration in the shoot of *Chromolaena odorata* found in our study was higher than that reported in its leaves by Bansah and Addo (2016).

In the case of As in the aboveground biomass, its highest concentration was observed in *Chromolaena odorata* with 62.1 mg/kg, followed by *Pueraria montana* (14.3 mg/kg), fern (14.6 mg/kg), *Lantana camara* (12.9 mg/kg) and *Alchornea cordifolia* (3.0 mg/kg). In roots, the highest As content was observed in *Pueraria montana* (23.7 mg/kg), and this was followed by *Lantana camara* (21.3 mg/kg), *Chromolaena odorata* (13.3 mg/kg), *Alchornea cordifolia* (10.0 mg/kg) and *Pityrogramma calomelanos*- fern (9.8 mg/kg). Arsenic is not an essential element, so it does not have any "expected" concentration in plants. In this respect, Kabata-Pendias (2011) reported that concentration of As in plants grown on uncontaminated soils usually range between 0 and 1.5 mg/kg. Higher As accumulation by *Pteris vittata* (2200 – 3030 mg As/kg) has previuosly been reported by Zhao et al. (2002).

Concentration of Ti in the above-ground biomass ranged between 8.1 and 13.9 mg/kg, with the highest concentration observed in fern and the minimum in *Alchornea cordifolia*. In roots, the highest Ti concentration was found in *Lantana camara* (13.1 mg/kg), followed by *Chromolaena odorata* (9.7 mg/kg), *Pityrogramma calomelanos*- fern (8.1 mg/kg), *Pueraria montana* (8.1 mg/kg) and *Alchornea cordifolia* (6.8 mg/kg). Kabata-Pendias (2011) reported that Ti concentration in plants vary within the range of 0.15 – 80 mg/kg. Titanium is relatively unavailable to plants and not readily mobile in them; this explains the little attention given to the element in many studies (Kabata-Pendias, 2011). Thus, to the best of our knowledge, our study is among the few works that have investigated the phytoremediation potential of *Chromolaena odorata*, *Lantana camara*, *Alchornea cordifolia*, *Pueraria montana* and fern for cleaning up Ti in contaminated mine spoil soils.

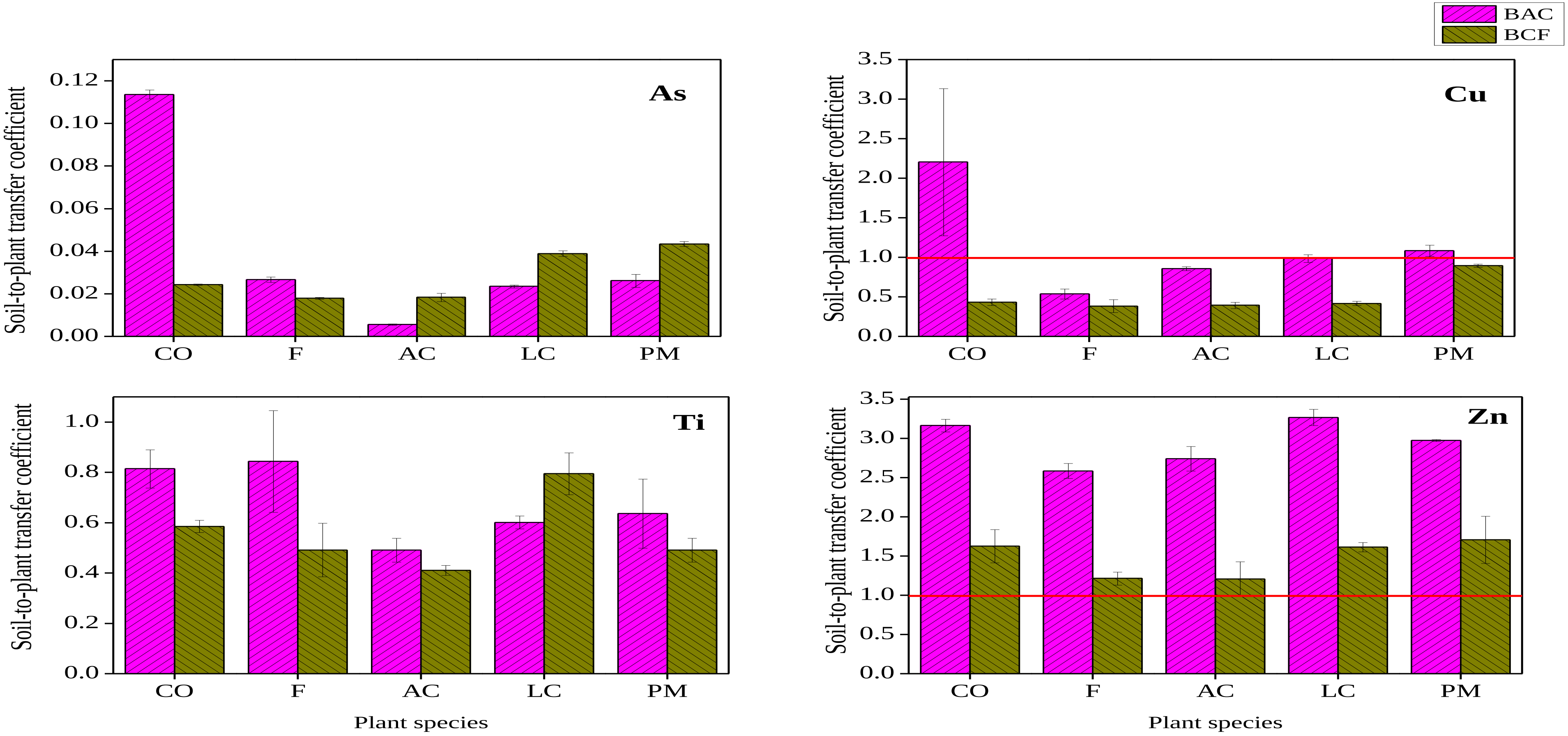

Fig. 3.5: Soil-to-plant transfer coefficients (TC) of toxic elements (As, Cu, Ti, and Zn) into shoots (bio-accumulation coefficient (BAC)) and roots (bio-concentration factor (BCF)) by the five native plant species near the abandoned mine spoil. Added line indicates the threshold above which plant is considered a phytoremediator. CO = Chromolaena odorata, F = fern, AC = Alchornea cordifolia, LC = Lantana camara, PM = Pueraria montana.

3.3.7.2 Phytoremediation potential of the native plants

As for TC, only Cu and Zn among the studied PTEs had values of > 1 (Fig. 3.5). This highlights the high mobility of these elements from the mine soil into the plants and indicates the ability of the plants to tolerate the elements even at their high concentrations. For As and Ti, their TCs were < 1, which may be attributed to their high contents in the mine soils. In this respect, Antoniadis et al. (2017a) reported that in highly PTE-enriched soils, soil-to-plant transfer is decreased due to seeming toxicities, and hence TCs become lower. For Cu, only *Chromolaena odorata* had a TC of > 1 for its shoot. This implies that it could be considered as a phytoremediation species for Cu. For Zn, all the tested native plant species may be possibly used for phytoremediation, as demonstrated by their high TCs of higher than 1 in both their shoots (BAC) and roots (BCF). Shaheen and Rinklebe (2015) found that TCs of sunflower and rapeseed were higher than 1 for Zn in a multi-element contaminated riparian soil, and they reported TC values (5 – 20) higher than those found in our work. However, Antoniadis et al. (2021) reported lower TC values (of <1) for twelve tested phytoremediation plants in Germany. Thus, it could be concluded that *Chromolaena odorata*, *Lantana camara*, *Pueraria montana*, *Alchornea cordifolia* and *Pityrogramma calomelanos*- fern near the abandoned mine spoil may be considered for cleaning up Zn from the soil, either through their shoots or roots. Particularly *Chromolaena odorata* and *Lantana camara* may be used for the phytoextraction of Zn, *Lantana camara* for the remediation through both shoots and roots, whilst *Pueraria montana* may be used for the remediation through roots.

For the multi-contaminated mine soils (with As, Cu, Ti, and Zn), phytoextraction may be achieved using *Chromolaena odorata* (TF for As = 4.7, Cu = 5.1, Ti = 1.4, Zn = 2.0) and fern (TF for As = 1.50, Cu = 1.4, Ti = 1.8, Zn = 2.1). Thus, *Chromolaena odorata* may be a better option than fern as demonstrated by their higher TFs for these elements. Moreover, with their TFs of higher than 1, *Alchornea cordifolia* and *Pueraria montana* may be used for the phytoremediation of Cu, Ti, and Zn. *Lantana camara* may also be an option for Cu and Zn (Fig. 3.6).

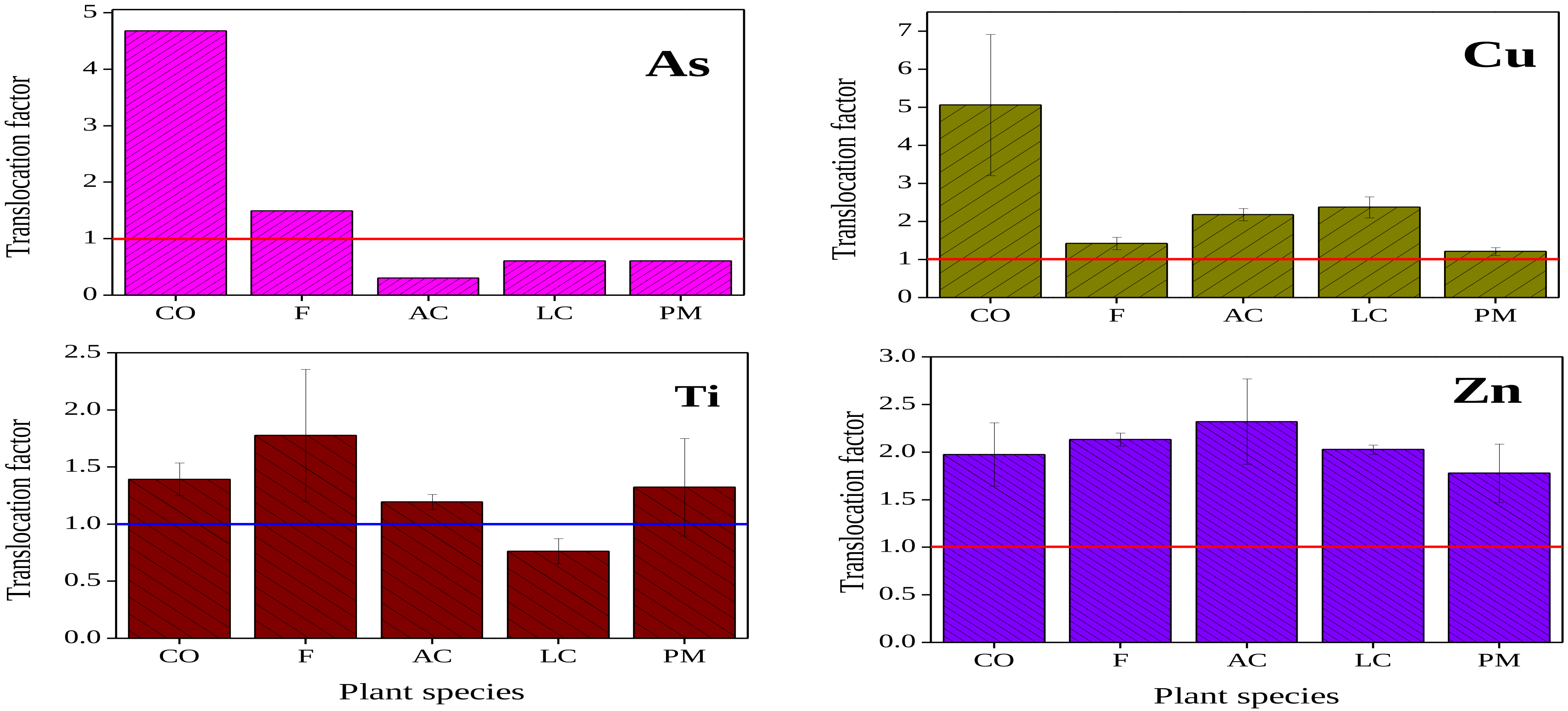

Fig. 3.6: Root-to-shoot translocation factor (TF) of toxic elements (As, Cu, Ti and Zn) into shoots by the five native plant species near the abandoned mine spoil. Added line indicates the threshold above which plant is considered a phytoremediator. CO = Chromolaena odorata, F = fern, AC = Alchornea cordifolia, LC = Lantana camara, PM = Pueraria montana.

3.4 Conclusions

We studied soil pollution with PTEs, their associated human health risk of sites near an abandoned gold mine spoil in Ghana. Additionally, we assessed possible remediation of these soils from PTEs using native and indigenous plant species growing near the mine spoil. We found that the sites located near the mine spoil were severely polluted and enriched with PTEs, particularly with As, Cd and Ti. These high PTE accumulations may have been caused by mobilisation and dry deposition from the abandoned mine spoil without any reclamation or vegetation cover. In other instances, the pollution has been caused by stockpiles of mine wastes that receive no proper protection, indiscriminate disposal of mine wastes and irresponsible mining practices such as illegal mining operations. These practices may have exacerbated the accumulation of PTEs and soil pollution in the mining sites. We also found very high hazard index (HI) values for children, adult males, and females, and this is an indication of elevated health risk posed by the soil PTEs on the residents in the mining communities. There is a potential of cleaning up these PTEs with native plant species. Particularly, local plants such as *Chromolaena odorata* and *Pityrogramma calomelanos*- fern may extract As, Cu, Ti and Zn from the multi-element contaminated mine soils and farms. This work may help to assess PTE environmental risk and their uptake into plants in this gold mining area. We recognize the need to conduct large-scale remediation experiments to test these native plant species to upscale their full potential and applicability for remediation of mine spoils at field level. Further research may also explore the geochemical fractionation, speciation, bioavailability, and potential mobilisation of the studied PTEs in the topsoil and down the soil profile.

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Supplementary Materials (Appendix A) of the manuscript (chapter 3):

Human health risk via soil ingestion of potentially toxic elements and remediation potential of native plants near an abandoned mine spoil in Ghana

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Table S3.1: Total contents of potentially toxic elements (mg/kg) in the soils and farms near the abandoned mine spoil at their 10th, 50th and 90th percentiles

Field	Percentile (th)	Al	As	Cd	Cr	Cu	Fe	Ni	Pb	Ti	V	Zn
Natural Forest	10	2352.0	10.8	0.2	6.6	3.4	6208.0	0.6	3.1	4.5	8.6	30.4
	50	2792.0	15.8	0.2	9.0	4.1	7656.0	0.8	3.8	5.1	10.4	41.6
	90	3174.4	22.2	0.2	11.5	5.5	10016.0	1.0	7.0	5.8	12.8	44.0
Mine surrounding	10	3860.8	76.4	0.6	23.5	20.2	26496.0	1.5	6.4	9.0	26.7	38.6
	50	6568.0	97.2	0.8	29.8	26.3	31560.0	2.3	9.0	11.2	29.4	45.2
	90	7264.0	2376.0	0.9	44.8	29.2	34928.0	11.1	20.6	20.5	37.3	67.4
Pueraria Field	10	4952.0	133.2	0.8	106.8	24.6	31320.0	5.8	6.0	24.2	63.1	45.6
	50	5128.0	162.4	1.0	171.2	31.0	37840.0	8.5	12.0	81.3	124.8	59.8
	90	6372.0	596.4	1.6	180.0	31.6	59480.0	14.5	13.0	167.6	174.0	197.0
Farm 1	10	4300.0	80.8	0.7	136.4	16.6	24360.0	5.2	12.5	37.8	73.6	47.4
	50	5216.0	143.2	1.2	172.8	18.3	46840.0	5.7	16.3	81.0	124.4	47.9
	90	9600.0	168.8	1.4	278.0	20.7	56600.0	8.8	28.0	95.2	130.8	58.4
Farm 2	10	4940.0	83.2	0.6	21.9	19.4	20720.0	2.0	8.0	13.9	21.2	37.4
	50	5532.0	89.2	0.6	29.1	23.0	23720.0	2.1	10.1	17.1	24.8	40.8
	90	8480.0	121.6	0.8	33.5	30.7	32800.0	2.8	22.5	31.9	31.3	64.7

Table S3.2: Correlation matrix between potential governing/controlling soil physico-chemical properties and potentially toxic elements in the various studied contaminated sites

	pH	C	Al	Ca	Fe	Mn	P
Al	ns	ns	1	ns	**0.71****	ns	**0.36****
	(26)	(50)	(52)	(52)	(52)	(50)	(52)
As	ns	ns	ns	**0.86****	ns	ns	**0.28***
	(26)	(50)	(52)	(52)	(52)	(50)	(52)
Cd	ns	**-0.54****	**0.64****	ns	**0.98****	**0.35***	ns
	(26)	(50)	(52)	(52)	(52)	(50)	(52)
Cr	**0.45***	**0-.69****	**0.29***	ns	**0.72****	**0.66****	**-0.45****
	(26)	(50)	(52)	(52)	(52)	(50)	(52)
Cu	ns	ns	**0.69****	**0.40****	**0.67****	ns	**0.47****
	(26)	(50)	(52)	(52)	(52)	(50)	(52)
Fe	ns	**-0.5****	**0.71****	ns	1	**0.32***	ns
	(26)	(50)	(52)	(52)	(52)	(50)	(52)
Ni	ns	ns	ns	**0.78****	**0.34***	**0.37****	ns
	(26)	(50)	(52)	(52)	(52)	(50)	(52)
Pb	ns	ns	ns	**0.54****	**0.33***	**0.68****	ns
	(26)	(50)	(52)	(52)	(52)	(50)	(52)
Ti	ns	**-0.64****	ns	ns	**0.69****	**0.28***	**-0.47****
	(26)	(50)	(52)	(52)	(52)	(50)	(52)
V	**0.52****	**-0.69****	ns	ns	**0.78****	**0.45****	**-0.46****
	(26)	(50)	(52)	(52)	(52)	(50)	(52)
Zn	**0.69****	ns	ns	ns	ns	ns	ns
	(26)	(50)	(52)	(52)	(52)	(50)	(52)

Ns: non-significant; *indicates significant correlations at $P < 0.05$; ** indicates correlations at $P < 0.01$; numbers in parenthesis indicates the number of observations

Table S3.3: Mean, minimum and maximum values of topsoil (0 – 20 cm) geo-accumulation index (*Igeo*) with potentially toxic elements in soils and farms near the abandoned mine spoil

Field	Statistics	Al	As	Cd	Cr	Cu	Fe	Ni	Pb	Ti	V	Zn
Natural Forest	Mean	-3.4	0.7	-0.7	-3.4	-3.8	-2.0	-5.7	-3.3	2.6	-3.7	-1.4
	SD	0.2	0.4	0.3	0.3	0.3	0.3	0.3	0.4	0.2	0.2	0.2
	Min	-3.7	0.1	-0.9	-3.8	-4.1	-2.3	-6.3	-3.7	2.4	-4.0	-1.8
	Max	-3.2	1.2	-0.3	-3.0	-3.4	-1.6	-5.3	-2.5	3.0	-3.4	-1.1
	n	10	10	10	10	10	10	10	10	10	10	10
Mine Surrounding	Mean	-2.3	4.1	1.3	-1.5	-1.2	0.0	-3.9	-2.1	4.0	-2.1	-1.1
	SD	0.3	1.9	0.3	0.6	0.4	0.3	1.2	0.6	0.8	0.3	0.3
	Min	-3.0	2.8	0.4	-2.1	-2.3	-0.9	-5.5	-2.7	3.1	-2.4	-1.5
	Max	-1.9	8.3	1.7	0.2	-0.7	0.4	-1.1	-0.9	6.9	-1.2	-0.5
	n	24	24	24	24	24	24	24	24	24	24	24
Pueraria Field	Mean	-2.5	4.5	1.8	0.7	-1.0	0.5	-2.3	-2.1	6.3	-0.3	-0.5
	SD	0.2	1.1	0.4	0.4	0.2	0.4	0.6	0.6	1.3	0.7	1.1
	Min	-2.6	3.7	1.4	0.2	-1.3	0.0	-3.0	-2.8	4.8	-1.1	-1.4
	Max	-2.2	5.9	2.4	1.0	-0.9	1.0	-1.5	-1.6	7.6	0.4	1.6
	n	6	6	6	6	6	6	6	6	6	6	6
Farm 1	Mean	-2.3	3.6	1.8	1.1	-1.7	0.4	-2.8	-1.2	6.3	-0.3	-1.0
	SD	0.5	0.5	0.5	0.5	0.2	0.6	0.4	0.5	0.6	0.4	0.2
	Min	-2.8	2.9	1.1	0.5	-1.9	-0.4	-3.1	-1.7	5.4	-1.1	-1.1
	Max	-1.6	4.2	2.3	1.6	-1.4	0.9	-2.2	-0.5	6.8	0.0	-0.6
	n	6	6	6	6	6	6	6	6	6	6	6
Farm 2	Mean	-2.3	3.2	1.1	-1.7	-1.3	-0.2	-4.3	-1.7	3.7	-2.4	-1.2
	SD	0.4	0.3	0.2	0.3	0.3	0.3	0.2	0.7	0.6	0.3	0.4
	Min	-2.6	3.0	0.9	-2.1	-1.7	-0.6	-4.5	-2.4	3.2	-2.7	-1.5
	Max	-1.8	3.6	1.4	-1.4	-0.9	0.2	-4.0	-0.8	4.9	-2.1	-0.7
	n	6	6	6	6	6	6	6	6	6	6	6

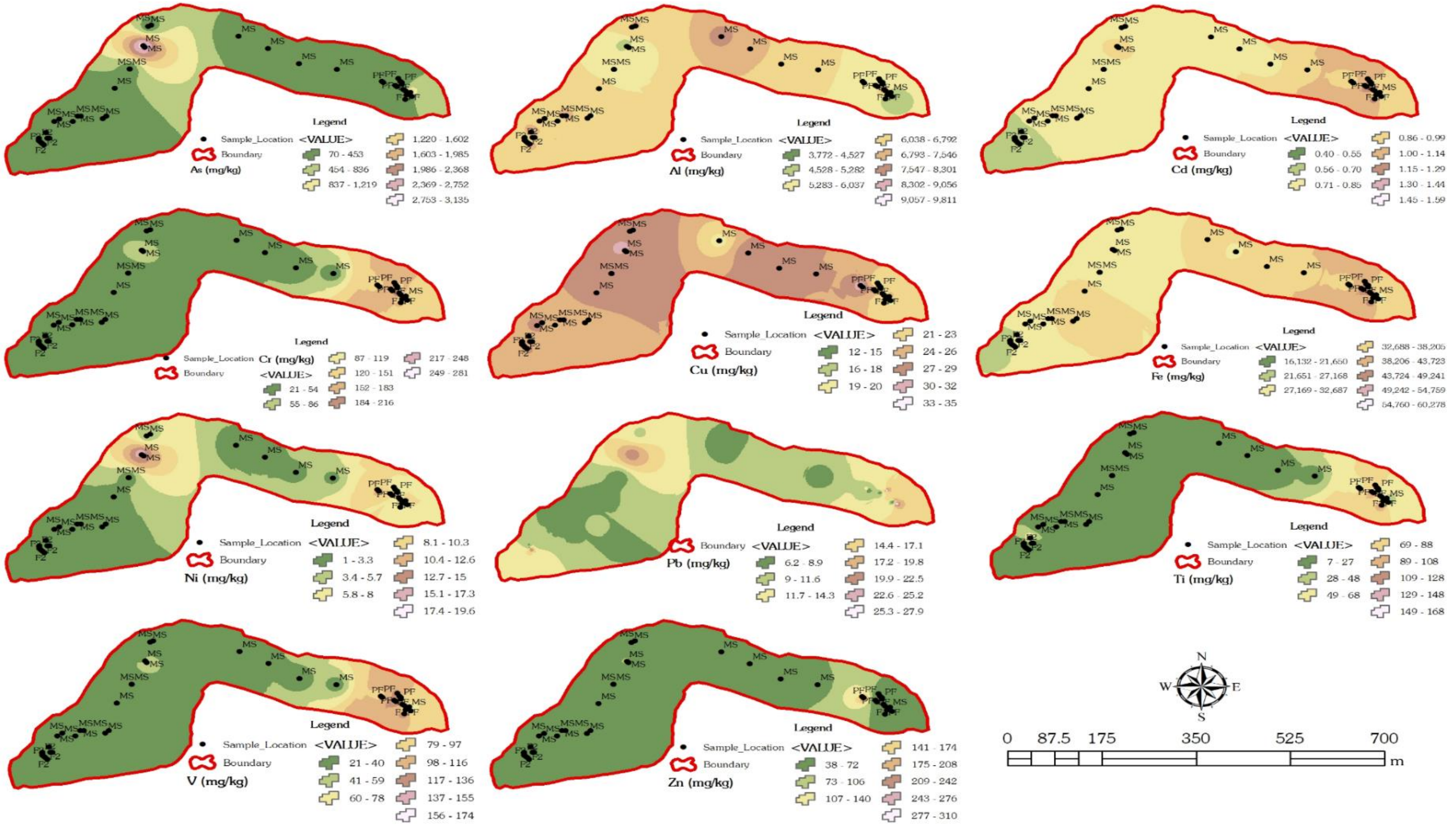


Figure S3.1: Map showing distribution of PTEs in individual sample points at farms and sites near the mine spoil. MS = mine surrounding; PF = Pueraria field; F = farm 1; F2 = farm 2

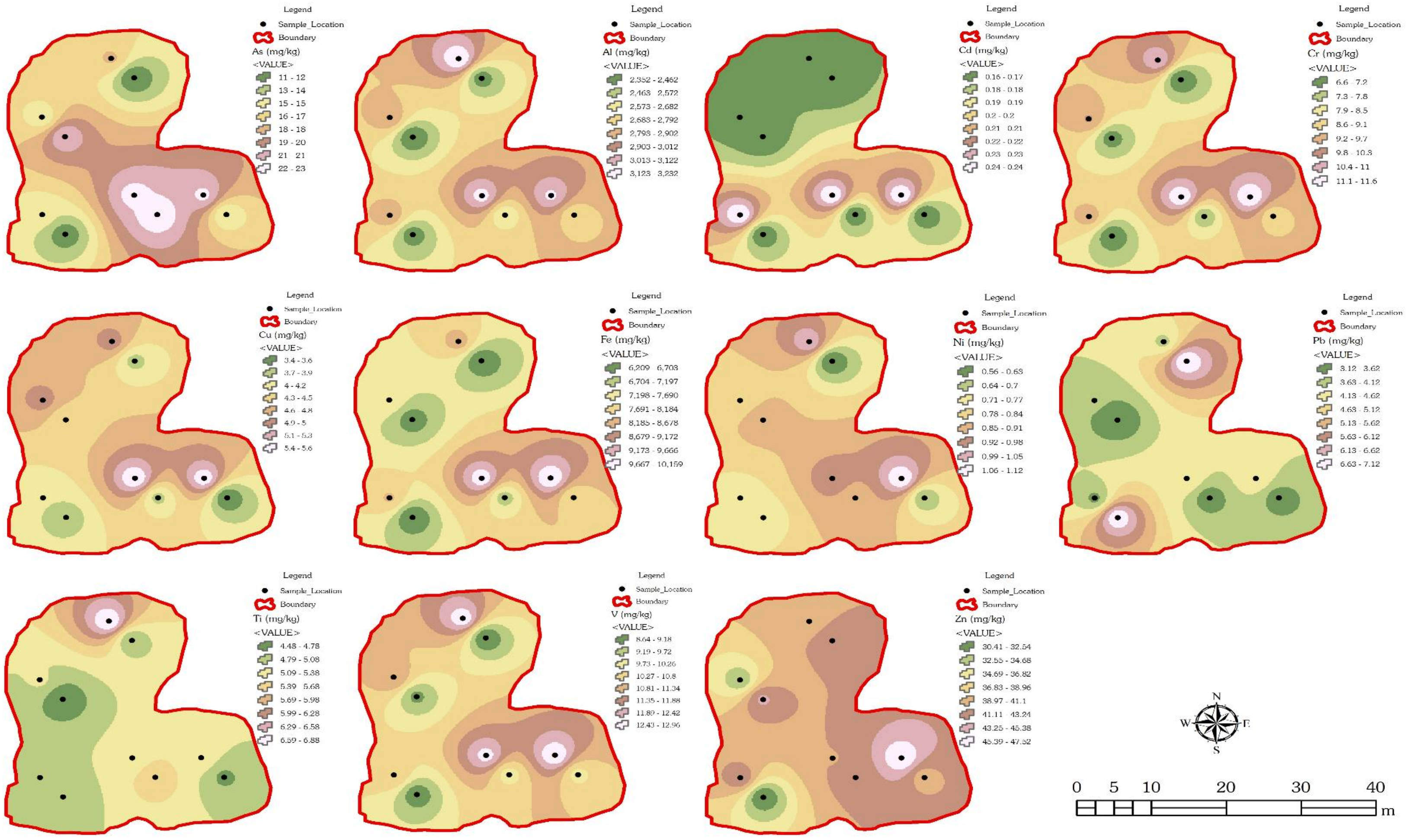


Figure S3.1 Cont.: Map showing distribution of PTEs in individual sample points in the natural forest

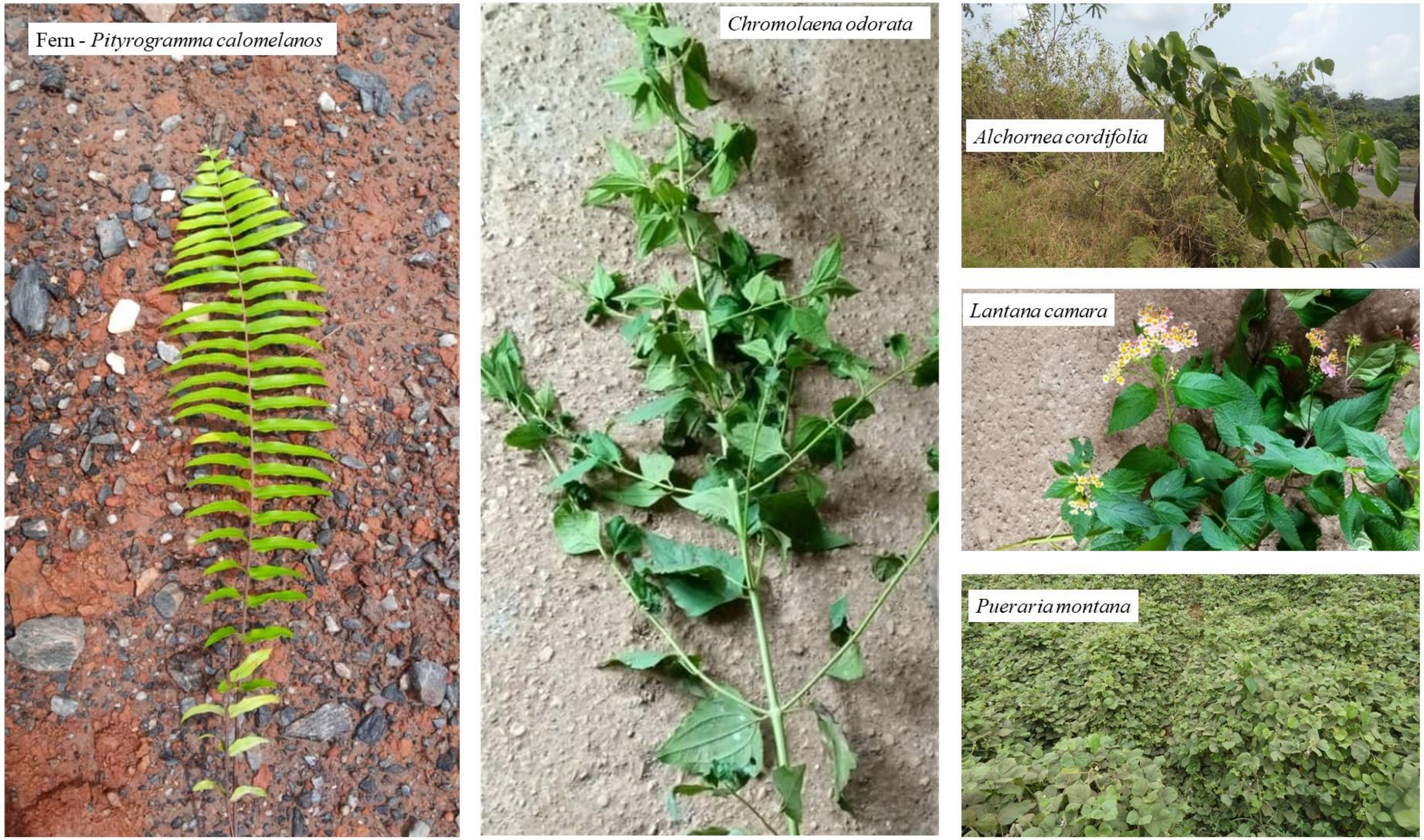


Fig. S3.2: Plant species growing near the abandoned mining spoil that were collected from the field and their pictures.

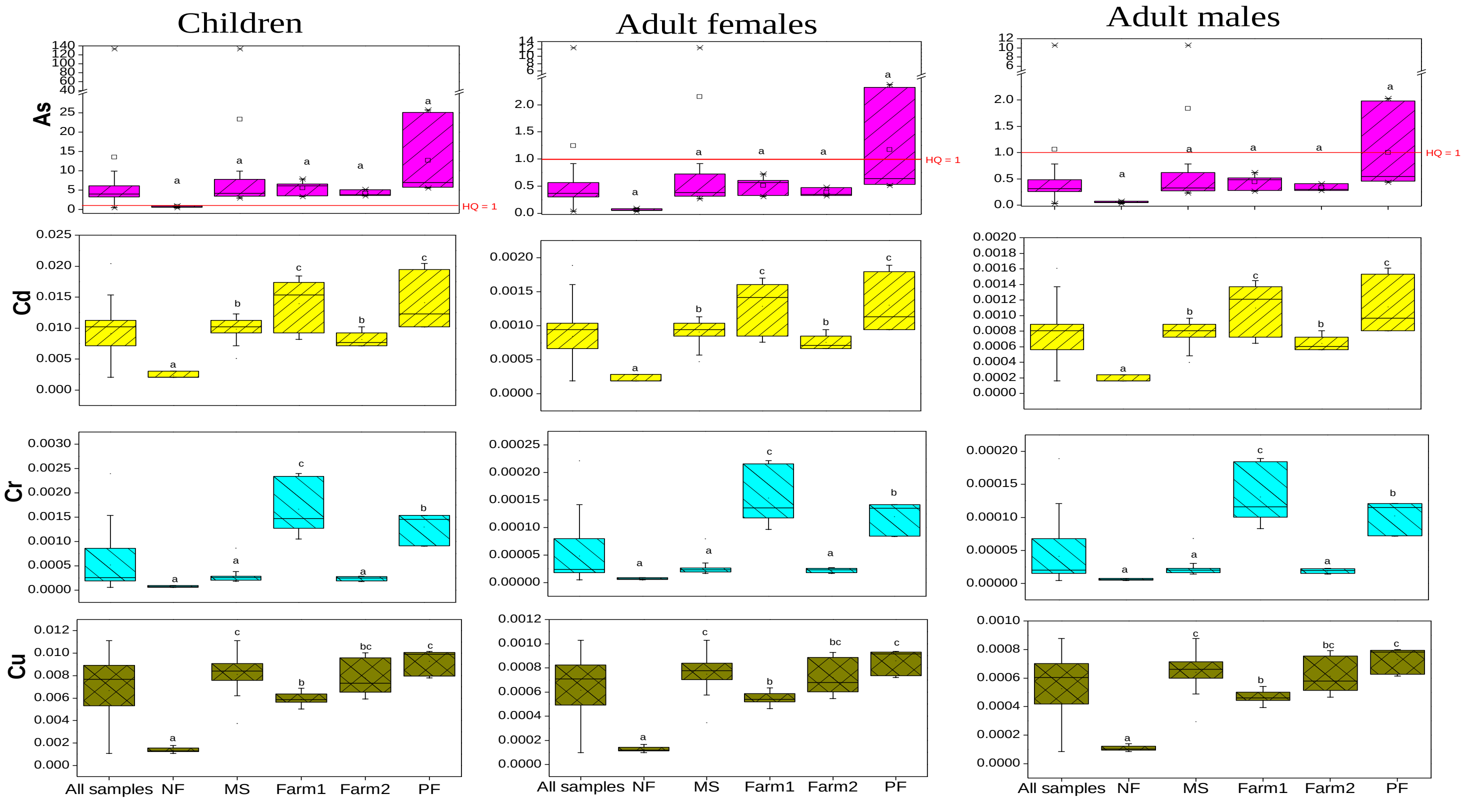
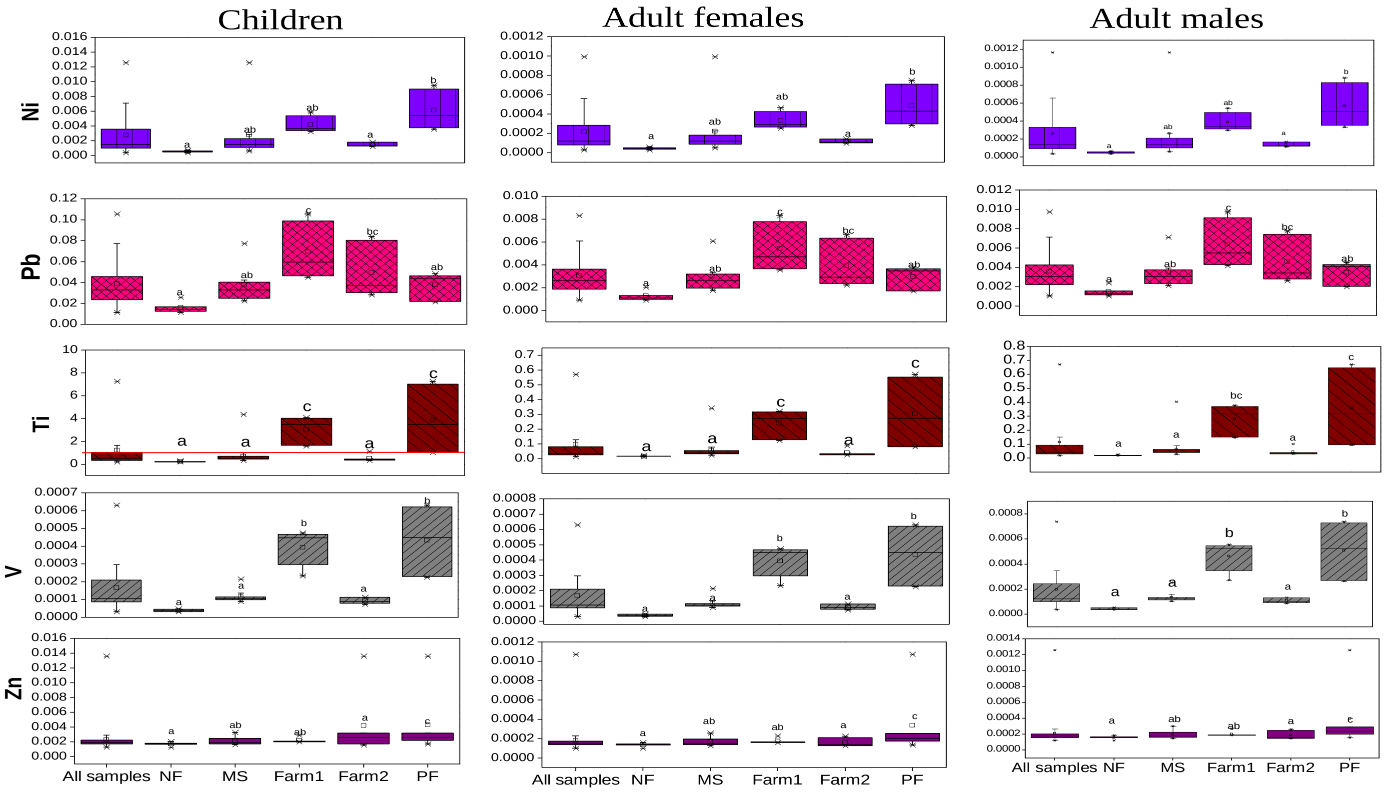


Fig. S3.3: Hazard quotient (HQ) of possible soil ingestion of PTEs by children, adult females and males living in the mining environments. NF = natural forest; MS = mine surrounding; PF = Pueraria field.



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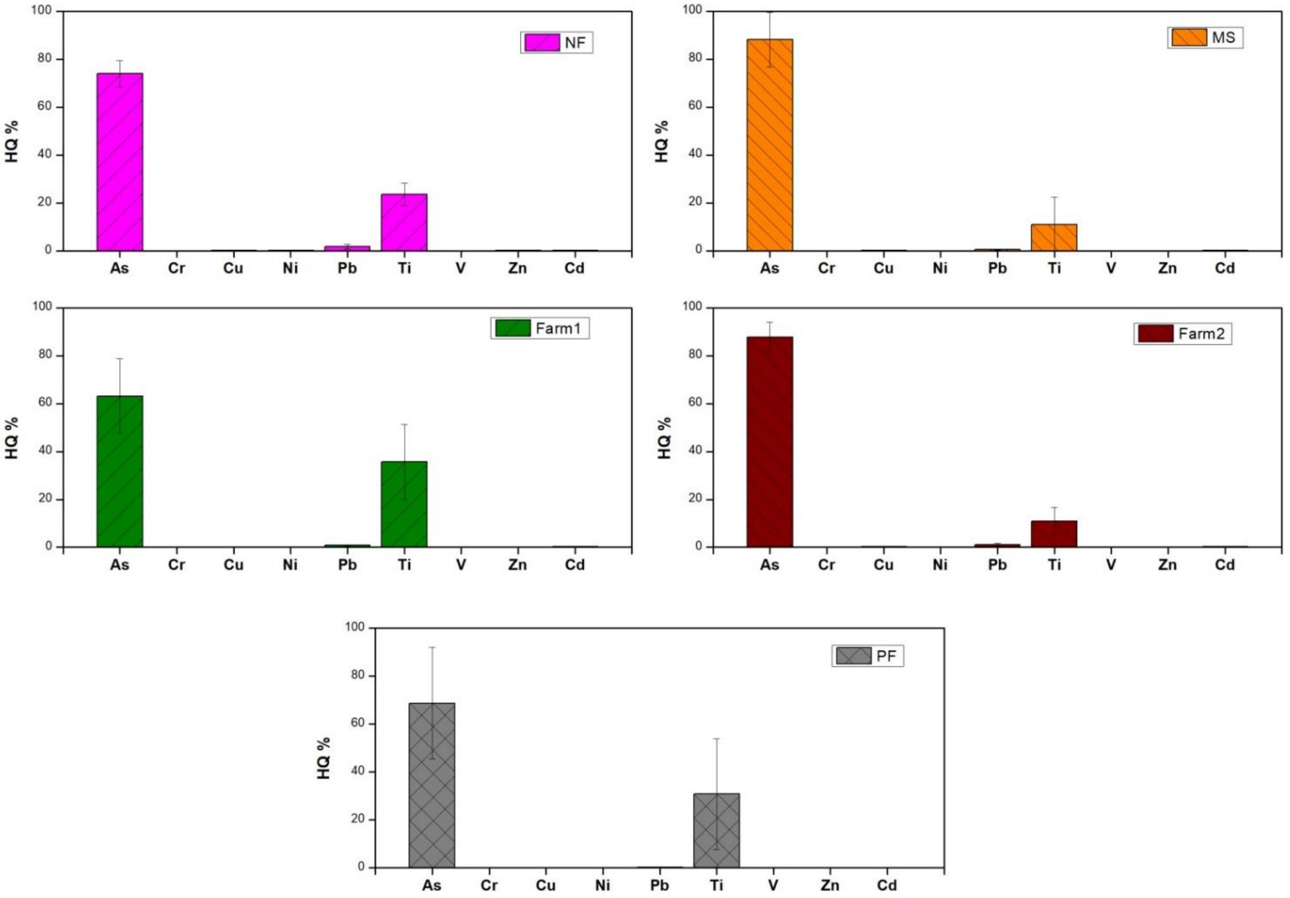

Fig. S3.4: Mean percentage contributions of hazard quotients of the studied PTEs to hazard index of the various mining environments. NF = natural forest; MS = mine surrounding; PF = Pueraria field.

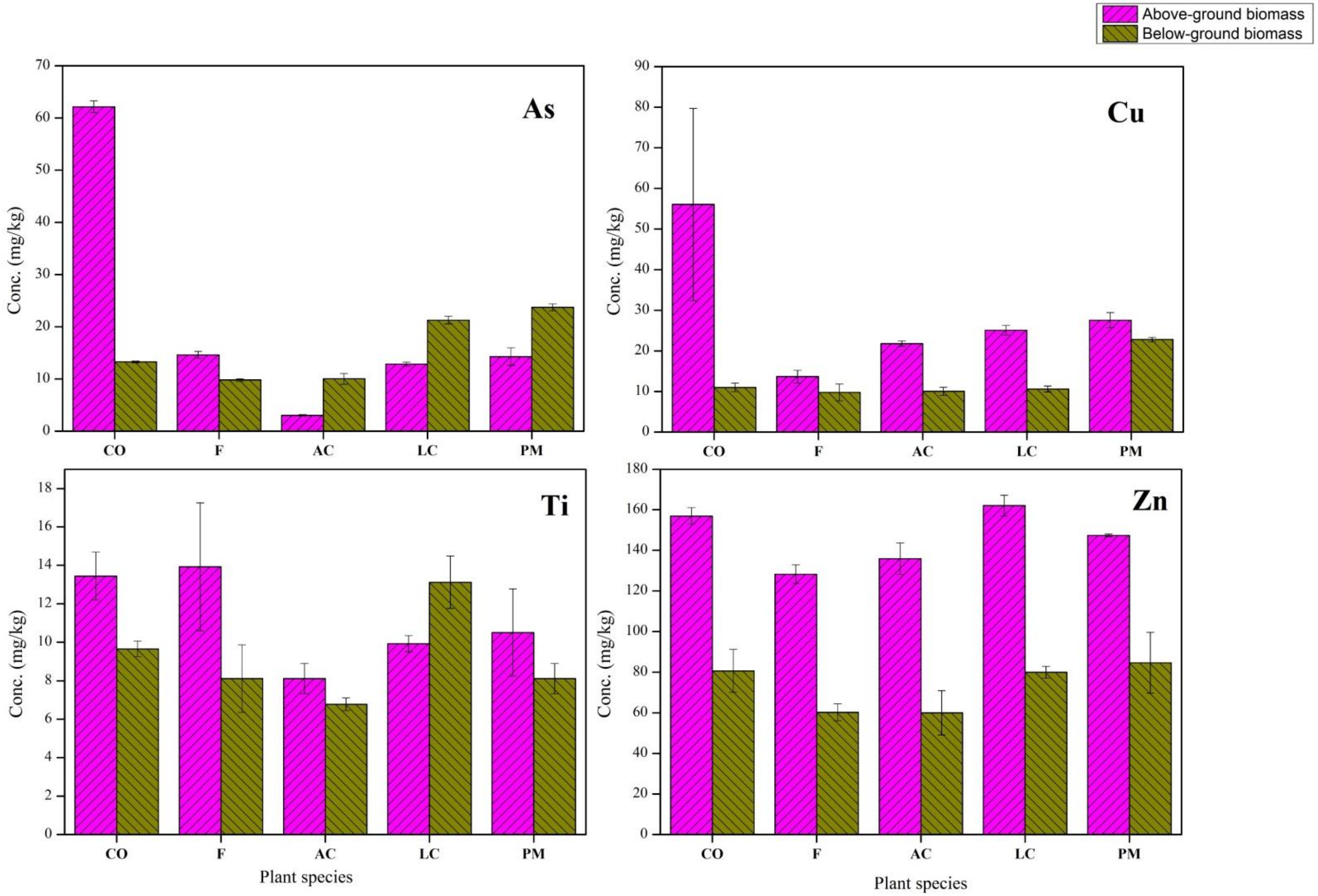

Fig. S3.5: Concentration of As, Cu, Ti and Zn (mg/kg) in the five native plant species growing near the abandoned mining spoil. CO = *Chromolaena odorata*, F = fern (*Pityrogramma calomelanos*), AC = *Alchornea cordifolia*, LC = *Lantana camara*, PM = *Pueraria montana*.

CHAPTER 4

Mobilisation and speciation of arsenic in an abandoned arsenic-contaminated gold mine spoil under reducing and oxidising conditions

This chapter is based on the manuscript: **Albert Kobina Mensah**, Bernd Marschner, Jianxu Wang, Jochen Bundschuh, Shan-Li Wang, Puu-Tai Yang, Sabry M. Shaheen, Jörg Rinklebe. Mobilisation and speciation of arsenic in an abandoned arsenic-contaminated gold mine spoil under reducing and oxidising conditions. Ready for submission to *Journal of Hazardous Materials.*

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) (-350 mV to +307 mV) on mobilisation of As and its dominant species in an abandoned spoil (with total As = 4,283 mg/kg) using an automated biogeochemical microcosm set-up. We observed that As mobilisation consistently increased at anoxic E_H conditions (maximum dissolved As at 136.7 mg/L), whilst it reduced during oxic conditions (minimum dissolved As was at 5.8 mg/L). Multiple stepwise regression showed that mobilisation of As was governed by dissolved Fe, which explained 97% of the data variance. Arsenic K-edge X-ray absorption near edge structure spectroscopy analysis showed that sorbed-As(V)-goethite, sorbed-As(III)-ferrihydrite, scorodite and arsenopyrite were the predominant As species in the mine spoil. As(V) dominated at anaerobic conditions and As(III) predominated at aerobic conditions, which may be attributed to either inability of arsenate bacteria to reduce As or incomplete reduction. Consequently, oxidized portion of As persisted during reducing conditions. Lower Fe/As molar ratios during anaerobic conditions show that the mine spoil may migrate As to watercourses during flooding. It is thus concluded that mitigation options should aim at limiting reducing conditions and encouraging aerobic conditions, which consequently restrict As mobilisation from the mine field.

Keywords: Redox chemistry, arsenic speciation, gold mining, groundwater pollution, flooding

4.1 Introduction

Arsenic (As) is a potentially toxic element whose presence in the environment presents severe health threats to humans (Mensah et al., 2020, 2021; Rinklebe et al., 2019; Shaheen et al., 2020), animals (Kumarathilaka et al., 2019), soil fauna (Su et al., 2014) and flora (Shrivastava et al., 2015). 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, 2021). 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 mine spoils causes consequent liberation of Fe^{2+}, As(III), and SO_4^{2-} into the soil solution and the environment as reported in DeSisto et al. (2017). Food chain contamination and ingestion of As causes skin lesions, cancer of the lungs, skin and urinary tracts, cardiovascular disease, and may interfere with proper functioning of DNA (Acosta et al., 2015; Huq et al., 2020). Additionally, exposure to As-contaminated soils and sediments during pregnancy may cause birth defects in new born babies such as low birth weights, anaemia, kidney cancer and cognitive problems (Khan et al., 2020).

In Ghana, poor handling of gold mine wastes (Mensah et al. 2015, 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., 2020, 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 mine spoils could thus be influenced by redox chemistry of the sites. This occurs via the direct changes of soil redox potentials and/or via redox-induced effects on soil pH, dissolved organic matter content, and soil chemistry of Al, Fe, Mn, and S (Rinklebe et al., 2017; Rinklebe & Shaheen, 2017; Shaheen et al., 2016). These conditions may also in turn influence migration of As into surface and groundwater, soil and lead to food chain contamination (Antoniadis et al., 2017; Shaheen et al., 2014b; Ye et al., 2012;

Zimmer et al., 2011). For instance, flooding and low redox potential conditions may reduce arsenate As(V) to arsenite As(III), lead to high As mobilisation and heighten its associated risks (Renock & Voorhis, 2017). Also, reducing conditions may cause a reductive dissolution of Fe/Al/Mn-oxyhydroxides. Consequently, As sorbed to these oxyhydroxides can be liberated into mobile forms (Frohne et al., 2011). 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).

Additionally, Renock and Voorhis (2017) reported that under SO_4^{2-}-reducing conditions, mobilisation of dissolved As is affected through formation of As-sulphide complexes including realgar (As_4S_4) and orpiment (As_2S_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). Thus, it can be hypothesised that reduction of sulphate into sulphides may play a key biogeochemical role to limit As mobilisation from contaminated spoils.

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; García-Sánchez et al., 2010, Gu et al., 2019). Thus, an increase in concentration of 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; Yu et al., 2007). 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 the 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 high-tech method to assess solubility of As (Itabashi et al., 2019; Yang et al., 2020), and 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, von der Heyden 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.

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 (Mensah et al., 2020) attempted this by studying the potential mobilization 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 mobilization and speciation as affected by various reducing and oxidizing conditions at the contaminated mining sites.

Moreover, previous works that studied As mobilisation and its speciation mainly were in temperate countries and ecosystems such as flood plains (Beckers et al., 2019; Frohne et al., 2011; Shaheen et al., 2014a,b; 2016), agricultural soils (Beiyuan 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. Therefore, our specific objectives were to: i) quantify the impact of different reducing and oxidising conditions on the mobilisation of As, ii) determine the mobilization dynamics of As as governed by the redox-impacted changes on pH, iron (Fe), manganese (Mn), aluminium (Al), sulphide (S), chloride (Cl^-), sulphate (SO_4^{2-}), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and specific ultra violet adsorption (SUVA), and iii) quantify the impact of different redox conditions on speciation of As in an As-contaminated gold mine spoil in Ghana.

4.2 Materials and methods

4.2.1 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 western Ghana. Detailed study area characteristics of the site are reported recently in Mensah et al. (2020, 2021). 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. Air-drying of the soil sample was then done for 48 hours; then they were crushed, homogenized, and sieved through 2-mm. The samples were then characterised 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 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/cm. 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 supplementary materials (Appendix A; Table S4.1) and more details about the soil are published in Mensah et al. (2020).

4.2.2 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 minutes 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 Divison). 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 fractions 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 S4.2). All procedures were done in triplicates and As recovery rate was calculated according to Mensah et al. (2020).

4.2.3 Redox experiment using an automated biogeochemical microcosm (MC) set-up

4.2.3.1 Redox MC setup

We simulated flooding of the As-contaminated mine spoil soil in the laboratory using the automated biogeochemical microcosm (herein, referred to as 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., 2014a, 2016; Yu & Rinklebe, 2011). Technical details of the set-up and how it works were also reported by Yu & Rinklebe (2011).

Three separate MCs were employed 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. Few grams of powdered wheat straw and 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 E_H, pH and temperature measured values for each separate MC were recorded every 10 minutes by a data logger connected via a computer to the system. Those data were used as measured by the calibrated sensors. The data were not calculated as a reference to the standard hydrogen electrode aiming to present the actual redox potential in relation to the solution. Nine pre-defined E_H windows between -350 mV to +307 mV +440 mV were set and examined. The windows were achieved 24 hours 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 hours before sampling for each window and their averages are reported in the Supporting information (Appendix A; Table S4.3).

4.2.3.2 Sampling and sample preparation

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 hours after attaining the pre-set E_H-window. Centrifugation of the collected sample was then done for 15 minutes at 5000 rpm. Samples were then filtered using the < 0.45 µm 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 µm filter paper, samples were sub-divided for subsequent analyses. 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. DOC and DIC were determined in the second sub-sample; 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). The whole filtration process happened in a glove box (MK3 Anaerobic Work Station, Don Whitley Scientific, Shipley, UK) to avoid exposure to oxygen.

4.2.3.3 Chemical analyses

Contents of dissolved As, Fe, Mn, Al, and S in the samples were analysed using the ICP-OES (Ultima 2, Horiba Jobin Yvon, Unterhaching, Germany). Contents of DOC and DIC were measured by a C/N-analyser (Analytik Jena, Jena, Germany). SUVA 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 (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).

4.2.3.4 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). Additionally, it establishes the ability 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 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.

4.2.4 Arsenic K-edge XANES analyses

Selected soil samples from the lowest (-220 mV), middle (0 mV) and highest (+220 mV) redox potentials were selected for As K-edge XANES analysis. The As XANES spectra were collected at beamline TLS 07A at the National Synchrotron Radiation Research Centre (NSRRC), Taiwan (https://www.nsrrc.org.tw/english/index.aspx). Details of the As-XANES and EXAFS methodology and speciation are reported in Mensah et al. (2020) and Yang (2020), and based on Kelly et al. (2008). Arsenic species dominant at -220 mV, 0 mV and +220 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 thus better).

4.2.5 Quality control and data treatment

We did quality control of the extraction efficiency of pseudo-total content of As 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 S4.4).

Mean E_H and pH values of samples measured 6 hours before the pre-defined E_H windows were calculated. Statistical analyses were performed with IBM SPSS Statistics 25 (NY, USA) and the figures were created with OriginPro 9.1 b215 software (OriginLab Corporation, Northampton, USA). Pearson correlation, simple linear regression and stepwise 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.

4.3 Results and discussion

4.3.1 Total contents, fractionation, and speciation of As in the mine spoil and at different redox conditions

The mine spoil soil contained high mean pseudo-total As concentration at 4,282.6 mg/kg (Appendix A; Table S4.1). 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 Altiplano-Puna plateau (Andean Highlands), South-America by Tapia et al. (2019). 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 study.

Arsenic was mainly distributed in the residual/sulphide fraction (FV; 60.5% of total As) and the low crystalline iron oxide fraction (FIII; 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. 4.1). 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 in 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).

The potential mobile fraction (non-residual fraction) of As (calculated as the sum of FI to FIV) from the mine spoil soil was 1793.52 mg/kg, and constituted 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. For instance, As in the potential mobile fraction may seep or become mobilised due to reductive dissolution of the Fe-bearing mineral (e.g. Shaheen et al., 2018). 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 (24.88 mg/kg) and FII (367.01 mg/kg). We thus hypothesize 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. High As mobile fraction and its potential mobilisation from As-contaminated gold mine spoils in Ghana had been reported in detail by Mensah et al. (2020).

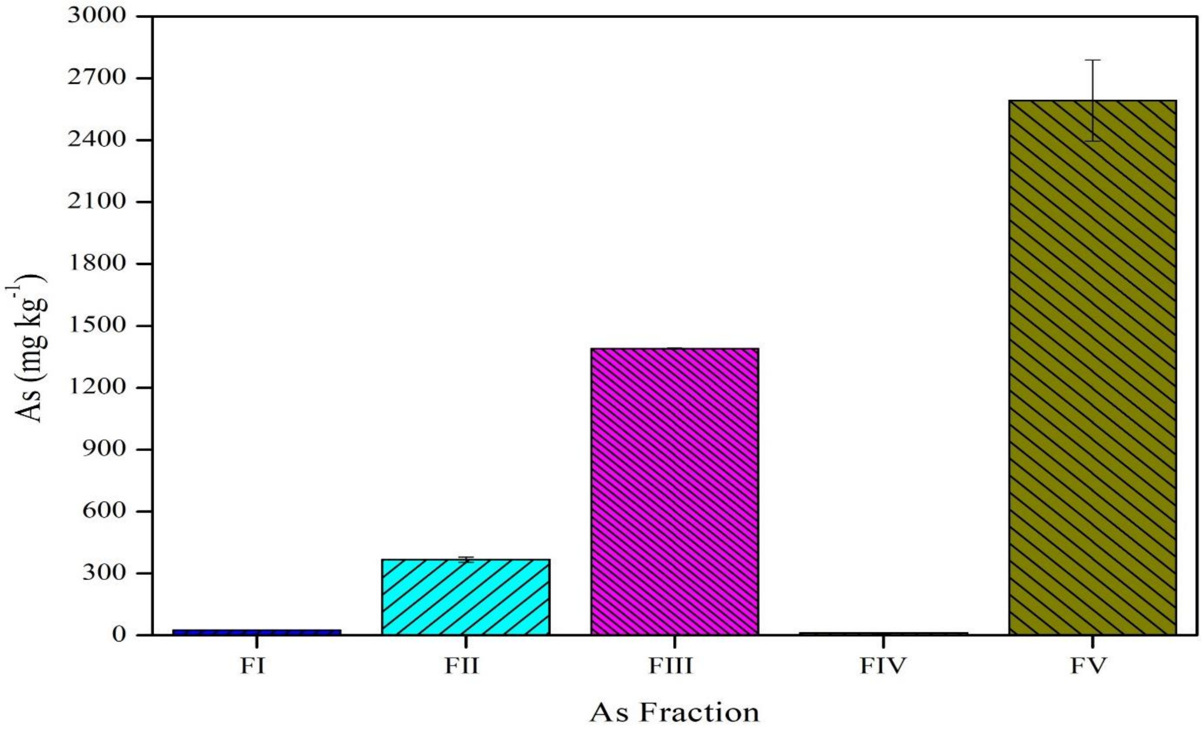

Fig. 4.1: Arsenic geochemical fractions in the As-contaminated mine spoil soil. Water-soluble and un-specifically bound As (FI); Specific-sorbed As/exchangeable fraction (FII); amorphous Fe oxide fraction (FIII); well-crystalline Fe oxide (IV); and As in residual fraction bound to sulphides (FV).

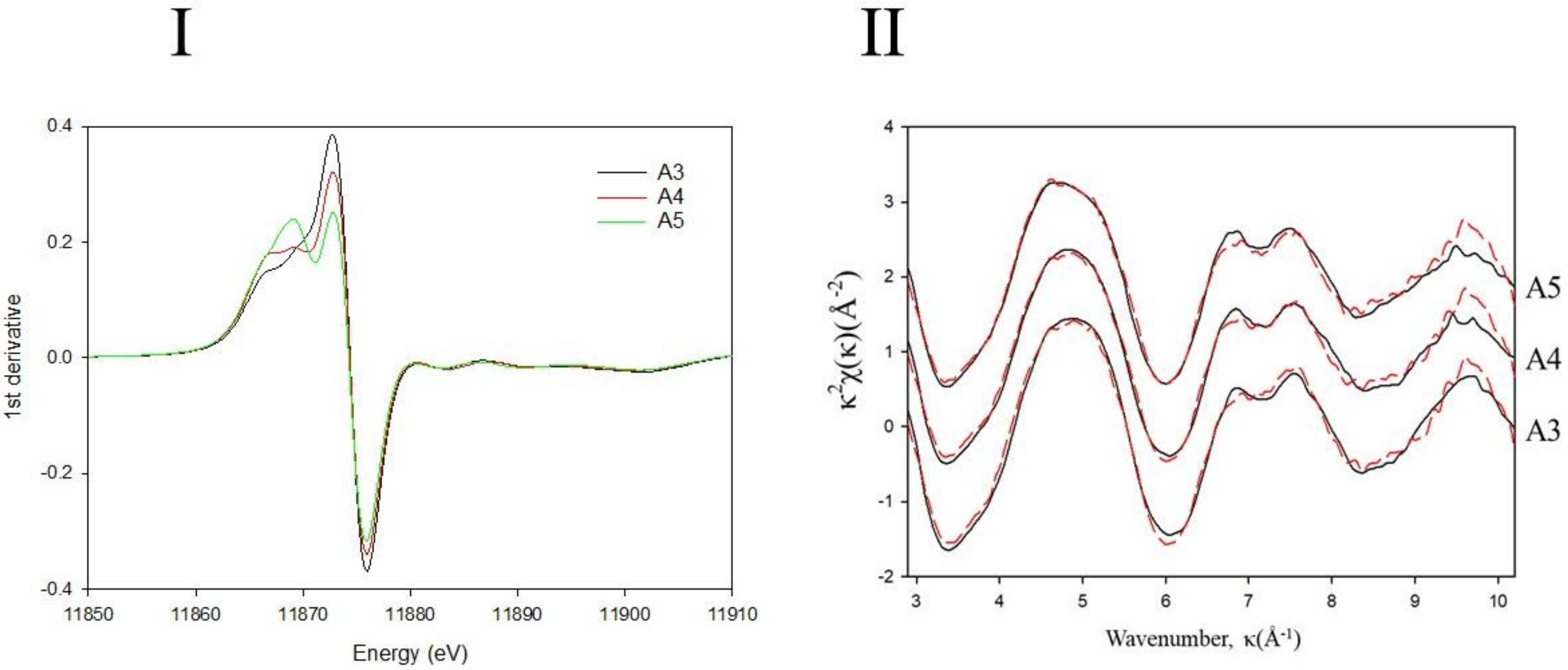

Fig. 4.2: (I): Arsenic K-edge XANES spectra of the mining spoil at different redox potential. II: Linear combination fitting results using the reference materials. A3 = -220 mV Eh; A4 = 0 mV Eh; and A5 = +220 mV Eh.

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. 4.2. As shown in the XANES spectra and the corresponding first derivatives, 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 supporting information (Appendix A; Table S4.5). Results showed that As is strongly associated with Fe in the mining spoil at both reducing and oxidising periods; similar observations were made by Yang et al. (2020). The dominance of iron 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).

From the LCF, we conclude that compounds of goethite-As(V), ferrihydrite-As(III), arsenopyrite and scorodite were the major As species found in the mine spoil. As shown in Table S4.5, the proportions of scorodite and arsenopyrite were relatively stable across E_H zones. At the lowest negative redox potential (-220 mV), As(V)-goethite dominated and accounted for 34%. This was followed by ferrihydrite-As(III) at 25%, arsenopyrite (23%) and scorodite at 18%. Similarly, arsenopyrite and sorbed-As(III) dominated the moderate reducing conditions (0 mV) at 29% and 30%, respectively. At the highest E_H (+220 mV), sorbed-As(III) dominated at 41%, and arsenopyrite and scorodite were 25% and 21%, respectively. The dominance of scorodite indicates oxidation of the As-bearing mineral (FeAsS) due to reintroduction and exposure to oxygen at higher E_H.

Generally, reduced species of As dominate during anaerobic conditions and vice versa (e.g., Reddy and Delaune, 2008; Renock and Voorhis, 2017). Sorbed-As(III)-ferrihydrite and arsenopyrite are common As species reported under anaerobic conditions (e.g., Fakhreddine et al., 2020; Yang 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).

In the solid-phase, it is possible that an oxidized portion of As (i.e., As(V)) may persist during reducing conditions (Fakhreddine et al., 2020). This may be due to inability of arsenate bacteria to reduce all the As in secondary minerals (e.g., scorodite in the bulk soil sample) and thus may result in incomplete reductive dissolution during the reducing periods. For instance, microbes may chelate Fe, bind As onto mineral surfaces (Nair et al., 2007; Malik, 2004), 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).

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 (187.5mg/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 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 $FeAsO_4$ by metabolites (e.g., ligands and organic acids).

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. 4.3. The E_H values varied between -306 and +307 mV and the pH ranged between 5.0 and 7.1 (n = 7,911) during the entire incubation study. Flooding decreased the mine spoil soil pH from the initial 7.1 to around 5.25 under reducing conditions at EH value of -150-mV. Overall, the pH decreased during oxidising conditions and increased during reducing conditions.

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 (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., Reddy and Delaune, 2008; Shaheen et al., 2014a).

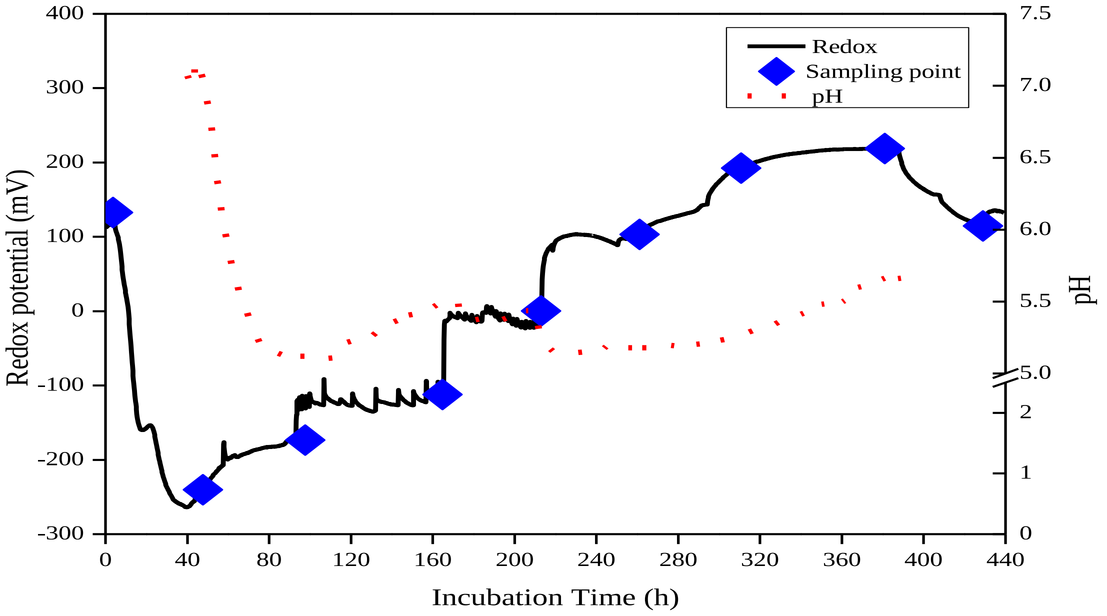

Fig. 4.3: Development and changes in EH and pH of soil slurry of the contaminated mine deposit during the incubation period. Data recorded every 10 min in a data logger, values were reported for means of an underling dataset (n = 7,911) of three replicate samples in the microcosms of the contaminated mine spoils.

4.3.3 Redox-induced mobilisation of As

4.3.3.1 Arsenic mobilisation as affected by E_H/pH dynamics

The minimum, maximum, and mean concentration of As in the dissolved fraction of the flooded mine spoil are given in Table 4.1. Contents of dissolved As were higher under reducing conditions (136.7 mg/L) than in the oxidising conditions (5.8 mg/L; Fig. 4.4). Mobilisation of As indicated a significant correlation with E_H ($r = -0.77$; $P < 0.01$; Fig. 4.5), whilst the impact of pH on As solubility was not significant. The high concentrations (maximum = 136.7 mg/L) 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.

We further assume that increasing As solubility under reducing conditions might be due to existence of As in the form of soluble As(III). Under such conditions, mobile forms of As such as H_2AsO_3, $H_2AsO_3^{2-}$ and AsO_3^{3-} may dominate (e.g., Reddy and Delaune, 2008; Renock and

Voorhis, 2017). Corkhill & 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_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 (Erbele, 2020). The impact of S on As mobilisation is further elaborated and discussed in sections 4.3.3.2.

Table 4.1: Mean, minimum, maximum and standard deviation of E_H, pH, As concentrations and potential governing factors (Fe, Fe^{2+}, Mn, Al, S, Cl^-, SO_4^{2-}, DOC, and SUVA) in the dissolved fraction of the contaminated mine spoil soil.

Parameter	Unit	Minimum	Maximum	Mean	SD	n
EH	mV	-306	306	20	173	27
pH		5.0	7.14	5.53	0.64	27
As	mg/l	5.80	136.68	58.46	52.05	27
Fe		0.23	324.87	132.20	127.40	27
Mn		0.29	15.86	9.29	3.61	27
S		206.47	360.36	253.93	36.27	27
Al		0.02	0.48	0.24	0.14	27
Fe^{2+}		1.35	172.32	61.94	54.24	27
Cl^-		27.29	133.56	75.61	30.09	27
SO_4^{2-}		572.58	1087.25	922.19	136.44	27
DOC		1118.99	2557.86	1636.05	360.94	27
SUVA	m^{-1} mg^{-1} L	0.05	0.24	0.10	0.04	24

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

4.3.3.2 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 206.47 to 360.36 mg/L, with the maximum value occurring at the reduced redox potential (E_H = -287.42 mV) (Table 4.1). Sulphate reduction is reported to be initiated by microbial communities at low E_H such as: < -150 mV as indicated by Mansfeldt (2004) or -220 mV as mentioned by Ross (1989). In this regard, we assumed 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. 4.4).

Therefore, neither sulphate nor sulphate reduction (formation of sulphides) affected the mobilisation of As in our study ($r = -0.02$; $P > 0.05$; $n = 27$; see Appendix A; Table S4.6 and Fig. 4.5). 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 ($r = +0.67$, $P < 0.01$; $n = 27$); and S and Al ($r = +0.54$, $P < 0.01$; $n = 27$) (Appendix A; Table S4.6). 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. 4.1) 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 and Rinklebe, 2014; Tack, 2010). The residual fraction of As is reported to be made up of greater proportions of FeAsS and FeAsO4 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.

4.3.3.3 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. As explained earlier in section 4.3.2, the higher contents of DOC at the reduction phase of the initial redox cycle may either be due to production of CO_2 from microbial activities (Grybos et al., 2009), decay of the organic straw (Reddy and Delaune, 2008), or release of organically bound carbon to reductively dissolved Fe-hydroxides (Rinklebe et al., 2020).

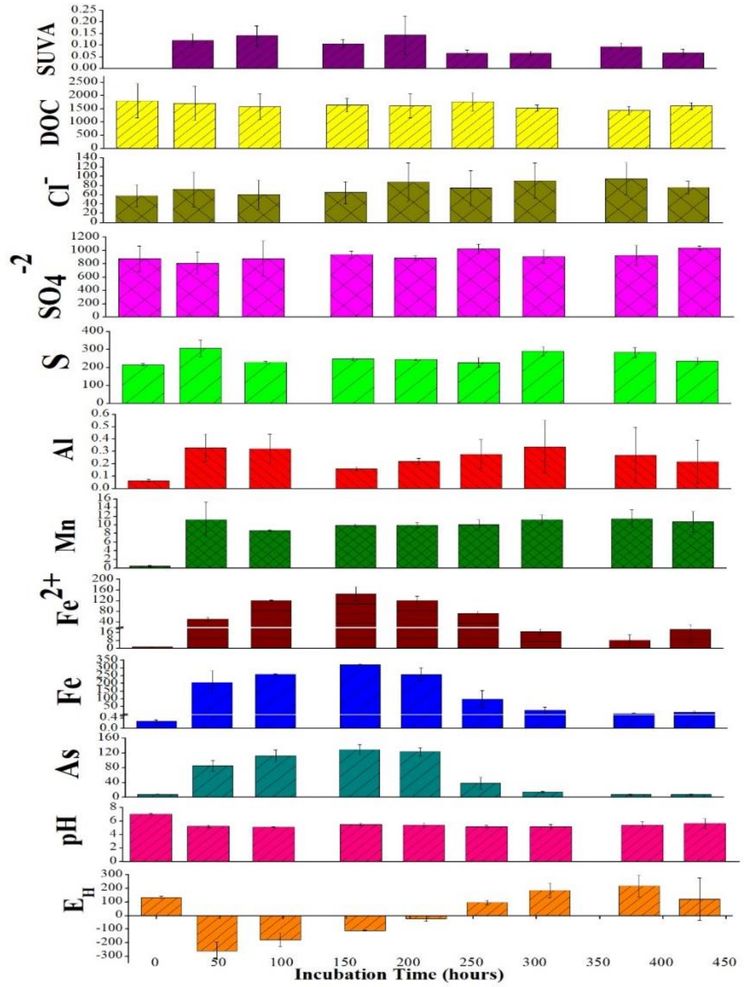

Fig. 4.4: Impact of different reducing and oxidising conditions on the release dynamics of arsenic (As) as affected by redox-induced (E_H) changes on pH, Fe, Fe^{2+}, Mn, Al, S, Cl^-, DOC and SUVA) in the contaminated mine spoil soil. Columns represent means and whiskers represent standard deviation of three replicates. Values of Fe, Fe^{2+}, Mn, Al, S, SO_4^{-2} Cl^-, and DOC are in mg/L; EH in mV; and SUVA in m^{-1} mg^{-1} L.

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 potential. Higher SUVA contents under reducing soil conditions were also previously reported by McKnight et al. (2002) and further explained by Weishaar et al. (2003). The DOC/SUVA-As correlation was non-significant (Fig. 4.5) and therefore, we conclude that As mobilisation from the mine spoil was not impacted by redox-induced changes in the dissolved organic matter.

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

Concentration of dissolved Fe ranged between 0.23 – 325 mg/L, and a mean value of 132.2 mg/L (Table 4.1). Concentration of dissolved Fe increased under reducing conditions and reduced under oxidising conditions (Fig. 4.4). Thus, Fe negatively varied significantly with E_H ($r = -0.77$, $P < 0.01$; Appendix A; Table S4.6). 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^{3+} oxides into Fe^{2+} as explained by Gu et al. (2019). It must be noted that flooding and water saturation in soils fill the soil pore spaces and thus may deplete 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^{2+} during the reducing phase of the redox incubation period. Concentration of Fe^{2+} ranged between 1.35 and 172 mg/L, with higher values observed under reducing conditions; and negatively correlated significantly with E_H (Appendix A; Table S4.6; $r = -0.61$; $P < 0.01$). This means that reductive dissolution of Fe-oxyhydroxides could result in excessive production of Fe^{2+}, 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; 2020). 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 ($r = -0.38$, $P < 0.05$; $n = 27$); pH and Fe^{2+} ($r = -0.37$; $P = 0.05$; $n = 27$) (Appendix A; Table S4.6). We assume that such phenomenon may cause carriers such as Mn/Fe/Al oxides to lose their ability to sorb As as explained by Violante et al. (2010).

Additionally, the Pearson correlation, linear and stepwise regression analyses demonstrate that dissolved contents of As correlated positively with both total Fe (Adjusted $R^2 = +0.94$, $P < 0.01$; $n = 27$) and Fe^{2+} (Adjusted $R^2 = +0.82$, $P < 0.01$; $n = 27$) (Fig. 4.5). Thus, redox-induced impacts of Fe chemistry may explain 94% of the contributions to As mobilisation from the mine spoils.

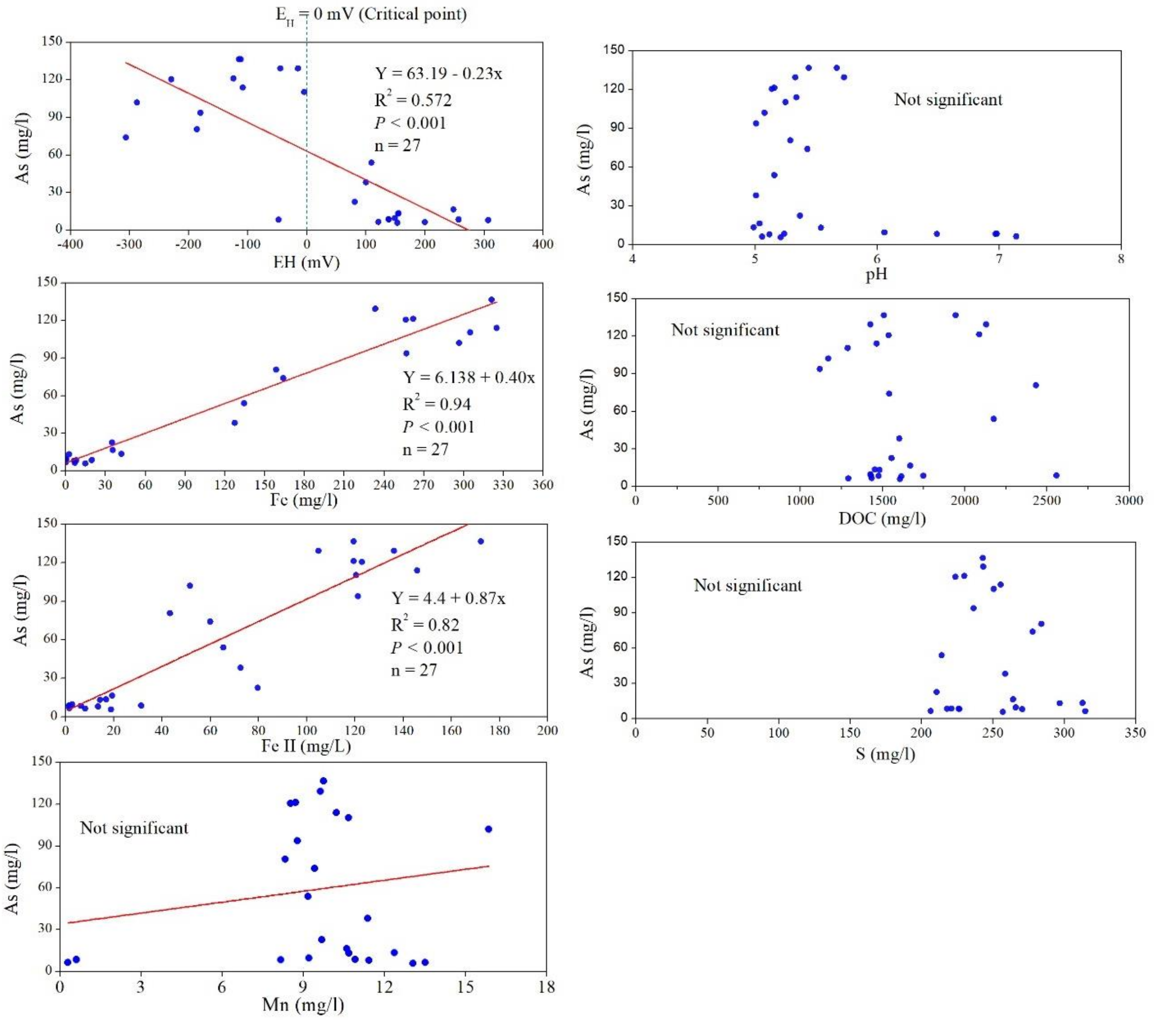

Fig. 4.5: As in solution as regressed to governing factors. For all bivariate linear regression analyses, n = 27, P value given by analysis of variance.

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 172 mg/L under the most reducing conditions (< -100 mV), at which time dissolved As contents were concurrently at its peak at 136.68 mg/L (Fig. 4.4). Reductive dissolution of Fe oxides and subsequent As release has been reported in other studies (e.g., Reddy and Delaune, 2008; Gu et al. 2019). Rinklebe et al. (2016) and Shaheen et al. (2014b, 2016) 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., 2018; 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 (Appendix A; Table S4.6). 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 from the mine spoil. In addition, this insignificant effect might be due to the smaller concentrations of Mn/Al (Mn range: 0.29 – 15.86 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: 0.23 – 324.87 mg/L, n = 27) (Table 4.1). 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 (0.26 – 3.3), reaching maximum value at 3.3 at the end of the incubation period (Fig. 4.6). 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 (0.26 – 2.54) 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. 4.6); oxidising condition with mean E_H = 120.8 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.

Multiple stepwise regression was further conducted among the changes in the factors (E_H, pH, Fe, Fe^{2+}, Mn, Al, S, Cl^-, 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 $R^2 = +0.94$, $P < 0.001$; n = 27) is given as:

$$As\ mobilisation/availability = 6.138 + 0.396\ (Fe) \tag{4.1}$$

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. 4.4). 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. 4.5). 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).

4.4 Conclusions

This is the first work that has explored how redox chemistry affects mobilisation and species of As from 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. The major As species in the mine spoil were goethite-As(V), ferrihydrite-As(III), arsenopyrite and scorodite. Interestingly, As(V) dominated at anaerobic conditions and As(III) predominated at aerobic conditions, which may be attributed to either inability of arsenate bacteria to reduce As, limited oxidation, or incomplete oxidation. Consequently, an oxidized portion of As persisted during reducing conditions and vice versa.

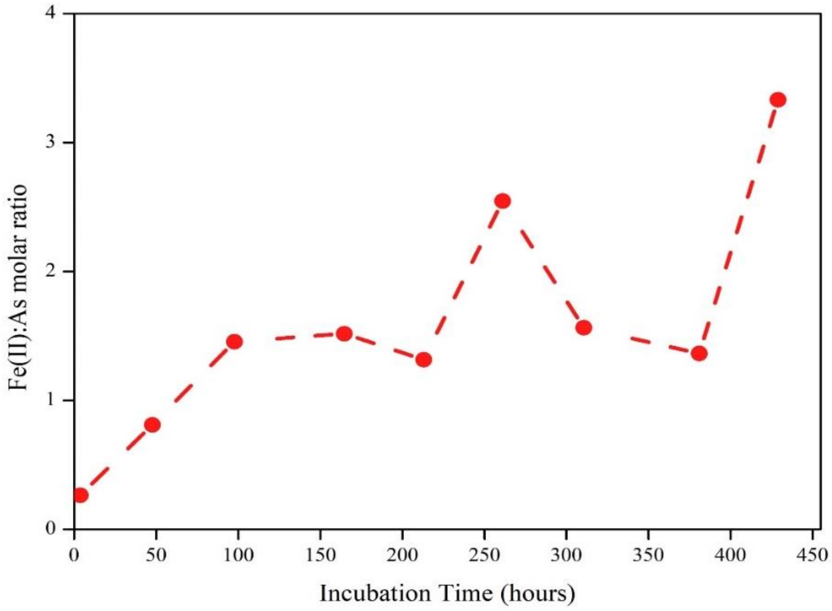

Fig. 4.6: Dynamics of Fe:As molar ratios in anaerobic incubation of the contaminated mine spoil soil. "As" in the Fe(II)/As ratio is the total dissolved As in the solution.

Thus, mobilisation and speciation of As in the Fe-As dominated mine spoil may solely be a function of direct 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. Future studies could investigate the field applications of varying redox conditions on As release from the contaminated mine gold mine spoil. 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.

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Supplementary Materials (Appendix A) of the manuscript (chapter 4):

Mobilisation and speciation of arsenic in an abandoned arsenic-contaminated gold mine spoil under reducing and oxidising conditions

Table S4.1: Physico-chemical properties of the contaminated mine spoil soil

Parameter	Unit	Value
Sand	%	62
Silt	%	36
Clay	%	3
pH ($CaCl_2$)		6.4
EC	dS/cm	1.9
Total C	%	1.2
Total P	mg kg^{-1}	13.4
Total element content	***mg*** kg^{-1}	
Fe		23,200
Ca		8,994
Mg		5,502
As		4,282.6

b.d.l = below detection limit
Values of trace elements are means of duplicates.

Table S4.2: Extraction scheme developed by Wenzel et al. (2001) used in the experiment.

As Fraction	Extracted fraction	Extracting Agent (Solution)	Procedure
I	Water-soluble and un-specifically bound arsenic	$(NH_4)_2SO_4$ 0.05 M	Shake at 20 °C for 4h
II	Specific-sorbed arsenic /exchangeable fraction	$(NH_4)H_2PO_4$ 0.05 M	Shake at 20 °C for 16h
III	Arsenic bound to amorphous oxides	NH_4-oxalate 0.2 M + oxalic acid 0.2 M; pH 3.25	Shake at 20 °C for 4h in the dark Wash with 12.5 ml of solution 3; pH 3.25
IV	Arsenic bound to crystalline iron oxides	NH_4-Oxalate 0.2 M + Oxalic acid 0.2 M + Ascorbic acid 0.1M; pH 3.25	Place for 30 min in a water bath (96 ° C) Wash with 12.5 ml of solution 3
V	Arsenic in sulphides and arsenides (Residual fraction)	Nitric acid conc. (HNO_3)	Digest in microwave

Table S4.3: Sampling number, incubation time, E_H-pH values 6 hours before sampling for each E_H window and averages for the three microcosms

Sampling number	Incubation Time (h)	EH (mV)	pH
0	3.7	132.8	7.0
1	47.7	-240.1	5.2
2	94.4	-173.5	5.1
3	164.7	-112.2	5.5
4	213.0	0.2	5.4
5	261.3	100.5	5.3
6	310.7	192.5	5.2
7	381.0	218.9	5.5
8	429.0	114.8	5.7

Table S4.4: Elements and their detection limits

Element	Detection limit [µg/l]
Al	28
As	53
Cu	5.4
Fe	6.2
Mn	1.4
P	50
Pb	42
S	60

Table S4.5. Linear combination fitting results for As K-edge XANES spectra of soil samples. 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	0.011837	0.014286	0.014234

A3 = -220 mV Eh; A4 = 0 mV Eh; and A5 = +220 mV Eh. Number in parentheses indicates uncertainty given by the Athena software.

Table S4.6: Pearson correlation (r) between E_H, pH, As and potential controlling factors (Fe, Fe^{2+}, Mn, Al, S, Cl^-, SO_4^{2-}, DOC, and SUVA) in the dissolved fraction of the contaminated mine spoil soil

Parameter	E_H	pH	As	Fe	Mn	S	Al	SUVA	FeII	n
E_H	1	ns	-0.77**	-0.77**	ns	ns	ns	-0.5*	-0.61**	27
pH	ns	1	ns	-0.38*	-0.86**	-0.45*	-0.78**	ns	-0.37 (ns)	27
As	-0.77**	-0.32	1	+0.97**	0.18 (ns)	ns	ns	ns	+0.91**	27
Fe	-0.77**	-0.38*	+0.97**	1	ns	ns	ns	0.30	+0.91**	27
Mn	ns	-0.86**	ns)	ns	1	+0.67**	+0.64**	ns	ns	27
S	ns	-0.45*	ns	ns	+0.67**	1	+0.54**	ns	ns	27
Al	ns	-0.78**	ns	ns	+0.64**	+0.54**	1	-0.118	ns	27
SUVA	-.498*	ns)	ns	ns	ns	ns	ns	1	ns	24
FeII	-0.62**	ns (ns)	+0.91**	+0.91**	ns	ns	ns	ns	1	27

*correlation significant at 0.05; **correlation significant at 0.01 level; ns = not significant correlation

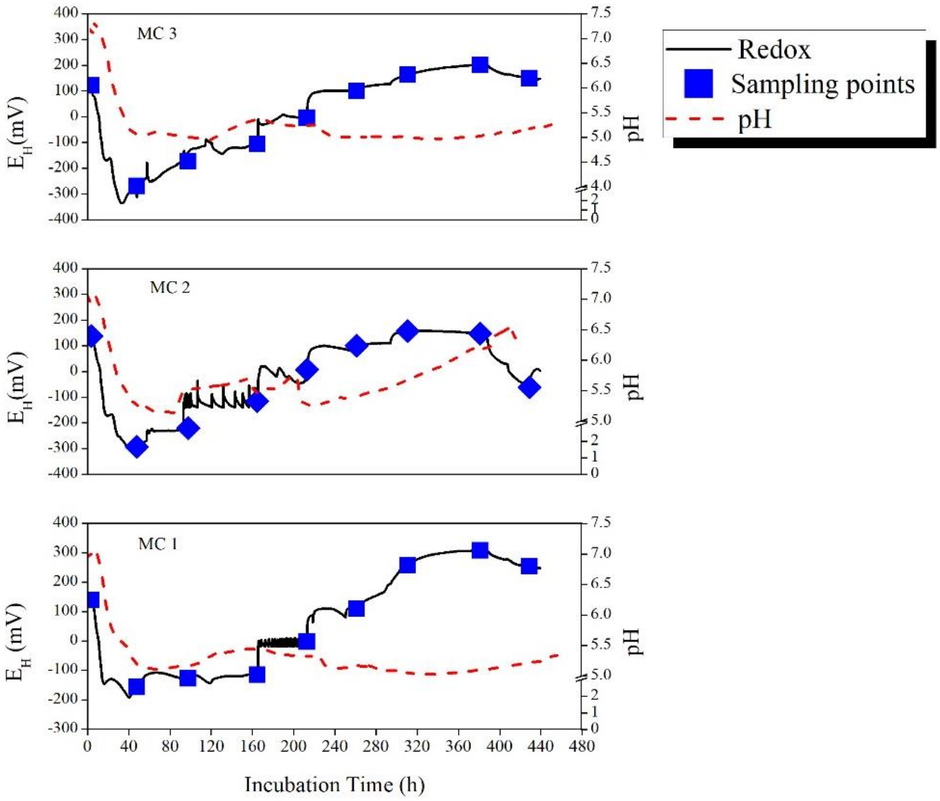

Figure S4.1: Development and changes in E_H and pH of soil slurry of the contaminated mine spoil during the incubation period. Data recorded every 10 min in a data logger, values were reported for an underling dataset (n = 2,637) of each of the three microcosms.

CHAPTER 5

Biochar, compost, iron oxide, manure, and inorganic fertilizer affect bioavailability of arsenic and improve soil quality of an abandoned arsenic-contaminated gold mine spoil

This chapter is based on the manuscript: **Mensah, A. K.**, Marschner, B., Shaheen, S. M., & Rinklebe, J. Biochar, compost, iron oxide, manure, and inorganic fertilizer affect bioavailability of arsenic and improve soil quality of an abandoned arsenic-contaminated gold mine spoil. Revised manuscript re-submitted to *Ecotoxicology and Environmental Safety*.

Abstract

Arsenic (As) contaminated mining spoils pose health threats to environmental resources and humans, and thus, mitigating this potential risk is worth investigating. Here, we studied the impacts of biochar, compost, iron oxide, manure, and inorganic fertilizer on the non-specifically (readily bioavailable)- and specifically- sorbed As and soil quality improvement of an abandoned mine spoil highly contaminated with As (total As = 1807 mg/kg). Compost, iron oxide, manure, and biochar were each applied at 0.5, 2, and 5% (w/w) to the contaminated soil; and NPK fertilizer at 0.1, 0.2, and 5.0 g kg^{-1}. The non-specifically (readily bioavailable)- and specifically- sorbed As were extracted sequentially and available P, total C and N, dissolved organic carbon, soil soluble anions, and exchangeable cations were extracted after 1- and 28-day incubation. Compost, manure, and biochar at 5% improved the total C and N and exchangeable K^+, Mg^{2+} and Na^+. However, manure, compost, and iron oxide at 5% reduced available P from 118.5 to 60.3, 12.6, and 7.1 mg/kg, respectively. As compared to the untreated soil, the addition of iron oxide doses reduced the readily bioavailable As by 93%; while compost, manure, inorganic fertilizers, and biochar increased it by 106-332%, 24-315%, 19-398%, and 28-47%, respectively, with a significantly higher impact for the 5% doses. Furthermore, compost reduced specifically-sorbed As content (14-37%), but the other amendments did not significantly affect it. The impacts of the amendments on the readily bioavailable As was stronger than on specifically-sorbed As; but these were not affected by the incubation period. Arsenic bioavailability in our soil increased with increasing the soil pH and the contents of Cl^-, DOC, and exchangeable K^+ and Na^+. We conclude that iron-rich materials can be used to reduce As bioavailability and to mitigate the associated environmental and human health risk in such mining spoils. However, the carbon-, and P-rich and alkaline materials increased the bioavailability of As, which indicates that these amendments may increase the risk of As but can be used to enhance phytoextraction efficiency of As in the gold mining spoil.

Keywords: Arsenic bioavailability, soil amendments, mining spoil, soil remediation, risk mitigation

5.1 Introduction

Chronic arsenic (As) toxicity of soil and water is one of the most environmental and human health hazards for many countries, including Ghana (Mensah et al., 2020, 2021; Natasha et al., 2021). World soil average of As in uncontaminated soils is reported at 6.8 mg kg^{-1} (Kabata-Pendias, 2011), but elevated contents arise from the natural weathering of As-rich parent materials, and anthropogenic sources such as gold mining, other industrial activities, and storage of contaminated sediments (Hou et al., 2020; Khan et al., 2021a; Mensah et al., 2021).

The total content method of assessing As risk on human and environmental health may overestimate the potential risk, and disregard the actual ecological toxicity effects (Hartley et al., 2010). Geochemical distribution of As among their various fractions in soils and water presents a more valid method to assess their true mobility and bioavailability (Liu et al., 2018; Shaheen et al., 2017; Wenzel, 2001). For instance, the non-specifically-sorbed (readily bioavailable) As content may represent the most important fraction connected to environmental risks (Wenzel, 2001; Khan et al., 2021b). As reported by Karak et al. (2011), the non-specifically-sorbed As fraction is the most mobile and toxic portion of As in soil and water systems. Further, the non-specifically-sorbed As extracted with ammonium sulphate can be used to predict the As leachability under field conditions (e.g., Wenzel et al., 2002).

The specifically- sorbed As or the exchangeable fraction, on the other hand, consequently, poses health risks to humans and animals via accumulation in the food chain (Antoniadis et al., 2017). Furthermore, it may provide vital clues on lability of As from the solid phase due to changes in soil and environmental factors such as the P, pH, and redox conditions (Mensah et al., 2020; Wenzel 2001). For instance, the soil pH may affect the solubility and mobility of As into the surrounding ecosystem as well as uptake by crops (Hou et al., 2020). Moreover, a much greater proportion of As is solubilized with ammonium phosphate due to the competitive exchange between phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) in soils (Bolan et al., 2014). In such scenario, the smaller size and higher charge density of phosphate makes it more preferred, and consequently arsenate is preferentially desorbed over phosphate (Manning and Goldberg, 1996).

Thus, the specifically-sorbed As, extracted with ammonium phosphate, may give a useful indication of As potential mobility due to anion exchange (e.g., Wenzel et al., 2001, 2002); therefore, phosphate fertilizers may increase As mobility and leaching from the highly contaminated mining spoil. The non-specifically- and specifically- sorbed portions of As form the most easily available fractions connected with environmental pollution and food chain contamination (Wan et al., 2017); hence, these two fractions may provide accurate estimation and useful guide towards remediation of As in contaminated sites.

Different kinds of organic and inorganic amendments are recommended for the treatment of contaminated sites. These include manures, compost, biosolids, sawdust, wood ash, lime, biochar, charcoal, zeolites, coal fly ash, and metal oxides/hydroxides such as those of Fe, Al, and Mn (Shaheen et al., 2015; Hou et al., 2020; Wang et al., 2021; Shaheen et al., 2022). As reported by Komárek et al. (2013), application of Fe oxides (e.g., iron grit) decreases the mobile and bioavailable fractions of As and thus minimizes their potential environmental risks and uptake by soil organisms, crops, and humans. Compost and manure could also immobilize As from soil by adsorption and/or complexation with particulate organic matter as reported by Gadepalle et al. (2008) and Hartley et al. (2010). Apart from immobilizing metals and metalloids, application of biochar may aid in improving soil quality and quicken revegetation of mine degraded sites owing to the introduction of organic matter into the soil (Mensah and Frimpong, 2018; Bolan et al., 2021; Shaheen et al., 2022). In effect, these amendments can correct soil pH problems, provide nutrients to improve quality of mine-contaminated sites, and aid in reducing phytoavailability of toxic elements to plants grown on degraded sites.

The gold mining sector in Ghana has caused myriad of land degradation problems and impacted immensely on the ecosystem and human health in gold mining communities. For instance, Mensah et al. (2020) reported high As median health hazard quotient values above unity for both children and adults in active and abandoned mine sites in Ghana. Additionally, Mensah et al. (2021) found that the As contamination accounted for more than 70% of the total health risks via soil ingestion for children, adult males and females living near abandoned mine sites in southwestern Ghana. Thus, more alternative options for remediation of these contaminated sites are needed to reduce the As-associated human health and environmental impacts in mining communities. Presently, no integrated study has attempted to assess and compare the potential of chemical methods including biochar, compost, manure, iron oxide and inorganic NPK fertiliser for cleaning As from these As-contaminated mine sites. Besides, the impacts of these amendments on As mobilization, bioavailability and remediation remain controversial in scientific literature. For instance, Palansooriya (2020) concluded that application of compost and manure to As-contaminated sites may vary in impacts depending on their compositions and the site's soil properties, as the compost/manure may either enhance or limit As mobilization. Moreover, Lv et al. (2021) found that low dosage of biochar (0.5%) showed limited effects in reducing As mobility whilst high dosage (5%) facilitated its release. Furthermore, even though application of phosphorus containing fertilizers (e.g., NPK 15:15:15) can boost P content in P-deficient mine degraded soils, P fertilizers are however widely reported to increase As mobility and could result in depletion of water quality.

In conclusion, the effects of these amendments on As mobility in mine contaminated spoils remain inconclusive and hence more scientific studies are needed to appropriately advise their safe use in mine land reclamation. Thus, we hypothesize that application of soil amendments to the contaminated-mine spoil may alter the As fractions, reduce its mobilization and thus its potential risk, and in parallel can improve and restore the soil quality in this contaminated area. Therefore, in this study, we employed incubation study to ascertain if treatment of an As-contaminated mine spoil with biochar, compost, iron oxide, manure, and inorganic fertiliser: i) provides a measure for remediation of the non-specifically (readily bioavailable) and the specifically-sorbed As contents, and ii) can enhance the soil quality of the abandoned mine spoil.

5.2 Materials and methods

5.2.1 Site characteristics and total element contents

Soil samples were collected from an abandoned As-contaminated gold mine spoil in the western region of Ghana. Soil pH was determined in a soil: 0.01 M $CaCl_2$ solution ratio of 1:5 using the pH meter. Total carbon and nitrogen were determined according to Wright and Bailey (2001). Soil texture was determined using the laser scattering method according to Zobeck (2004). Total element contents were determined using the nitric acid method (120 °C + 15 minutes digestion; 10 ml conc. HNO_3 + 10 ml dilution with de-ionized water) (USEPA, 2007).

The texture of the site is sandy with sand, silt, and clay percentages as 62, 36, and 3%, respectively (Table 5.1). The soil has a neutral pH at 7, total carbon at 1%, total organic carbon at 5 mg/l, total Fe at 19,348 mg/kg, total Al at 3,390 mg/kg, total Ca at 10,893 mg/kg and total Mn at 357 mg/kg. More details about the site, sample collection and preparation, climatic conditions and physico-chemical properties of the site are reported in Mensah et al. (2020, 2021).

The site is highly contaminated with As and contains 1807 mg/kg (Table 5.1). Arsenic contamination in the site is sourced from many years of accumulation and stockpiling of the mine tailings (Mensah et al., 2020) and the site has been abandoned since 2002. Arsenic geochemical fractions were determined using sequential extraction procedure according to Wenzel et al. (2001). Arsenic is mainly distributed in the amorphous iron oxide fraction (FIII; 49% of total As) and the residual fraction (FV; 38.5% of total As). This was followed by the exchangeable fraction (FII; 10.7%), non-specifically sorbed As (FI; 1.2%); then, the high-crystalline Fe oxide fraction (FIV; 0.5%) (Appendix A, Fig. S5.1). These indicate that As in the contaminated mine spoil was highly related with the amorphous iron oxide and the residual fractions as also found by Mensah et al. (2020).

The potential mobile fraction of As (∑FI – FIV) from the mine spoil soil is 1183.6 mg kg^{-1} (61.5%). Arsenic in the potential mobile fraction may become solubilised due to reductive dissolution of the Fe-bearing mineral (e.g., Shaheen et al., 2017). Thus, this As component may become available under varying reducing and oxidising conditions and might consequently pose toxicological and environmental risks. The content of the mobile fraction of As (FI + FII) was 229 mg kg^{-1} (12% of total As).

2.2 Soil amendment characterization

The soil amendments used in the study were rice husk biochar, iron oxides, NPK fertiliser (15:15:15), compost, and cow dung manure. Biochar was made from rice husks at 500 °C as reported by Manka'abusi et al. (2020). Compost was obtained from partially decomposed small animal (rabbits, rats, and guinea pigs) manure, poultry manure, domestic bio-wastes, soil, and plant litter. The manure was a cow dung obtained from a cattle farm. Iron oxide was bought from Amazon market in Germany and was principally made up of iron and oxides. The iron oxide had a pH of 7 and electrical conductivity of 0.0024 dS/cm. Additionally, it was made up of the following constituents: Fe_2O_3 = 82%, SiO_2 = 9.8%; CaO = 2%, Al_2O_3 = 2.6%, MgO = 1.5%, K_2O = 0.5% and BET was 10.6 g/100g. The inorganic NPK fertiliser had a neutral pH at 7, EC of 1.1 dS/cm and principally contained the following: 15% ammonium nitrogen, 15% P_2O_5 (neutral-ammonium citrate and water-soluble phosphate), 15% water-soluble K_2O, and 11% S.

The amendments were oven-dried at 80°C, crushed, homogenised, and passed through < 0.63 mm sieve. They were later characterised for their pH, electrical conductivity, total carbon and nitrogen, total elements, and heavy metals, as in the case of the soil. Total carbon in the amendments were generally high with highest contents in biochar (42%), followed by manure (40%) and compost (24%). Total contents of nitrogen were 1%, 2%, and 3%, for biochar, compost, and manure respectively. Iron contents were highest in compost (15,120 mg/kg), manure (570 mg/kg) and biochar (313 mg/kg). Composts contained the highest proportion of Al, Mn and P at 5,888 mg/kg, 1864 mg/kg, and 27,360 mg/kg, respectively (Table 5.1). Heavy metal contents in the soil amendments were all below detection except compost, which contained 3 mg As/kg.

Table 5.1: Basic physico-chemical properties and element total contents in the soil amendments used in our experiment

Parameter	Unit	Soil		Biochar		Compost		Manure	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
pH	-	7	0.3	7	0	7	0	8	0
EC	µS/cm	632	0.6	900^a	74.7	1946	57	207	1
DOC	mg/l	5	0.5	ND	-	ND	-	ND	-
C/N	-	44	2.2	59	1	11	0	16	0
TC	%	1	0.2	42	1	24	1	40	1
TN		0	-	1	0	2	0	2	0
Sand		62	15	NA		NA		NA	
Silt		36	14	NA		NA		NA	
Clay		3	1	NA		NA			
Ash content $^{a, b, c}$		NA		45.2	0.8	ND		ND	
Volatile matter $^{a, b, c}$		NA		23.2	2.6	ND		ND	
Total element contents									
As	mg/kg	1807	26	< 0.5	-	3	0.1	< 0.5	-
Al		3390	41	304	25	5888	91	722	26
Ca		10,893	88	1344	3	36,880	2376	30,720	0
Fe		19,348	86	313	3	15,120	3281	570	68
K		388	12	6488	714	11,492	226	14,920	419
Mg		6174	46	847	26	1864	283	5920	475
Mn		357	4	359	12	3752	215	174	1
P		305	7	1277	208	27,360	679	7408	68
Al_d	mg/kg	233		ND					
Al_o		150		ND					
Fe_d		4919		ND					
Fe_o		5110		ND					
Mn_d		73		ND					
Mn_o		105		ND					

Value represents mean of three replicates; NA = not applicable; ND = not determined; SD = standard deviation; Fe_d/Al_d/Mn_d = Fe/Al/Mn oxides with warm dithionite extraction (this is made up of both crystalline and amorphous iron oxides); Fe_o/Al_o/Mn_o = Fe/Al/Mn oxides extracted with oxalate (made up of only amorphous iron oxides); EC = Electrical conductivity; DOC = dissolved organic carbon; TC = total carbon; TN = total nitrogen.

^{a} = data as obtained from Akoto-Danso et al. (2018).

$^{a, b, c}$ = data as obtained from Asirifi et al. (2021), Manka'abusi et al. (2020) and Akoto-Danso et al. (2018).

5.2.3 Experimental design/incubation study

The study employed an incubation study and laboratory experiments. There were five different treatments, three different levels, and three replications each. Compost, iron-oxide, manure, and rice husk biochar were each applied at the rates of 0.5, 2 and 5% (w/w) to 300 g soil; and NPK (+S) (15:15:15+11) fertilizer was applied at 0.1, 0.2, and 5.0 g kg^{-1}. Thus, the soil amendments were applied at low, medium, and high rates and the rates were selected based on application rates in previous studies (e.g., Mensah and Frimpong, 2018; Li et al., 2020). These application rates were carefully chosen to test if low, moderate, and high rates will suppress or enhance As mobilization. The highest rate of biochar (5%), for instance, was selected to test the hypothesis that application rates above 3% increases mobilization of As (e.g., El-Naggar et al., 2021; Lv et al., 2021). The application rates for the inorganic fertiliser were based on the normal application range by farmers in Ghana (i.e., 200 – 560 kg/ha). Water was added to bring the soil water content to a 70% field capacity and the setups including the control were kept in a dark room at 20°C and arranged in a complete randomized design for 28 days. The incubation time were based on that previously used by Lv et al. (2021). Thus, there were six total treatments and 16 total experimental set-ups: control with no addition of soil amendments (Co), compost (C), manure (M), rice husk biochar (B), and iron oxide (F) (Appendix, Table S5.1).

5.2.4 Chemical analyses

5.2.4.1 Analyses of soil properties

Soil samples for analyses were collected at 1-day and 28-day intervals to determine their gravimetric moisture content, pH, electrical conductivity, dissolved organic carbon, and soluble anions (F^-, Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}). For the pH, electrical conductivity, dissolved organic carbon, and anions, 10 g of the wet soil was weighed into a 100 ml PE bottle and 50 ml of de-ionised water added. The contents were shaken for 2 hours at room temperature and then filtered through 0.45 µm filter paper. From the filtrates, pH, EC, DOC, and anions (F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) were determined. Additionally, portions of the soils after the 28-day incubation were collected, saved and oven-dried at 60°C and later analyzed for their exchangeable cations, cation exchange capacity (CEC), total C, N, and available P.

The soil available P was determined using the P-Bray method (Pierzynski, 2000). Soil moisture contents were determined using the gravimetric water content method after oven-drying at 105°C for 48 hours, exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) by the Hexamincobalt (III)-chloride method based on *DIN EN ISO 23470* (Jaremko and Kalembasa, 2014), and cation exchange capacity estimated from the summation of all exchangeable cations. Soil pH was measured with pH meter (Sentix 41, WTW GmbH, Weilheim, Germany), electrical conductivity was determined with EC meter (TetraCon 325, WTW GmbH, Weilheim, Germany), dissolved organic carbon, total carbon and nitrogen were measured by an elemental analyzer (Vario max cube, Elementar Analyse systeme GmbH, Hanau, Germany), and anions were measured with the Ion Chromatography (Metrohm, 881 Compact IC Pro).

5.2.4.2 Determination of non-specifically-sorbed (readily bioavailable) As and specifically-sorbed As

In determination of non-specifically-sorbed As (readily bioavailable) and specifically-sorbed As in the incubated samples, 2 g of the collected wet samples were used. These contents were determined according to the method of Wenzel et al. (2001) to study operationally defined associations of As from mine waste in south-west England. For non-specifically-sorbed As, 25 ml of 0.05 M $(NH_4)_2SO_4$ solution was added to the 2-g wet soil, shaken for 4 hours at 20°C, centrifuged at 4000 rpm for 15 minutes, and then filtered through 0.45 µm filter paper.

After extracting the non-specifically-sorbed As, the same soil sample was used to extract the specifically-sorbed As sequentially using 25 ml 0.05 M of $(NH_4)H_2PO_4$. After 16h shaking at 20°C, the samples were centrifuged at 4000 rpm for 15 minutes, and then filtered through 0.45 µm filter paper. Phosphate solutions are reported to be very efficient in extracting As from different soils as explained earlier in section 1 and demonstrated by Wenzel et al. (2001). From the filtrates, As contents were determined with the ICP-OES. The moisture content was determined and As concentrations were calculated based on the dry weight.

5.2.4.3 Determination of soil As/pH solubility

The pH of the As contaminated soil was adjusted using the acid neutralization capacity (ANC) method (James and Riha, 1986). ANC describes the ability of the soil to buffer acid intake within a short period. In this method, the amount of acid or base necessary to adjust the soil to a certain pH is specified. The effect of pH on As solubility was determined in a series of batch extraction tests (1:5 m/v), in which 25 g of air-dried soil was mixed with various volume doses of 1 M HCl or 0.1 M KOH. These were diluted in appropriate amounts of distilled water to obtain a total solution volume of 50 ml, to which contained additions of 5ml 0.1M KCl as the background electrolyte. The volumes of acid added were in the range 0.5 – 10 ml; and the base in the range of 0.5 – 5ml; which corresponded to 0 – 10 mmol H^+ or OH^-/25 kg of soil. The samples were shaken overnight for 22 hours; thereafter, the suspensions were centrifuged and filtered. The concentrations of As, as well as pH values, in the extracts (filtrates) were determined. All the procedures were carried out in triplicates.

5.2.5 Data treatment and statistical analyses

As a quality control, blank and standard solutions, and triplicate samples were employed in all extraction procedures. In addition, we used the standard reference material, SRM 2710a, for baseline trace elements concentrations (National Institute of Standards and Technology, USA) to verify concerns of data quality. Our ICP had calibration range between 0 mg/L and 2mg/L; 3.36 µg/L As detection limit and 95% recovery rate.

We performed a one-way ANOVA between means of different treatment rates (control, biochar, compost, manure, iron-oxide and NPK fertiliser). Before running ANOVA, we conducted test for normality of data using the Shapiro-Wilk Test. For these tests, variables with $P > 0.05$ were considered normally distributed and those with $P < 0.05$ were not normally distributed. We further performed multiple range tests using the Tukey's Honestly Significant Difference (HSD) test among means of treatments at $P < 0.05$.

Additionally, we ran a Pearson moment correlation matrix between non-specifically-sorbed (readily bioavailable) As, specifically-sorbed As and other potential As-controlling soil factors such as moisture content, pH, electrical conductivity, dissolved organic carbon, soluble anions such as F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, available P, exchangeable cations, and cations exchange capacity. We further calculated percentage changes (either increase or decrease) in the readily bioavailable As, specifically sorbed-As, and in the other soil quality parameters of the mine spoil soils due to addition of the soil amendments relative to no addition of amendments (i.e., the control soil). Statistical analyses were performed using IBM SPSS Statistics 25 (NY, USA), and figures displaying means of measured values were presented using OriginPro 2021b (OriginLab Corporation, Northampton, USA) software.

Table 5.2: Absolute values and their associated percentage changes in treatment (%) (inc/dec) in readily bioavailable As, specifically sorbed-As, and soil quality parameters of the amended mine spoil soils relative to the un-amended control at the end of the 28-day incubation

Treatment	Readily bioavailable As	Inc/dec	Specific sorbed-As	Inc/dec	K	Inc/dec	Mg	Inc/dec	Na	Inc/dec	%N	Inc/dec	%SOC	Inc/dec	C/N	Inc/dec	Avail P	Inc/dec
Control	25		393		1		22		1		0.0		1.4		44		118	
C0.5	52	106	338	-14	3	511	27	20	2	121	0.0	19	1.5	4	38	-13	78	-34
C2	108	332	302	-23	11	1795	33	47	3	296	0.1	92	1.7	20	27	-38	42	-64
C5	90	260	249	-37	25	4285	50	122	5	625	0.1	227	2.2	58	21	-52	13	-89
F0.5	12	-52	413	5	1	2	28	25	0	-39	0.0	3	1.5	4	44	1	68	-42
F2	5	-82	405	3	2	212	25	12	1	25	0.0	13	1.5	5	40	-7	24	-80
F5	2	-93	380	-3	1	0	27	19	1	-12	0.0	29	1.6	14	39	-11	7	-94
M0.5	31	24	432	10	2	173	28	23	1	105	0.0	42	1.6	12	34	-22	118	-1
M2	67	169	342	-13	6	928	32	42	4	497	0.1	132	1.9	37	26	-41	73	-38
M5	104	315	347	-12	12	2099	38	68	8	1082	0.1	344	3.0	115	21	-52	60	-49
N0.1	24	-4	416	6	1	53	21	-6	1	-19	0.0	-6	1.4	-4	45	3	91	-23
N0.2	30	19	392	0	1	89	23	2	0	-33	0.0	-3	1.4	-3	43	-1	92	-22
N5	125	398	349	-11	12	2060	33	46	1	22	0.1	65	1.4	1	27	-39	94	-21
B0.5	34	35	395	1	1	43	25	10	0	-47	0.0	7	1.5	10	45	3	124	5
B2	32	28	394	0	2	167	21	-5	0	-46	0.0	26	2.1	51	52	19	111	-6
B5	37	47	341	-13	3	402	20	-10	0	-54	0.1	59	2.8	99	54	25	124	4

C0.5, C2, C5 = soil treatment with compost at 0.5%, 2% and 5%, respectively; F0.5, F2, F5 = iron oxide at 0.5%, 2% and 5%, respectively; M0.5, M2, M5 = manure at 0.5%, 2% and 5%, respectively; N0.1, N0.2, N5 = NPK fertiliser at 0.1g/kg, 0.2g/kg and 5 g/kg, respectively; and B0.5, B2, B5 = rice husk biochar at 0.5%, 2% and 5%, respectively. (-) means percentage increase as compared to the control; (+) means percentage decrease as compared to the control. Percentage increase/decrease at the end of the incubation was =

$$\frac{Measured\ value\ in\ treatment\ sample - Measured\ value\ in\ the\ control\ sample}{Measured\ value\ in\ the\ control\ sample} \times 100$$

5.3 Results and discussions

5.3.1 Impact of amendments on soil quality

5.3.1.1 Soil pH, salinity, soluble anions, and exchangeable cations

Changes in the soil pH, electrical conductivity (EC) and soluble anion contents (Cl^-, NO_3^-, SO_4^{-2}) following treatment with the soil amendments within 1 day and 28-day incubations are shown in Fig. 5.1 and Table S5.2 (Appendix A). Within the 24-hour period, the soil pH ranged between 6.1 and 7.6, where the highest pH was observed in 5% iron-oxide and lowest in 5% compost addition. In the 28-day incubation period, addition of compost, manure, and biochar at 5% significantly ($P < 0.05$) increased the soil pH from 6.8 to 7.9, 7.8 and 7.5, respectively. The increase in the mine spoil soil pH due to addition of compost, manure and biochar may be due to presence of positive charges on their surfaces. The higher pH caused by the amendment addition may lead to the release of As. This is because the change of ambient pH could change the protonation of functional groups on biochar, compost, or manure, and could thus alter the chemistry of As (Niazi et al., 2018; Bolan et al., 2021). For instance, Van Vinh et al. (2014) and Bolan et al. (2021) indicated that the surface of biochar could be negatively charged under relatively alkaline conditions. Electrical conductivity varied between 1.2 and 2.3 dS m^{-1} during the entire incubation period (Appendix A, Table S5.2). Addition of inorganic NPK fertiliser at 5 g kg^{-1} and manure at 5% significantly ($P < 0.05$) increased the EC to 2.3 dS m^{-1} and 2.1 dS m^{-1}, respectively, at the end of the 28-day incubation period.

Concentration of chloride was increased upon increasing addition of compost, manure and NPK fertilizer. For instance, during the day-1 incubation period, 5 g kg^{-1} NPK fertilizer increased the Cl^- content to 425.5 mg kg^{-1}, whilst it increased it to 441.7 mg kg^{-1} at the 28-day period. Thus, the higher contents in chloride were associated with manure and NPK fertilizer. The implication of these is that Cl^- may displace As-anions from positive sorption sites particularly the manure and inorganic fertilizer amended soils, and may enhance its subsequent uptake, availability, and release. These indicate that the chemistry of chloride may greatly influence the release pattern and environmental ecotoxicology of As from the mining spoil.

In this respect, the presence of Cl^- may affect mobilization of As from the soil either via competition with As(V) or As(III) for available adsorption sites or they may alter the electrostatic charge on soil minerals (Niazi et al., 2018); this will be explained later in section

5.3.2.3. However, addition of biochar and iron-oxide significantly reduced content of chloride in our soils. Thus, the addition of iron oxide and biochar to the soil could restrict the release of dissolved Cl^- from the soil solids into the soil solution; which mechanism limits the production of negative ions. Therefore, we hypothesize that biochar and iron oxide could be very useful in safeguarding environmental safety and reducing As food chain contamination in the surroundings of the abandoned mining spoil (see detail explanation in section 5.3.2.3).

At the end of the 28-day incubation period, addition of soil amendments did not significantly affect the soil exchangeable Ca^{2+} or the overall CEC (Appendix A, Fig. S5.2). However, compost and manure at 5% increased the soil exchangeable K^+, Mg^{2+} and Na^+. This may have been caused by the relative higher contents of K^+, Mg^{2+} and Na^+ in the compost and manure used in our study (Table 5.1). Additionally, relative higher contents of K^+, Mg^{2+} and Na^+ in the compost and manure amended soils may be attributed to their release into the soil exchange sites from the functional groups such as those complexed with carboxylic and phenolic acid on the surfaces of organic matter (Liu et al., 2012). Similarly, Mensah and Frimpong (2018) found that higher rate of compost application (at 2%) increased the soil exchangeable Mg, K, and Na contents in degraded soils in Ghana.

High contents of soil exchangeable K^+, Mg^{2+} and Na^+ may have environmental implications in controlling the soil pH, retaining nutrients (and thus prevent loss of cations and other nutrients) and in controlling the fate of As transport and mobilization in contaminated mining soils. For instance, compost application has a liming effect due to its richness in alkaline cations such as Ca, Mg, and K; which are liberated from organic matter due to high rates of mineralization (e.g., Mensah and Frimpong, 2018). Consequently, high pH has the potential to increase As solubility and mobilization as will be explained later in section 5.3.2.3. Additionally, the presence of K^+, Mg^{2+} and Na^+ may contribute to raising the soil cation binding capacity and enhancing sorption ability for As (Palansooriya et al., 2020).

5.3.1.2 Carbon, nitrogen, and phosphorus

At the end of the 28-day incubation period, compost, manure, and biochar improved the mine spoil total C contents concomitantly with higher doses of amendment addition. For instance, C content increased by 58% upon addition of 5% compost, 115.7% upon addition of 5% manure and 99% with 5% biochar treatment (Table 5.2; Fig. 5.2). Thus, highest increments in the mine spoil C contents were attained with high doses of manure and biochar, which we may attribute to the greater C contents in the biochar (42%) and manure (40%) used in the experiments, as also reported by others (e.g., Rogovska et al., 2011). We thus further calculated the carbon balance by comparing the actual C-inputs with the C-output.

Fig. 5.1: Changes in the mine spoil soil pH, DOC, sulphate, and chloride contents during the 1-day and 28-day incubation period following treatments with biochar, compost, iron oxide, manure, and inorganic fertiliser. Co = control; C0.5, C2, C5 = soil treatment with compost at 0.5%, 2% and 5%, respectively; F0.5, F2, F5 = iron oxide at 0.5%, 2% and 5%, respectively; M0.5, M2, M5 = manure at 0.5%, 2% and 5%, respectively; N0.1, N0.2, N5 = NPK fertiliser at 0.1g/kg, 0.2g/kg and 5 g/kg, respectively; and B0.5, B2, B5 = rice husk biochar at 0.5%, 2% and 5%, respectively. Charts represent means of three replicates and error bars represent their standard deviations. Means with different letters differ significantly among treatments at $P < 0.05$ and same letters indicate no significant differences among means according to the Tukey's Honestly Significant Different test.

We found that addition of 5% biochar containing 42% C led to a lesser C output (8.4 g C kg^{-1}) than the manure amended soils (9.1 g C kg^{-1}). Additionally, 5% biochar addition sequestered more C (1.53 C kg^{-1}) than the manure-amended soils (0.54 C kg^{-1}) (data not shown). Thus, higher amount of C was used and mineralized by the soil microbes than in the biochar-amended soils, where much of the C were recalcitrant as demonstrated by the C/N values (Rogovska et al., 2011)

Dissolved organic carbon in our experiment was significantly affected by addition of 5% compost and manure (Fig. 5.1). Compost at 5% during the 24-hour period, for instance, significantly increased DOC from 11.2 mg L^{-1} to 44.7 mg L^{-1}, whilst 5% increased it to 114.4 mg L^{-1}. Similar observations were made during the 28-day incubation period. But 0.5% iron-oxides significantly decreased DOC by 86.6%, whilst 5% biochar decreased DOC by 80%. The reduction in the soil DOC contents by the iron oxide may be due to adsorption, whilst the higher Al/Mn/Fe contents and presence of basic cations in the biochar may have similarly reduced the DOC contents. It is thus reported that Fe-and Mn oxyhydroxides strongly adsorb organic matter and reduce its subsequent solubilization (Gu et al., 2019). In this respect, the reduction in dissolved carbon due to biochar application indicates biochar's ability to reduce loss of carbon from the mine spoil and will contribute to its sequestration.

Additionally, reduction in DOC leads to increased stabilization of C, increased immobilization of C, decreased microbial decomposition (Bolan et al., 2012), and consequent reduction in mobility of sorbed-As. In this regard, sequestration, and reduction in loss of dissolved carbon upon addition of iron oxide and biochar will consequently contribute to reducing the associated readily bioavailable As content and its migration into available groundwater, as will be discussed more in section 5.3.2. The higher DOC in the manure treated soils may be due to availability and release from mineralization of the C content and thus contributed to its impact in increasing the readily bioavailable As content as will be discussed in section 5.3.2. The higher DOC in the manure treated soils may be due to availability and release from mineralization of the C content and thus contributed to its impact on increasing the readily bioavailable As content as will be discussed in section 5.3.2.

Similar findings were made for the soil total N contents where higher doses of compost, manure and biochar led to significant appreciation in the mine spoil N contents. For instance, addition of compost, manure, and biochar at 5% each led to percentage increase in the mine spoil N by 227%, 344% and 59%, respectively (Table 5.3; Fig. 5.2). The increment in the site's total N content upon addition of higher doses of compost, manure and biochar indicate their potential in ameliorating the deficient N contents in the mine spoil. Mining spoils present an extremely hostile environment for plant establishment and survival (Mensah, 2015).

Soil amendments increase soil productivity and stimulate microbial activity which provides essential nutrients (e.g., N and P) and organic carbon to the soil (Sheoran et al., 2010). Thus, compost, manure and biochar could be used to improve the nitrogen status of the degraded mining sites, enhance their soil quality, and to consequently quicken revegetation and growth of plants on the sites. In this regard, Alhar et al. (2021) found that biochar applied at 5% facilitated growth and increase in dry matter yield of ryegrass grown in abandoned mining spoils in the United Kingdom. These effects are more pronounced when biochar is co-applied with manure and/or compost (e.g., Mensah and Frimpong, 2018; Zhao et al., 2020).

Additionally, higher biochar treatments led to increases in the spoil C/N ratio (+25%), whilst higher addition of compost, manure and NPK fertilizer resulted in significant reduction of the C/N ratios (Appendix A, Fig. S5.3; Table 5.2). The compost and manure contained relatively higher inherent N contents and may indicate a higher rate of nitrogen mineralization than the biochar. This explains the relative higher C/N ratio in the biochar amended soils and may hence indicate possibility of lower rate of decomposition and mineralization. The implication of these findings is that nutrients held in compost and manure amended soils may easily be lost through leaching, infiltration, and runoff, whilst those applied in biochar may be held and stored for a longer period or many seasons for crop use (Duku et al., 2011; De Gryze et al., 2010). In this respect, De Gryze et al. (2010) reported that the recalcitrant nature and longer half-life of biochar make it possible to hold nutrient in soils for longer period, resulting in positive benefits on crop yields in the long run.

Soil available P in our study ranged between 7.1 mg/kg and 123.8 mg/kg, with the lowest value observed in 5% iron-oxide and highest value in the 5% biochar (Fig. 5.2). Soil available P decreased proportionally upon higher doses of compost, iron-oxide, and manure. Thus, sorption sites may have been provided for P by manure, compost, and iron-oxide. We may attribute these reductions to the high contents of Al, Fe and Mn in the compost and manure used in the study; whilst the highest reduction by FeO may mainly be due to its high Al, Fe and Si contents. High contents of Al, Fe and Mn may bind P to the soil exchange sites and consequently reduce their availability, as also assumed by others (Shaheen et al., 2021; Zhang et al., 2021). Furthermore, available P may be complexed/precipitated on the surfaces of compost and manure treated mine spoil soils due to the presence of surface positive ions such as Ca^{2+}, K^{+}, Mg^{2+} and Na^{+}.

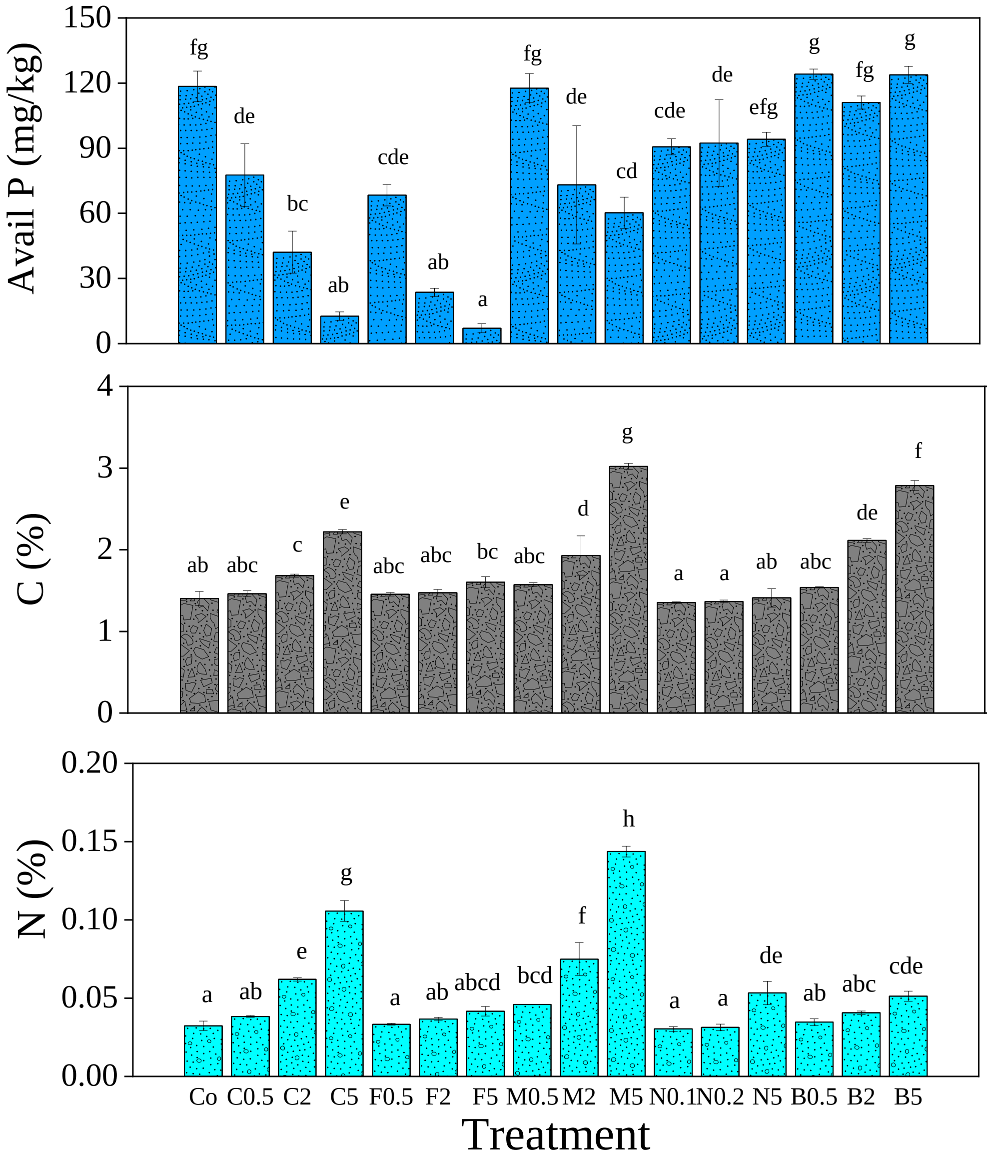

Fig. 5.2: Changes in the mine spoil soil total carbon, total nitrogen, and available phosphorus at the end of the 28-day incubation period following treatments with biochar, compost, iron oxide, manure, and inorganic fertilizer. Co = control; C0.5, C2, C5 = soil treatment with compost at 0.5%, 2% and 5%, respectively; F0.5, F2, F5 = iron oxide at 0.5%, 2% and 5%, respectively; M0.5, M2, M5 = manure at 0.5%, 2% and 5%, respectively; N0.1, N0.2, N5 = NPK fertilizer at 0.1g/kg, 0.2g/kg and 5 g/kg, respectively; and B0.5, B2, B5 = rice husk biochar at 0.5%, 2% and 5%, respectively. Charts represent means of three replicates and error bars represent their standard deviations. Means with different letters differ significantly among treatments at P < 0.05 and same letters indicate no significant differences among means according to the Tukey's Honestly Significant Different test.

5.3.2 Impacts of soil amendments on non-specifically-sorbed (readily bioavailable) As and specifically-sorbed As

5.3.2.1 Non-specifically-sorbed (readily bioavailable) As

The amendments showed contradictory effects on the non-specifically-sorbed (readily bioavailable) As (Fig. 5.3a). 5% iron oxide reduced the readily bioavailable As by 93%, while addition of the different doses of compost, manure, inorganic fertilizers, and biochar increased it by 106-332%, 24-315%, 4-398, and 28-47% as compared to control, respectively (Table 5.2). The readily bioavailable As was therefore reduced with increasing proportions of iron oxide during the entire incubation period (Fig. 5.3a). The mine spoil already contains a high amount of total Fe (i.e., 19,343 mg kg^{-1}, Table 5.1). The geochemical fractionation results (Appendix A, Fig. S1) also indicated greater quantities of As bound to amorphous iron-oxides (45%), and 0.5% represented the non-specifically-sorbed As. Thus, we assume that additional treatment of the mine spoil with iron oxide contributed to reducing the 0.5% As content further.

In this regard, Danila et al. (2020) and Komárek et al. (2013) reported that high Fe contents in mine soils concomitantly lead to its high immobilization efficiency for As. The binding and sorption of As by FeO may be attributed to the presence of many positive charges on the surfaces of iron oxide. The presence of positive charges is more dominant under acidic conditions as explained earlier in section 5.3.2.3. The stability of FeO on As immobilization is highly dependent on the pH. At high pH, As bound to the surfaces of FeO may be liberated due to the dissociation of the positively charged binding sites and thus become available (El-Naggar et al., 2019). Additionally, iron oxyhydroxides in soil can slowly transform into more crystalline Fe oxides (e.g., hematite) that have a lower specific surface area (Danila et al., 2020). This can cause the release of previously sorbed As and increase its leaching over time.

On the other hand, the increase of readily bioavailable As by 5% compost, manure, and NPK fertilizer may be related to rise in salinity and chloride contents associated with addition of the amendments and the fertilizer to the soil. These are further confirmed by the higher EC values and chloride contents of compost, manure and NPK fertilizer treated soils (Table 5.1). These high salinity and chloride contents may enhance desorption of As anions from positively charged binding sites, leading to liberation of As. Moreover, there were high significant positive relationships between readily bioavailable As with EC and chloride (Fig. 5). Thus, readily bioavailable As in our study may be highly governed by salinity and Cl^- contents, and that increasing salinity and chloride contents in the mine spoil may result in increasing As solubility and vice versa. In a similar study, El-Naggar et al. (2021) found a positive relationship between available As, EC and chloride in an amended multi-contaminated mining soil in South-Korea. High content of salinity and Cl^{-} in the soil may lead to high As solubility in the soil solution and facilitate its subsequent mobilization (e.g., El-Naggar et al., 2021).

Moreover, the increased in readily bioavailable As may be related to the high C content in the compost and manure used in our study, and as explained earlier in section 3.1.2. 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; Gu et al., 2019). Hartley et al. (2010) reported high concentration of As in compost treated soils in brownfield site in the UK and attributed the increase to formation of As-DOC complexes on the surfaces of compost. In our present study, we also found a positive significant relationship between the readily bioavailable As and DOC ($r = +0.53$, $P < 0.01$; Fig. 5.5). The positive relationship may imply that As content might have formed complexes with DOC in the compost- and manure-amended soils.

Consequently, high DOC content subsequently leads to high As availability under various environmental changes such as the pH. Alternatively, DOC is largely anionic and therefore can displace As from binding sites through competition, like that of Cl^-. In this regard, El-Naggar et al. (2021) reported that As forms complexes with DOC (As-DOC complexes) and thus solubilization of DOC concurrently creates high available As and leads to their subsequent release. In addition, Guo et al. (2019) reported that the DOC could increase the release of As via desorption of As-sorbed organic matter, particularly during reductive dissolution of As-bearing oxides in reducing conditions. In conclusion, four assumptions may account for the high DOC and the concomitant high As mobilization (positive relationship between DOC and As): 1) there was release of As adsorbed on the surfaces of the dissolved organic matter; 2) there was release of As from C that is co-precipitated on the surfaces of reductively dissolved Fe/Al/Mn-oxyhydroxides; 3) there was release of soluble organic metabolites produced by soil reducing bacteria, subsequently leading to release of any sorbed-As; and 4) there was As release via desorption of organic matter from soil mineral surfaces due to changes in soil pH.

Furthermore, 5% biochar addition significantly increased As solubility by 75% in the 1-day and by 48% during the 28-day period. The increase in As solubility by biochar may be related to deprotonation of positively charged binding sites (Beiyuan et al., 2017) due to pH increase of the mine spoil. Thus, the high concentration of dissolved As in the alkaline treatments was higher than that in the control. Biochar increases pH of soils and has liming effects as reported by Mensah and Frimpong (2018). This may be attributed to the presence of basic cations in the ash produced during biochar making process (Tack and Egene, 2018).

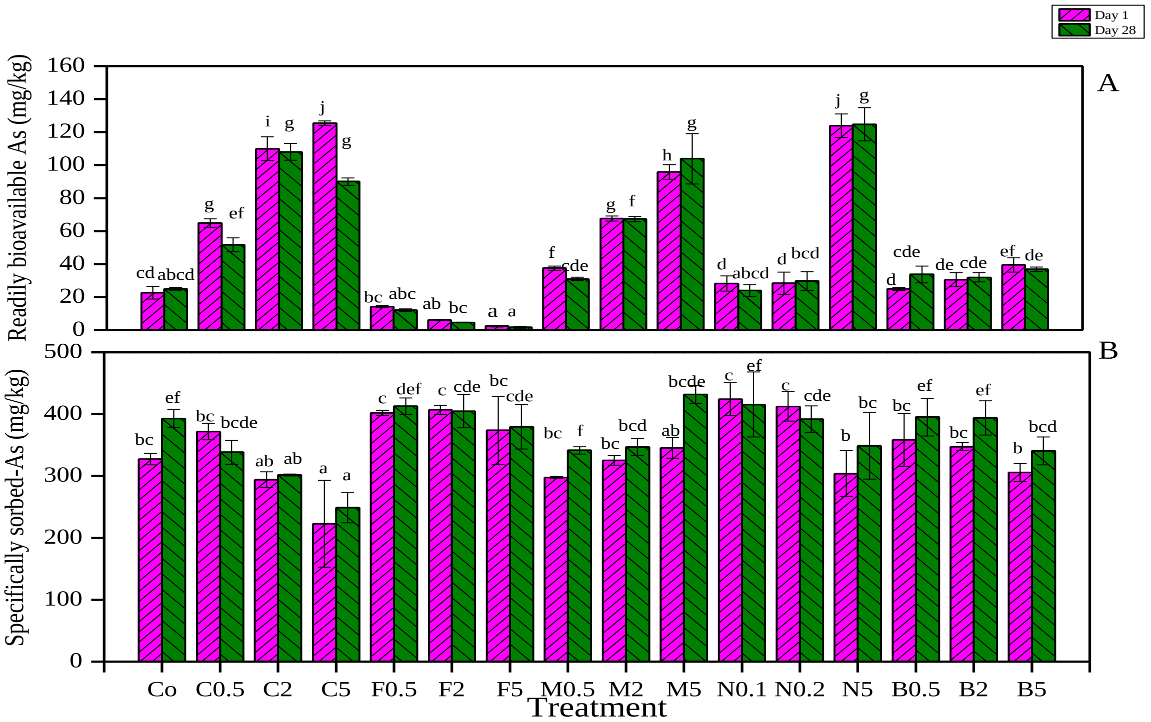

Fig. 5.3: Changes in the mine spoil non-specifically (readily bioavailable)- and specifically- sorbed As contents during the 1-day and 28-day incubation period following treatments with biochar, compost, iron oxide, manure, and inorganic fertiliser. Co = control; C0.5, C2, C5 = soil treatment with compost at 0.5%, 2% and 5%, respectively; F0.5, F2, F5 = iron oxide at 0.5%, 2% and 5%, respectively; M0.5, M2, M5 = manure at 0.5%, 2% and 5%, respectively; N0.1, N0.2, N5 = NPK fertiliser at 0.1g/kg, 0.2g/kg and 5 g/kg, respectively; and B0.5, B2, B5 = rice husk biochar at 0.5%, 2% and 5%, respectively. Charts represent means of three replicates and error bars represent their standard deviations. Means with different letters differ significantly among treatments at P < 0.05 and same letters indicate no significant differences among means according to the Tukey's Honestly Significant Different test.

Consequently, increase in pH may facilitate As solubility from the mine spoil during the 28-day incubation period, and as also confirmed in other studies (e.g., Beiyuan et al., 2017). This is further demonstrated by the high significant positive correlation (r = +0.64, $P < 0.01$) between pH and readily bioavailable As (Fig. 5.5 and demonstrated in section 5.3.2.3). Therefore, the increase in dissolved As under high pH is attributed to 'anion exclusion' resulting from the electrostatic repulsive force between negatively charged amendment and the dominating negative As species, including $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} (Beiyuan et al., 2017; Wen et al., 2021).

Additionally, we speculate that the application of this P-rich amendments, particularly compost (total P = 27360 mg/kg; Table 5.1) and manure (total P = 7408 mg/kg; Table 5.1), and biochar (total P = 1277 mg/kg; Table 5.1) may increase the phosphate content in soil, which would compete with As anions for the binding sites on soil (Pan et al., 2021; Yang et al., 2021), and thus increase its solublity and biovaiability. In this regard, Palansooriya (2020) advised against application of phosphate-rich materials to sites contaminated with As, as such actions may exacerbate surface and groundwater pollution.

5.3.2.2 Specifically-sorbed As

Addition of 5% compost reduced mine spoil specifically-sorbed As from 393 to 249 mg kg^{-1} (-37%) (Fig. 5.3b; Table 5.2). We may attribute this reduction to higher contents of Al/Fe/Mn in the compost amendments used as shown in Table 5.1. High content of Al/Fe/Mn may have provided sorption sites for the specifically-sorbed As in the soil and thus contributed to its reduction. Additionally, the compost is made up of organic materials and contained relatively high contents of carbon (24%). High soil carbon content can become carriers of As, and thereby reduce their availability as explained earlier in section 5.3.2.1. This is further demonstrated by the significant negative relationship ($r = -0.6$, $P < 0.05$; Fig. 5.5) between the soil total carbon and specifically-sorbed As. Thus, the higher the C content, the lower the content of available As for exchange, bioavailability, and possible food chain contamination. In this regard, Karczewska et al. (2017) reported that soil amendment with organic materials such as compost was effective in reducing soil available As in ryegrass cultivated fields. Similarly, Gadepalle et al. (2008) found low available As in soils treated with 5% compost.

At the 28-day incubation period, 5 g kg^{-1} NPK and 5% biochar slightly reduced specifically-sorbed As by 11% and 13%, respectively (Table 5.2). It is thus reported that As acts as a P analogue (Pan et al., 2021). Furthermore, the reduction in specifically-sorbed As by biochar and manure may have been caused by the relatively high carbon content and presence of positive ions such as Al, Fe and Mn (Table 5.1) on the surfaces of biochar and manure. In this respect, Beesley et al. (2013) found that addition of biochar to a contaminated mining soil decreased the soil As availability, and consequently led to reduced uptake and toxicity-transfer risk into tomato plant.

Biochar may have demonstrated some effectiveness for reduction in specifically-sorbed As, but care must be taken regarding their application to As contaminated soils. This is because of potential increase in soil pH associated with liming effects of biochar (Mensah and Frimpong, 2018) and production of soluble C (Beesley et al., 2011); which may concomitantly lead to high As mobilization. It is reported earlier (section 5.3.2.1) that high soil pH may lead to increased liberation of As and may concomitantly increase its ecotoxicological effects. In this regard, Beesley et al. (2011) suggested that combination of biochar with iron oxides may be a good option to achieve mutual benefit as iron oxides can reduce As availability.

5.3.3 Soil pH and As solubility

Arsenic solubility in our study may be governed by contents and biogeochemical changes in the mine spoil pH, Cl^-, EC, exchangeable K^+ and Na^+ (Fig. 5.5). Thus, we further demonstrated the impact of pH on As solubility using the acid neutralization capacity test (Fig. 5.4). Results from the extraction tests indicated that As solubility increases with increasing pH. With 0.00 and 0.04 mg kg^{-1}, As contents were lowest at pH of 5.47 and 5.87, respectively. In the alkaline range, As more or less continuously increased by a factor of >10 from 1.25 mg kg^{-1} at pH 7.02 till 14.08 mg kg^{-1} at pH 10.03. This indicates higher potential environmental risks of As under alkaline conditions and this was further confirmed by a significant positive correlation between pH and soluble As ($r = 0.92$, $P < 0.01$, $n = 12$; data not shown). We propose three main hypotheses to explain As release and mobilization at higher pH: deprotonation of Al/Fe/Mn oxides, solubilization of Fe/Mn oxides, and development of negative charges on the soil colloids.

It is well known that As compounds adsorb to oxyhydroxides of Al, Fe and Mn, humic substances, and clay minerals (Kabata-Pendias, 2011). At high pH, sorption capacity of Fe oxides for As is lost due to deprotonation of Fe (Kabata-Pendias, 2011). Tack (2010) reported that As sorption unto the soil colloids decreases with higher pH due to carbonates acquiring a more negative charge and production of hydroxyl ions at high pH. This phenomenon can make exchangeable As become available (Mensah et al., 2020). Also, Gersztyn et al. (2013) found that considerable amounts of As were released at a pH of about 9. This is not always the case, as Gersztyn et al. (2013) reported that soil liming with $Ca(OH)_2$, which principally supplies calcium, does not result in As solubilization, because calcium humates are hardly soluble in alkaline conditions.

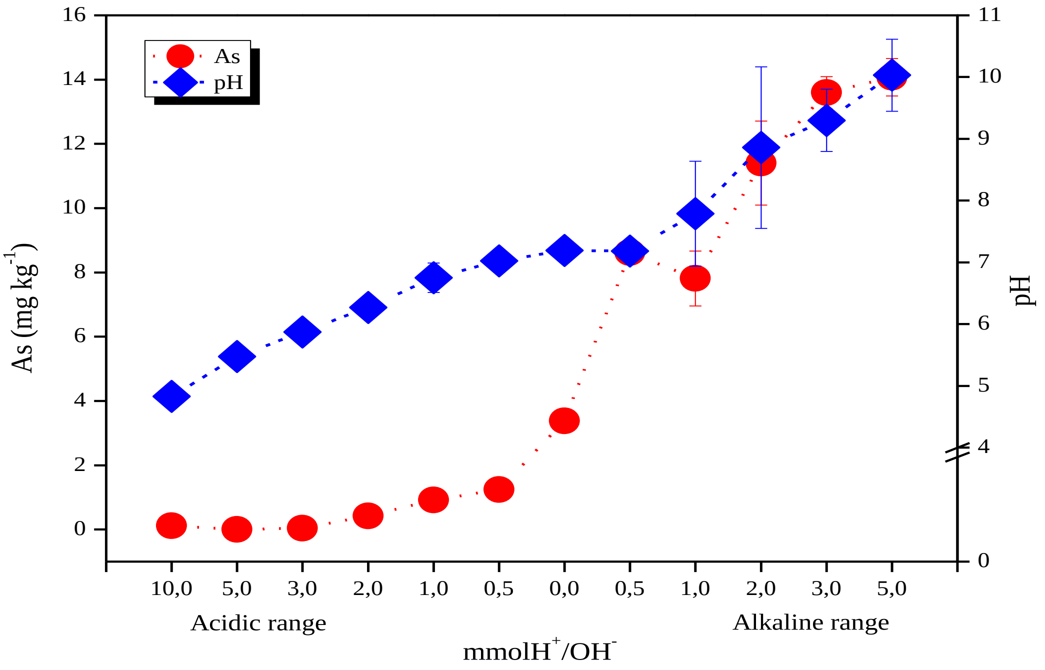

Figure 5.4: Dynamics of As solubility due to pH changes (impacts of pH changes on As solubility). Values are means of three replicates and error bars represent the standard deviations.

5.4 Conclusions

In soils from an abandoned gold mine spoil in Ghana, we determined arsenic (As) mobilization and soil quality improvement, as impacted by different rates (low, medium, and high) of biochar, compost, iron oxide, manure, and inorganic fertilizer. The high total content (1807 mg/kg), readily bioavailable (25 mg/kg) and specifically sorbed As (393 mg/kg) in this spoil may lead to a high environmental and human health risks. The increase in the soil pH, carbon and P content induced by the amendments (compost, manure, biochar), increased the bioavailability of As and may lead to an elevated risk to the surrounding ecosystem and human health. Nevertheless, these carbon-, and P-rich and alkaline materials can be used to enhance the phytoextraction efficiency of As in the gold mining spoil. However, the addition of iron-rich materials decreased the bioavailability of As and thus can be effective solution to reduce As loss and migration into surface and groundwater and consequently mitigate the potential As-associated environmental and human health risks in such mining spoils. We thus recommend a combination of methods such as biochar in combination with compost/and or manure, or biochar in mixture with iron oxide; such measure (s) may encourage vegetation re-establishment on the degraded mining sites to aid restore ecological system functions and consequently reduce As availability to the surroundings.

This study provides first baseline success guide regarding the use of organic based material and inorganic amendments for soil remediation of As-contaminated gold mining spoils in Ghana. We propose large-scale field applications and longer-term study to better evaluate the long-term applicability of the treatments on As mobilization into the surrounding ecosystem and restoring soil quality. Additionally, the impacts of the soil amendments on geochemical distribution of As and potential mobilization in the contaminated gold mining spoil should be investigated in detail. Finally, modern sophisticated technologies such as synchrotron radiation X-ray spectroscopy may be employed in the future to investigate the dominant species of As in the abandoned mining spoil as impacted by the various treatments.

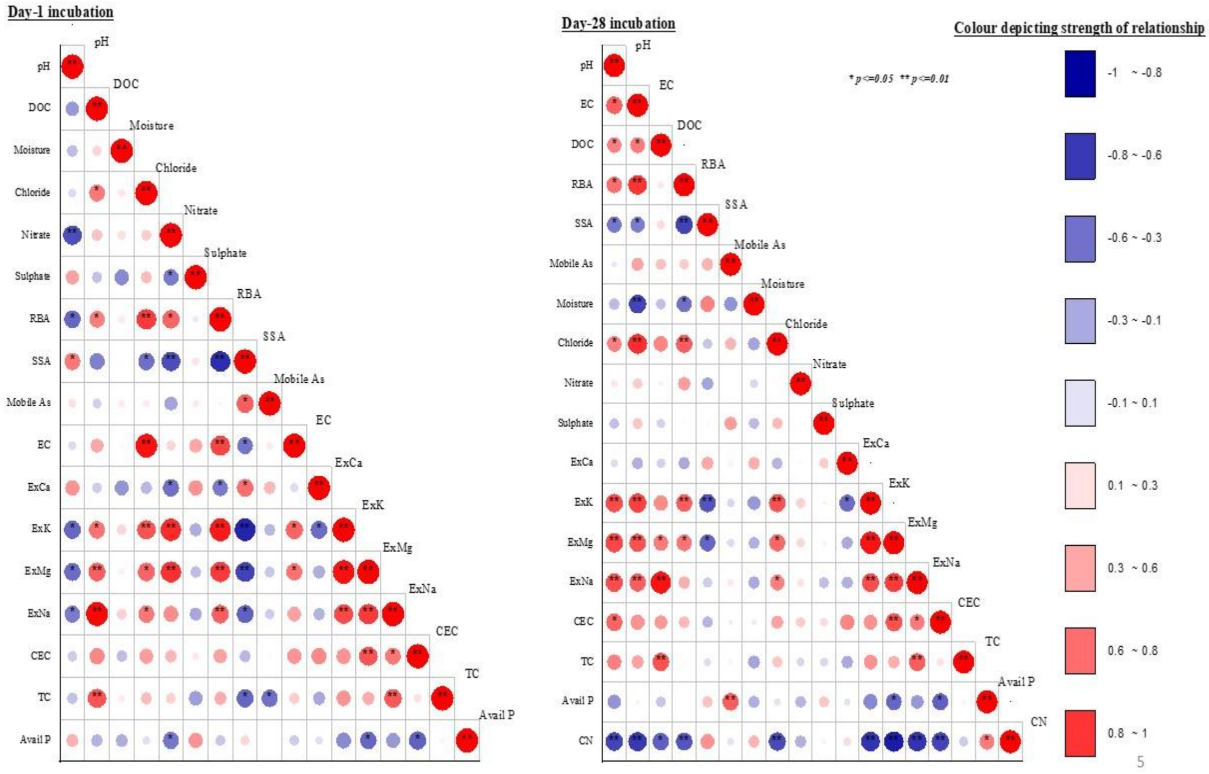

*Figure 5.5: Correlation matrix between readily bioavailable As, specifically sorbed-As, and relevant As-governing soil chemical factors at the beginning (Day-1) and the end (Day-28) of the incubation period. *indicates significant relationships at P < 0.05; ** indicates significant relationships at P < 0.01; DOC = dissolved organic carbon; EC = electrical conductivity; RBA = Readily bioavailable As; SSA = specifically-sorbed-As; ExCa = exchangeable calcium; ExK = exchangeable potassium; ExMg = exchangeable magnesium; ExNa = exchangeable sodium; CEC = cation exchange capacity; TC = soil total carbon; avail P = soil available P*

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Supplementary Materials (Appendix A) of the manuscript (Chapter 5):

Biochar, compost, iron oxide, manure, and inorganic fertilizer affect bioavailability of arsenic and improve soil quality of an abandoned arsenic-contaminated gold mine spoil

Albert Kobina Mensah et al. Revised manuscript submitted for review in *Ecotoxicology and Environmental Safety*

Table S5.1: Treatments, dosages and replications of compost, iron-oxide, manure, biochar, and inorganic fertiliser used in our experiment

Treatment	Added dose (%; w/w)	Abbreviation	Replicate
Control soil		Co	3
NPK fertiliser (N)	0.01	N0.1	3
	0.02	N0.2	3
	0.50	N0.5	3
Compost (C)	0.5	C0.5	3
	2.0	C2	3
	5.0	C5	3
Manure (M)	0.5	M0.5	3
	2.0	M2	3
	5.0	M5	3
Rise husk biochar (B)	0.5	B0.5	3
	2.0	B2	3
	5.0	B5	3
Iron oxide (F)	0.5	F0.5	3
	2.0	F2	3
	5.0	F5	3

Table S5.2: Changes in soil physico-chemical parameters (moisture, EC, and nitrate) following treatments with biochar, compost, iron oxide, manure, and inorganic fertiliser

Treatment ID	Incubation day	Mean	SD	Incubation day	Mean	SD	Incubation day	Mean	SD
Nitrate (mg/kg)				EC (µS/cm)			Moisture (%)		
Co	Day 1	9.6efg	0.8	Day 1	1612.7ghijkl	51.9	Day 1	23.31abcd	0.81
	Day 28	7.8efg	1.9	Day 28	1577.3ijkl	35.9	Day 28	21.9abcd	1.5
C0.5	Day 1	21.9c	3.6	Day 1	1686fghijk	60.8	Day 1	23.9abcd	1.8
	Day 28	18.1cd	3.8	Day 28	1844cdefgh	73.7	Day 28	18.9cd	7.2
C2	Day 1	55.4b	3	Day 1	1756defghij	47.3	Day 1	23 abcd	0.4
	Day 28	55b	2.1	Day 28	1863cdefg	74.1	Day 28	23 abcd	1.9
C5	Day 1	126.8a	3.2	Day 1	1839.3defgh	55.8	Day 1	24.2 abcd	0.4
	Day 28	6.1fg	0	Day 28	1981.3cd	41.9	Day 28	21.5 bcd	0.5
F0.5	Day 1	10.5ef	1.8	Day 1	1704efghijk	9	Day 1	21.8 bcd	1.4
	Day 28	9efg	1.4	Day 28	1245.3op	138.5	Day 28	33ab	1.4
F2	Day 1	9.5efg	0.9	Day 1	1589hijkl	6.6	Day 1	23 abcd	1.3
	Day 28	8.1efg	0.6	Day 28	1317.3mnop	53.2	Day 28	36 a	4.5
F5	Day 1	8.9efg	1.3	Day 1	1697.7efghik	34	Day 1	23.8 abcd	2
	Day 28	8.3efg	0.3	Day 28	1266.7nop	61.2	Day 28	27.3 abc	11.8
M0.5	Day 1	8.6efg	1.6	Day 1	1642fghijkl	14.7	Day 1	11.5d	1.1
	Day 28	7.9efg	3.2	Day 28	1711.7efghijk	55.2	Day 28	22.9 abcd	0.2
M 2	Day 1	10.9efg	3	Day 1	1784.3defghi	37	Day 1	23.5 abcd	0.3
	Day 28	6fg	1.7	Day 28	1895.3cdef	96.6	Day 28	23.5 abcd	0.2
M 5	Day 1	14.4de	3.6	Day 1	1952.3cde	44.7	Day 1	25.5 abcd	0.7
	Day 28	8.9efg	3	Day 28	2101bc	197.5	Day 28	22.7 abcd	0.7
N0.2	Day 1	10.2ef	0.6	Day 1	1580.7ijkl	166.4	Day 1	25.2 abcd	2.6
	Day 28	6.9fg	0.8	Day 28	1207.3p	56.1	Day 28	32.4 abc	9.2
N0.1	Day 1	8.2efg	0.9	Day 1	1522jklmn	70.5	Day 1	27.4 abc	3.7
	Day 28	7.9efg	1.9	Day 28	1238.3op	60.1	Day 28	29.7 abc	15.2
N5	Day 1	9.2efg	1.1	Day 1	2410a	10	Day 1	22.6 abcd	6
	Day 28	7.9efg	1	Day 28	2275.7ab	107.9	Day 28	21.9 abcd	1.7
B0.5	Day 1	6.5fg	0.3	Day 1	1426.3lmnop	196.8	Day 1	22.7 abcd	1.1
	Day 28	7.2fg	4	Day 28	1538ijklm	11.8	Day 28	22.5 abcd	0.5
B2	Day 1	6.9fg	1.3	Day 1	1557.7ijklm	51.5	Day 1	22.1 abcd	1.3
	Day 28	4.5fg	0.9	Day 28	1484klmno	28	Day 28	22.2 abcd	0.9
B5	Day 1	4.8fg	0.8	Day 1	1716efghik	37.4	Day 1	22.3 abcd	1.1
	Day 28	3g	0.3	Day 28	1515jklmn	44.5	Day 28	23.2 abcd	0.4

Co = control; C0.5, C2, C5 = soil treatment with compost at 0.5%, 2% and 5%, respectively; F0.5, F2, F5 = iron oxide at 0.5%, 2% and 5%, respectively; M0.5, M2, M5 = manure at 0.5%, 2% and 5%, respectively; N0.1, N0.2, N5 = NPK fertiliser at 0.1g/kg, 0.2g/kg and 5 g/kg, respectively; and B0.5, B2, B5 = rice husk biochar at 0.5%, 2% and 5%, respectively. EC = electrical conductivity, SD = standard deviation. Means with different letters differ significantly among treatments at $P < 0.05$ and same letters indicate no significant differences among means according to the Tukey's Honestly Significant Different test.

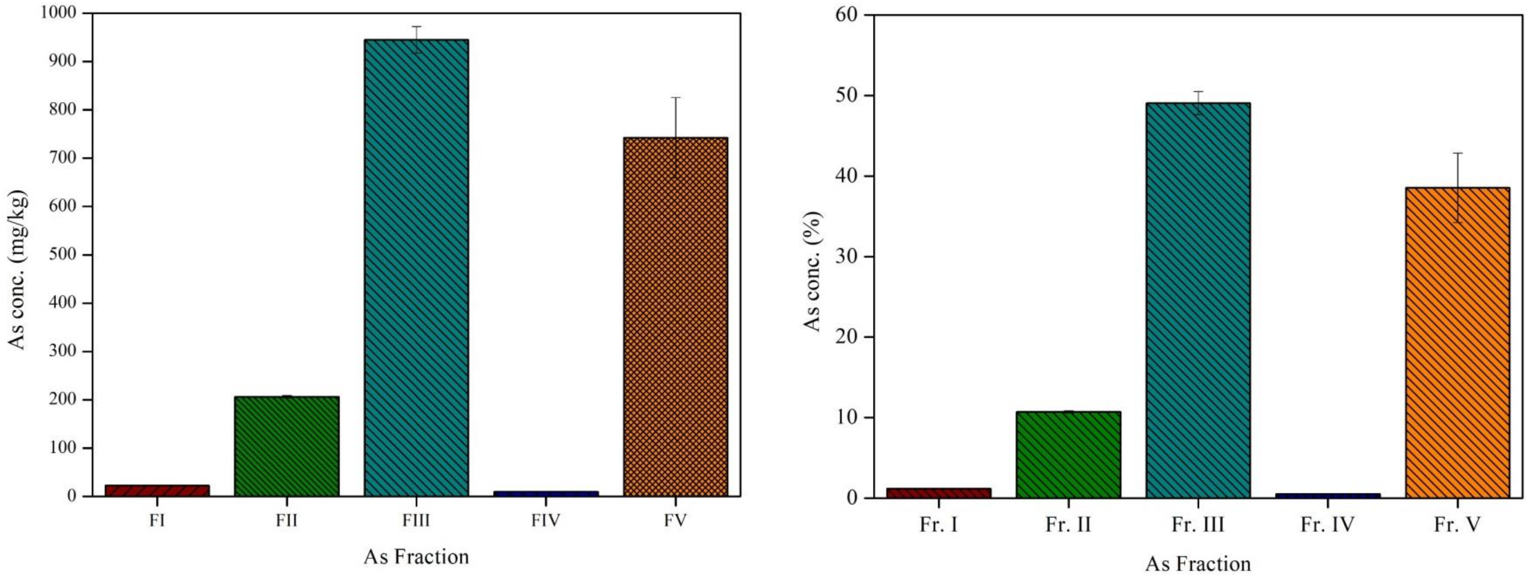

Fig. S5.1: Distribution of As geochemical fractions in the mine spoil in mg/kg. Fr. I = non-specifically sorbed As, Fr. II = specifically sorbed-As, Fr. III = amorphous iron oxide fraction, Fr. IV = high-crystalline Fe oxide fraction, FV = residual fraction.

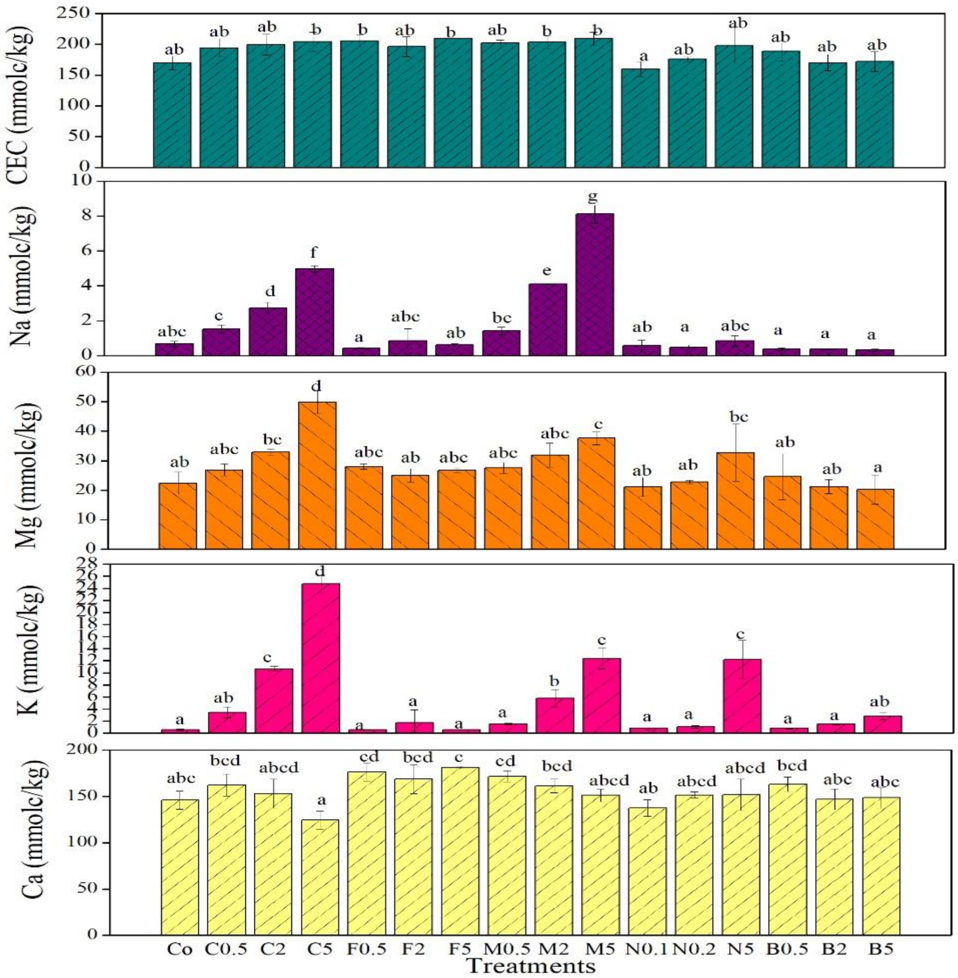

Fig. S5.2: Changes in the mine spoil soil exchangeable cations and cations exchange capacity at the end of the incubation period following treatments with biochar, compost, iron oxide, manure, and inorganic fertiliser. Co = control; C0.5, C2, C5 = soil treatment with compost at 0.5%, 2% and 5%, respectively; F0.5, F2, F5 = iron oxide at 0.5%, 2% and 5%, respectively; M0.5, M2, M5 = manure at 0.5%, 2% and 5%, respectively; N0.1, N0.2, N5 = NPK fertiliser at 0.1g/kg, 0.2g/kg and 5 g/kg, respectively; and B0.5, B2, B5 = rice husk biochar at 0.5%, 2% and 5%, respectively. Means with different letters differ significantly among treatments at $P < 0.05$ and same letters indicate no significant differences among means according to the Tukey’s Honestly Significant Different test. Error bars represent the standard deviation of the means of three replicates.

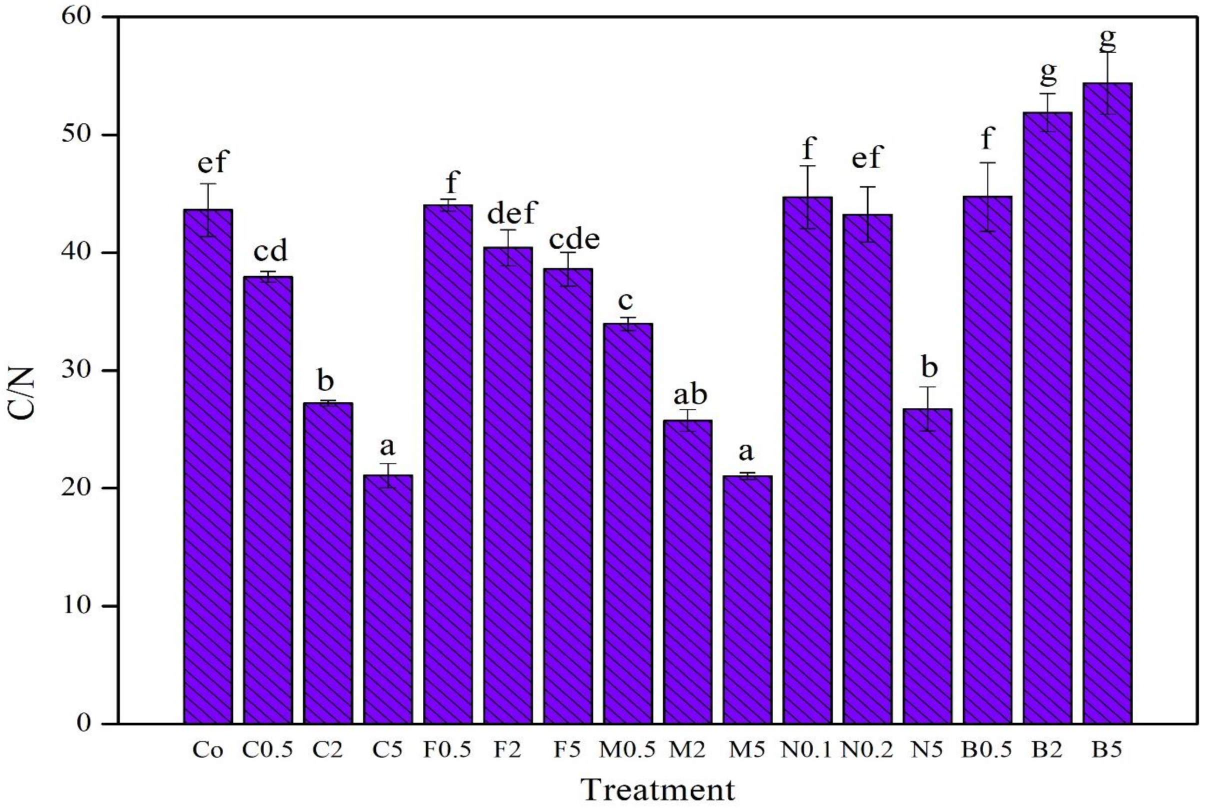

Fig. S5.3: Changes in the mine spoil soil C/N contents at the end of the incubation period following treatments with biochar, compost, iron oxide, manure, and inorganic fertiliser. Co = control; C0.5, C2, C5 = soil treatment with compost at 0.5%, 2% and 5%, respectively; F0.5, F2, F5 = iron oxide at 0.5%, 2% and 5%, respectively; M0.5, M2, M5 = manure at 0.5%, 2% and 5%, respectively; N0.1, N0.2, N5 = NPK fertiliser at 0.1g/kg, 0.2g/kg and 5 g/kg, respectively; and B0.5, B2, B5 = rice husk biochar at 0.5%, 2% and 5%, respectively. Means with different letters differ significantly among treatments at $P < 0.05$ and same letters indicate no significant differences among means according to the Tukey's Honestly Significant Different test. Error bars indicate standard deviation of the means of three replicates.

CHAPTER 6

General discussions, conclusions, and recommendations

6.1 General discussions

Gold mining presents varied environmental and human health threats in the areas where the mining takes place. Water pollution and increased cost of water treatment, cyanide spillage from mine tailings, tailings collapse, pollution of aquatic biodiversity, mercury pollution, depletion of fertile lands, food crop contamination, soil pollution; and many neurological, genetic, and skin diseases are common in mining areas. These come from irresponsible mining practices such as bad management of mine wastes and neglect of mine sites at the decommissioning phase of the mineral extraction. Consequently, these affect the well-being of the populace in mining communities and deprive them of their livelihoods (shown and explained in Fig. 1.3 in chapter 1). To investigate this hypothesis in detail, I first collected samples from an abandoned mine tailing (10 individual sampling points and bulked together into one) that measures 126,000 m^2. Initial analyses on the samples indicated total As content at 1809 mg/kg, whilst other heavy metals in the mining tailing were either below or equal to the recommended threshold. Thus, As pollution is a major problem in the mining region, and therefore studying it in detail and devising a sustainable remediation/mitigation strategy will be worth pursuing. This led to the study in chapters 2, 3, 4 and 5; summarised in the subsequent sections.

Chapter two reported findings from investigation on As contamination in the abandoned and active gold mine sites and explored their pollution and related potential human health threats. Here, I collected additional samples from both the abandoned and active mining spoils. I collected 32 samples from individual spots (0-20 cm depth) from the abandoned mine spoil, dug two pits up to 1 m depth and collected samples from every 20-cm depth till 100 cm, and collected 10 samples from individual spots from active mining tailing (surface: 0 – 20 cm depth). The samples were prepared, further separated into bulk, fine (silt and clay) and coarse (sand) fractions, and analysed for total As contents, and five geochemical fractions. Additionally, selected samples from both mining sites were further analysed for their dominant As species using synchrotron x-ray adsorption near edge spectroscopy. These were collected in NSRRC in Taiwan. Further, valuation of soil pollution and health implication of both the active and old mine tailings was done. Results from the study indicated that the mining sites posed a major threat on the health of the people in the mining areas. More particularly, the old, abandoned mining spoil posed greater risks especially on children and women. The risks were confirmed by the total As contents, the operationally defined components, and their dominant species in the mine spoils. Elevated total As concentration (1807 – 8,400 mg/kg), high mobile and potential mobile As fractions, and high As dominant species ($FeAsSO_4$ = 65-76%; FeAsS = 24-35%) in mining sites contributed to their high risks. Additionally, the risk of pollution was in order: active mine spoil < profile < abandoned mine spoil. Thus, even though both mine spoil contained As contents in many folds above the recommended thresholds, extent of contamination and risks were more pronounced in the surface soils and profiles.

The higher As content in the surface soils may come from many years of accumulation and stockpiling of the mining waste materials. This was demonstrated by the higher contents of topsoil As contained in the residual fraction of both fine (52%) and coarse particles (56%) of the abandoned site (see Fig. 2.5). Moreover, extent of pollution was higher in the abandoned site than in the active mine. It was assumed that these differences might have arisen from difference in either ore characteristics, historical extraction procedures (Mensah et al., 2020), age of the mine spoils (Antoniadis et al., 2017) or different tailing depositional times as reported in Edraki et al. (2014).

Further, As total contents and potential mobility were greater in the fine separate than in the coarse portion. This was attributed to greater proportions of $FeAsSO_4$ and FeAsS, and extracted As in the amorphous and residual fractions in the fine fraction relative to the contents in the coarse fraction. A high significant positive association between As and Fe ($r = 0.98$; $P < 0.01$, see Table S2.5) was observed. This implies that As total and potential mobility were hugely a function of the content of Fe. The dominance of Fe in the fine fraction may also be due to higher content of clay which may increase positive charges. The presence of surface positive charges then increases sorption capacity for As and increases As content in the fine fraction. It is thus explained and elaborated earlier (see section 2.3.4.2 in chapter 2) that soils with superior clay fraction hold elevated proportions of As.

Consequently, the increased potential mobility in the fine fraction designates potential mobilisation and release of the sorbed-As under changing environmental conditions (e.g., pH, E_H and changes in contents of P). For example, during flooding and rainfall, the high total As, As contained in the species (e.g., $FeAsSO_4$ and FeAsS), the extracted As in the amorphous and residual fractions in the fine fraction may be liberated and become available for polluting the surrounding soils and surface and groundwater as demonstrated in chapter 4 and also explained in other studies (e.g., Rinklebe et al., 2016, 2017).

The mobile and potential mobile fractions of As in the coarse particles of the profile samples increased down the profile while it declined in the fine particles. Here, I attributed this observation to the impact of weathering, reduction and oxidation processes occurring in the soil coarse particles. Such processes occur in the soil more strongly at the surface topsoil than in the subsoils. The amorphous iron oxide contents for example, may be subjected to different oxidation and reduction processes. These processes may subsequently lead to liberation and migration of As that are loosely-bound from the surface soils. The released As may be lost from the soil surface through runoff and erosion processes or leach downwards to the soil sub-layers. These reasons may have accounted for decreased As mobile and potential mobile fractions down the profiles in the fine fractions, and increased mobility in the coarse fractions down the soil profiles. In conclusion, the mining spoils pose threats to the livelihood of the people in the gold mine dominated region and remediation action should be explored to protect the environment, restore livelihoods, and safeguard the health of animals and residents.

Chapter three studied the human health risk via soil ingestion of potentially toxic elements and remediation potential of native plants near the abandoned mine site. The intent of this chapter was to look at the spread of the contamination from the abandoned mining spoil into nearby sites- soils and farms. Additionally, I explored how indigenous and native plant species could be used to remediate and clean the contaminated fields in the mining area. I embarked on another sampling campaign to Ghana, and collected 52 soil samples from sites and farms within the vicinity of the abandoned mining spoil and from a natural forest, which is located 3.4 km away from the mine sites. Additionally, native plants growing near the mine site were harvested: *Chromolaena odorata, Pityrogramma calomelanos, Alchornea cordifolia, Lantana camara* and *Pueraria montana*. I determined the total element concentration in the sites, calculated their associated-soil contamination and enrichment factors, geo-accumulation index, pollution load index and assessed the human health risk via intentional or accidental soil ingestion by calculating the hazard quotients (HQ) and hazard index (HI). Total element concentration in the native plants were determined and their remediation efficiencies were assessed by calculating their bioaccumulation, bioconcentration and translocation factors.

In summary, mean element total concentrations in the fields were observed to follow the order: Fe > Al > As > Cr > Zn > V > Ti > Cu > Pb > Ni > Cd. Iron concentration in the sites surpassed the threshold average. Mean total As in the sites exceeded the recommended threshold of 6 mg/kg. At the 90th percentile, Zn total concentration in the Pueraria field, and maximum values in the mine surrounding exceeded their mean and maximum allowable concentration thresholds (see chapter 3; Fig. 3.1). Cadmium and Ti in the mining sites also exceeded their world soil average. Particularly, the fields were contaminated with As, Cd, Fe, Ti and Zn. Arsenic contamination in the soils and farms near the abandoned gold mine land supports our findings and conclusions in chapter 2. The contamination of the sites with As was thus attributed to either mobilisation by runoff/and or by action of water erosion, rainfall or through deposition by wind into the surrounding environments. Additionally, contamination of the sites with Cd, Fe, Ti and Zn was attributed to either illegal gold mining activities taking place in the surroundings, indiscriminate disposal of mine wastes, poor handling of mine wastes or dry deposition from the mining spoil. In other instances, these toxic elements may have been deposited over a period through dust emission generated from motor vehicles. The lack of vegetation cover of mine sites, abandonment of mine lands without protection and the many untarred roads found in the area may further exacerbate the wide pollution of the sites and farms in the mining area with toxic elements.

These have deleterious effects on food crops grown, available water sources, and agricultural soils found in the area, with consequent on health of the people (see also Mensah et al., 2015 on environmental impacts of mining in mining communities in Ghana). These were further confirmed with the findings from the health impacts calculations. In the soil-to-human health appraisal, hazard quotient (HQ) and hazard index (HI) in all sites for especially children and women were above the critical threshold of 1 (see chapter 3; Fig. 3.4). These high HI values were largely contributed by As (range: 63.2% – 88.1%); thus indicated an extremely greater health risk consequences linked with soil ingestion of As for women and children in the mining areas. In conclusion, I speculate that women and children in the mining areas may be susceptible to As health-related problems. Women and children may thus be exposed to As-health threats such as that of Buruli ulcer, other skin diseases, genetic disorders, neurological problems, birth deformities in new-born babies and cognitive dysfunctions among children. In this regard, Duker et al. (2004) observed that instances of Buruli ulcer were greater in As-enriched drainages and farmlands in mining districts in Ghana. Additionally, cases of bladder and lung cancers, reproductive outcomes, and declined cognitive function were reported among As-exposed population in Latin America (e.g., Bundschuh et al., 2021; Khan et al., 2020). The chapter concluded that there is a potential and the possibility of using native plant species, more particularly, *Chromolaena odorata*, to reclaim these heavily-laden metal and metalloid-polluted sites.

In chapter four, I investigated the mobilisation and speciation of As in the abandoned gold mine site under reducing and oxidising settings. Humid tropical climates are characterised by high rainfall regimes. These events cause flooding of many urban areas including farmlands and mining fields. Flooding and high rainfall regimes create various reducing and oxidizing conditions of mine contaminated sites and may thus induce mobilisation and release of toxic elements including As-laden sediments and slurry into the environment. Consequently, such redox processes exacerbate pollution of nearby water courses and available groundwater, with subsequent threats on human health and livelihoods. Thus, in this chapter, I investigated impacts of various reducing and oxidising conditions created by flooding regimes on the mobilisation and speciation of As in abandoned mining sites. In summary, I explored the biogeochemistry and dynamic behaviour of As in a contaminated mine spoil when it rains, or when the site is flooded or drained. This study was conducted using the novel automated biogeochemical microcosm experimental set-up. This set-up has been employed successfully in the past to study biogeochemistry and mobilisation of other potentially toxic elements into groundwater (e.g., Yu et al., 2007; Yu and Rinklebe, 2011). The system enables the researcher to investigate in a controlled environment, how the various biogeochemical processes may influence mobilisation and control the fate of transport of As during flooding. This equipment allows the simulation of anoxic/oxic conditions by adjusting the E_H automatically with nitrogen to decrease E_H or synthetic oxygen to increase E_H. Contents of dissolved As, Fe, Mn, Al, and S; SUVA, DOC and DIC; Cl^- and SO_4^{2-}; as well as Fe^{2+} in the soil solution and suspension were measured. Additionally, selected soil samples from the lowest, middle, and highest redox potentials were selected for As K-edge XANES analysis in NSRRC in Taiwan Light Photo Source.

It was observed that As mobilisation increased under reducing conditions whilst it decreased under oxidising conditions. This mobilisation was mainly regulated by the chemistry of Fe, which explained almost 100% of the data variation according to the multiple stepwise regression analyses (see chapter 4; Fig. 4.5; equation 4.1). This was further confirmed by the XANE results where greater proportions of As were bound to Fe-dominant minerals such as arsenopyrite, scorodite, goethite and ferrihydrite under both anaerobic and aerobic conditions.

It was further observed that Fe^{2+} consistently increased during reducing periods and decreased during oxidizing conditions. The implication of this is that during reductive dissolution, any As sorbed or co-precipitated with Fe mineral will be made loose and thus becomes mobilised for polluting groundwater. This hypothesis was further demonstrated by the Fe/As ratio (see chapter 4; Fig. 4.6), where lower values were realised under reducing conditions and higher values were detected under oxidising conditions. Lower values of Fe/As during reducing periods thus imply possible migration of As into watercourses during flooding commonly created by high rainfall events in tropical humid climates.

When the contaminated mining fields are drained of water and/or the floods, Fe/As values increase, As consequently becomes precipitated/co-precipitated again due to reintroduction of oxygen which oxidises Fe. In conclusion, remediation measures to reduce As mobilisation and associated ecological impacts should aim at limiting situations that create anaerobic conditions in the mining fields. For instance, vegetation cover or revegetation of the mining sites may improve organic matter of the field, improve the soil structure, conserve soil moisture, reduce surface runoff, encourage soil microbial activities, thus create oxidising conditions, and consequently may limit As mobilisation and curtail its associated health risks.

Various soil remediation options exist for reducing As bioavailability and thus limiting its consequent environmental and human health risks, and in chapter five, I explored the potential of biochar, compost, iron oxide, manure, and NPK fertilizer to lessen bioavailability of As and to improve soil quality of the degraded mining site. These amendments are readily available and possess properties that make it possible to be used for remediation of contaminated sites (see for e.g., Hou et al., 2020; Palansooriya et al., 2020; Wang et al., 2021). The amendments were each applied at different rates- lowest (0.5%), moderate (2%), and highest (5%); and NPK at 0.1, 0.2, and 5.0 g/kg. The non-specifically (readily bioavailable)- and specifically- sorbed As were extracted in sequence. Additionally, soil available P, total C and N, dissolved organic carbon, soil soluble anions, and exchangeable cations were extracted after 1-day and 28-day incubation periods. As discussed in chapter 2 (see sections 2.3.4), the non-specific and specific-sorbed fractions of As represent the most mobile fractions and they are easily available for causing pollution due to changing environmental conditions.

The most promising soil amendment was iron oxides, which highest dose application drastically reduced the readily bioavailable As by 93% (see Table 5.3 and Fig. 5.3). The reduction in As bioavailable by iron oxides was attributed to sorption effect. In this regard, the presence of positive charges on the surfaces of iron oxides increases its binding and sorption strength, and thus reduces As availability. The iron oxides used in the experiments contained greater percentages of Fe, Si, Ca, Al, Mg, and K (see Table 5.1 and section 5.2.2); these positive charges increase sorption capacity, become carriers of As and consequently reduce As mobility. Iron oxides may also reduce As availability through the process of co-precipitation (Yang et al., 2022). However, the stability of FeO highly depends on the pH of the medium. For example, under high pH media, there is reduction in positive charges and increase in negative charges due to production of OH^- and CO_3^{2-}; and there is deprotonation of Fe due to loss of protons. In this regard, Lindsay et al. (2015) reported that under moderately acidic to circumneutral pH conditions, the mobility of dissolved oxyanions such as $H_2AsO_4^-$ is restricted due to sorption onto positively charged mineral surfaces.

These findings have implications in the remediation of As in Fe-As bearing dominated mining tailings and spoils. Acid mine drainage (AMD), for instance, is a common ecological hazard that occurs from gold mine fields. This process creates oxidative dissolution of FeAsS and releases As into the environment, causes soil acidity and increases the concentration of Fe. The decrease in soil pH during this process causes negative ions such as carbonates to be depleted; and thus reduces the acid neutralization capacity (Lindsay et al., 2015). Lindsay et al. (2015) reported that AMD develops in mine deposits where the neutralization capacity of carbonate minerals is depleted. In contrast, neutral mine drainage (NMD) occurs in mine deposits where carbonate dissolution efficiently counterbalances acid generated by sulfide oxidation. Such spoils are concomitantly characterized by high concentration of weakly hydrolyzing substances including Fe(II) and As (see Lindsay et al., 2015; and this has been elaborated in detail in chapter 4).

Thus, application of FeO is affected by pH and changes may consequently reduce or increase mobility of As. Mitigating As bioavailability in the mine sites with Fe and reducing ecological pollution may be achieved in acidic range. Neutral to alkaline conditions may be encouraged to enhance bioavailability for phytoextraction. This observation is confirmed by Mamindy-Pajany et al. (2011), when they reported that As adsorption by FeO is effective at lower pH. I conclude that iron-rich materials can be used to reduce As bioavailability and mitigate the associated environmental and human health risk in the mining spoils. However, biochar, compost, manure, and the inorganic fertilizer increased the bioavailability of As, which indicates that these amendments may increase the risk of As but can be used to enhance phytoextraction efficiency of As in the gold mining spoil.

6.2 Final conclusions and recommendations

This study was conducted to explore the mobilisation of heavy metals and metalloids in gold mine sites in Ghana, their dominant species and associated soil and human health risks. Additionally, options for remediation of the mining spoils were investigated. It was observed that the gold mining sites, active and abandoned, were severely contaminated with As, with a total content ranged from 1,807 - 8,407 mg/kg; the extent of contamination was higher in the abandoned site than the active one. Arsenic was associated with the amorphous Fe oxide and the residual/sulphide components; this suggests that solubility of As in the contaminated sites is controlled by content of amorphous iron oxides and sulphides. These findings confirm the dominant As species in the mining sites, which were mainly arsenopyrite- the primary mineral and scorodite- the secondary mineral. These two As species are mainly sulphide As ores which weathering, and breakdown coupled with abandonment, poor handling and processing may exacerbate ecosystem pollution with As (see sections 1.2.1.1 and 1.33 in chapter 1; Fig. 1.3 and equations 1.1 and 1.2).

High As total contents, dominant species, high mobile and potential mobile fractions in the bulk soil, coarse and fine fractions demonstrate their ability to increase their ecotoxicological threats to plants and the surrounding ecosystem. There is the potential of As to leach down the profile to existing groundwater due to probable changes in soil redox potential and pH. Furthermore, the human wellbeing valuation showed that even though all the mine sites posed health danger, the abandoned mine spoil posed highest danger to residents in the mining area.

These risks may be exacerbated under changing conditions of pH, redox potential, dissolved organic matter, sulphur, aluminium/iron/manganese and soluble anions such as chlorides, carbonates, phosphates, sulphates, and nitrates. For instance, chlorides and other soluble anions (e.g., P) will increase the negative charges, reduce positive charges, and displace As from the soil colloid and facilitate its availability. This was evident in the manure and compost amended soils (chapter 5), where As availability was enhanced in such treated soils. Therefore, remediation measures should be taken to reduce migration of As into watercourses, offer protection against pollution of nearby communities, to restore soil quality of the sites and to ultimately protect human health.

In conclusion, local plants (e.g., *Chromolaena odorata* and *Pityrogramma calomelanos*) can be considered to clean As from the spoils and the polluted sites. Remediation efforts can make use of C, P-rich and alkaline materials to boost the As phytoremediation effectiveness of the plants. Also, Fe-rich materials can be employed to decrease the bioavailability of As, to reduce losses and migration into surface and groundwater and mitigate the potential associated environmental and human health risks. Such remediation efforts should take into consideration the wet and dry conditions prevailing at the contaminated sites. More precisely, options should limit anaerobic conditions and encourage aerobic conditions at the site. This cautious plan will thus reduce the pH, raise the redox potential, and consequently restrict As mobilisation from the mine spoil.

6.3 Future research recommendations

The following recommendations are made for future research considerations:

i. Future research should investigate in detail the roles of biogeochemical parameters such as organic matter content, content of Fe, content of Si and content of S could affect mobilisation of As in the mining sites.
ii. There is the need to conduct comprehensive pot and field experiments on native plant species to upscale their full potential and applicability for remediation of mine sites. The efficiency of *Chromolaena odorata*, *Pityrogramma calomelanos* and other indigenous plants inhabiting the mining areas could be investigated in detail.
iii. There is the need to explore field application of varying redox conditions on As release from the mine spoil. The mobilisation and dominant species of As in the subsoils as affected by varying redox environments can be investigated. Further, various remediation options and impacts on As mobilisation under different redox environments should be explored.
iv. A large-scale field remediation experiment involving the use of organic and inorganic materials will better help to appraise the long-term applicability of such treatments on As mobilization.
v. Synchrotron radiation X-ray spectroscopy may be employed in the future to investigate the dominant species of As in the abandoned mining spoil as impacted by various soil remediation efforts.
vi. Further investigation could be conducted on food crops, surface and groundwater, plants in the mining area. This will aid to assess the extent of pollution in the mining region.

References

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Duker, A. A., Carranza, E. J. M., & Hale, M. (2004). Spatial dependency of Buruli ulcer prevalence on arsenic-enriched domains in Amansie West District, Ghana: Implications for arsenic mediation in Mycobacterium ulcerans infection. *International Journal of Health Geographics*, *3*, 1–11. https://doi.org/10.1183/1476-072X-3-19

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CURRICULUM VITAE

Albert Kobina Mensah

(M.Sc., Kenya; B.Sc., Ghana)

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Google Scholar: https://scholar.google.de/citations?user=wJmx7UkAAAAJ&hl=en
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RESEARCH FOCUS

Soil science; soil chemistry, soil trace elements; soil potentially toxic elements and remediation; phytoremediation; environmental risk assessment; redox chemistry of potentially toxic elements; artisanal and small-scale mining sustainability

PRESENT POSITION

Doctoral Researcher: Ruhr-Universität Bochum, Institute of Geography, Soil Science/Soil Ecology Department, Universitaetsstr. 150, 44801 Bochum, Germany.

PREVIOUS ACADEMIC POSITIONS

- Course Tutor, Department of Soil Science/Soil Ecology, Ruhr-Universität Bochum, Germany (April 2019 – August 2020).
- Research Stay, Department of Soil Science, University of Cape Coast, Cape Coast (Ghana) (March 2016 – March 2017)
- Science Tutor, Holy Child School (Ghana Education Service), Cape Coast, Ghana (September 2012 – September 2013)
- Teaching Assistant, Department of Soil Science, University of Cape Coast, Cape Coast (Ghana) (October 2011 – August 2012)
- Chemistry Teaching Assistant, Prestea Senior High Technical School, Ghana (May 2010 - July 2010).
- English and Agricultural Science Teacher, Prestea Islamic Junior High School, Ghana (October 2005 - July 2007).

EDUCATION

- PhD Fellow (Environmental soil science), Ruhr University Bochum, Bochum (Germany). October 2017 – December 2021.
- German as a Foreign Language, Carls Duisberg Centre, Cologne, Germany. April 01 – September 2017
- Master of Science (Water resources/watershed management), Kenyatta University, Nairobi (Kenya). September 2013 – July 2016
- Bachelor of Science (Agricultural Science). University of Cape Coast, Cape Coast, Ghana. August 2007 – May 2011
- Senior Secondary School Certificate (SSSCE). Prestea Secondary Technical School, Prestea, Ghana. September 2001 – July 2004
- Basic School Certificate Examinations (BECE). Prestea Anglican Basic School, Prestea, Ghana. 1992 – 2001

TEACHING, RESEARCH AND PROFESSIONAL EXPERIENCE

- **Doctoral/PhD Researcher, Department of Soil Science/Soil Ecology, Ruhr-Universität Bochum, Germany (October 2017 – present).**
  - Researches into spatial distribution of potentially toxic elements in mining tailings and spoils from mining communities in Ghana.
  - Runs experiments on various factors such as redox chemistry as a factor of arsenic mobilisation using the novel redox automated microcosm experiments.
  - Runs various laboratory, incubation studies and pot experiments on remediation of arsenic-contaminated gold mining spoils and tailings
  - Runs experiments on various green soil amendments for remediation of arsenic in a contaminated gold mining sites.
  - Involved in writing and preparation of manuscripts of scientific research findings for publication in very high impacts journals
  - Involved in data manipulation and rigorous statistical analyses of data
  - Involved in proposal development for soliciting for research grants and funding
  - Successfully run and executed doctoral research project, and independently wrote and published a high quality and standard doctoral dissertation for assessment and for the award of PhD degree.
  - Presented papers and gave oral presentations at international conferences, internal faculty, and departmental colloquium.

- **Course Tutor, Institute of Geography, Ruhr-Universität Bochum, Germany (April 2019 – August 2020).**
  - Designed and lectured university course in mining and water resources in Africa (mining and environmental protection in Africa) for the faculty.
  - Initiated the development of the new course curriculum, including student learning objectives for mining and water resources in Africa/mining and environmental protection in Africa
  - Supervised students' semester term papers

- **Research stay, Department of Soil Science, University of Cape Coast, Cape Coast, Ghana (March 2016 – March 2017)**
  - Supervised field workers and enumerators in land preparation, data collection, and setting up experimental field
  - Designed and supervised field and pot experiment works
  - Researched and taught soil science courses for undergraduate students
  - Prepared proposal for research funding
  - Prepared periodic field project reports
  - Prepared and drafted manuscript for publication
  - Supervised students' projects and research theses

- **Science Tutor, Holy Child School (Ghana Education Service), Cape Coast, Ghana (September 2012 – September 2013)**
  - Taught Integrated Science (Agricultural Science) to forms 1 and 2
  - Set quiz, mid-semester, and end of year examination questions, marked, and provided grades to the students
  - Served as an assistant examiner for West Africa Secondary School Certificate Examinations Integrated Science Paper III for two years
  - Took the students through practical agricultural science sessions
  - Attended workshops and conferences on integrated science for the school
  - Provided career guidance to the students

- **Teaching Assistant (National Service), Department of Soil Science, University of Cape Coast, Cape Coast, Ghana (October 2011 – August 2012)**
    - Organized tutorials for undergraduate students in agricultural and biological sciences in soil science (soil chemistry, soil and water engineering, problem soils, soil management, irrigation, and drainage engineering)
    - Conducted research on soil, land use, environmental sciences, and plant losses
    - Handled lectures at times and invigilated undergraduates' exams
    - Supervised undergraduate students' dissertations
    - Helped lecturers with research activities for their consultancy services
    - Monitored soil erosion at prone zones
    - Advised farmers on water and soil conservation measures

- **Internship, Environmental Department, Prestea Sankofa Gold Limited, Prestea, Ghana (June 2010 – August 2010)**
    - Carried out water sampling from mining catchment areas to assess and monitor the effects of gold mining activities on water quality in the surrounding villages/communities.
    - Ensured environmental compliance by employees
    - Wrote and reviewed environmental reports
    - Monitored rehabilitation of degraded gold mined lands of the company
    - Carried out desktop research and made recommendation on some plant species for gold mined soil fertility remediation and restoration (E.g., Vetiver grass, Leucaena, Acacia sp., etc.)
    - Supervised filling/control of gullies created around tailings dam to aid avoid collapse of the dam
    - Carried out tailings dam maintenance to avoid spillage and pollution of surrounding environment.
    - Supervised planting of cover grasses, legumes, and trees around the tailings dam to help conserve moisture and to prevent water erosion around the dam, to prevent spillage, etc.

- **Internship, Environmental Protection Agency, Tarkwa (Ghana) (June 2009 – August 2009)**
    - Formed part of the team to educate the public on environmental conservation.
    - Assisted in carrying out environmental audit and report writing.
    - Reviewed environmental reports submitted by the mining companies
    - Carried out water quality assessment from mining catchment areas.
    - Carried out field and desktop research on reclamation of degraded gold mined soils for the agency
    - Conducted field monitoring and supervision of degraded mined lands under rehabilitation by the mining companies in the district.
    - Monitored small scale mining sites to assess the measures put in place for environmental management before granting them environmental permit for full operation.

PEER-REVIEWED PUBLICATIONS

- **Mensah, A. K.**, Marschner, B., Antoniadis, V., Stemn, 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. *Science of The Total Environment*, 798, 149272
- **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. *Environmental Pollution*, 261, 114116.
- Owusu, O., Bansah, K. J., & **Mensah, A. K.** (2019). “Small in size, but big in impact”: socio-environmental reforms for sustainable artisanal and small-scale mining. *Journal of Sustainable Mining*, 18(1), 38-44.

- **Mensah, A. K.,** & Frimpong, K. A. (2018). Biochar and/or compost applications improve soil properties, growth, and yield of maize grown in acidic rainforest and coastal savannah soils in Ghana. *International Journal of Agronomy*.
- Owusu, O., Wireko, I., & **Mensah, A. K.** (2016). The performance of the mining sector in Ghana: A decomposition analysis of the relative contribution of price and output to revenue growth. *Resources Policy*, *50*, 214-223.
- Kakaire, J., **Mensah, A. K.,** & Menya, E. (2016). Factors affecting adoption of mulching in Kibaale sub-catchment, South Central Uganda. *International Journal of Sustainable Agricultural Management and Informatics*, *2*(1), 19-39.
- **Mensah, A. K.** (2015). Role of revegetation in restoring fertility of degraded mined soils in Ghana. A review. *International Journal of Biodiversity and Conservation*, 7(2): 57-80.
- **Mensah, A. K.,** Mahiri I. O., Owusu, O. Mireku, D. O., Wireko I. and Appiah, K. E. (2015). Environmental impacts of mining: a study of mining communities in Ghana. *Applied Ecology and Environmental Sciences*, 3(3): 81-94.
- Kakaire, J., Makokha, G. L, Mwanjalolo, M., **Mensah A. K**., and Menya, E. (2015). Effects of mulching on soil hydro-physical properties in Kibaale sub-catchment, South Central Uganda. *Applied Ecology and Environmental Sciences,* 3 (5): 127-135
- **Mensah, A. K.**, Kissi, E. A., Krah, K., & Mireku, O. D. (2015). The extent of groundwater use for domestic and irrigation activities in Thiririka sub-catchment, Gatundu South District, Kiambu County, Kenya. *African Journal of Environmental Science and Technology*, *9*(6), 519-530.

PUBLISHED ABSTRACTS

- **Mensah, A. K.,** Marschner, B., Shaheen, S. M., and Rinklebe, J. (2021). Compost and manure addition enhanced arsenic phytostabilization potential of ryegrass grown in a contaminated gold mine spoil. ASA, CSSA, SSSA International Annual Meeting, Salt Lake City, UT. https://scisoc.confex.com/scisoc/2021am/meetingapp.cgi/Paper/133911
- **Mensah, A. K.,** Marschner, B., Wang, J., Shaheen, S. M., and Rinklebe, J. (2020). Mobilization, release, and speciation of arsenic in an As-contaminated gold mine spoil under varied soil redox conditions, EGU General Assembly 2020, Online, 4–8 May 2020, EGU2020-1360, https://doi.org/10.5194/egusphere-egu2020-1360
- **Mensah, A. K**., Marschner, B., Shaheen, S. M., Wang, J., & Rinklebe, J. (2019). Mobilisation and release of arsenic from an arsenic-contaminated gold mine spoil under varied soil redox conditions. Available at: https://scisoc.confex.com/scisoc/2019am/meetingapp.cgi/Paper/119005. ASA-CSSA-SSSA International Annual Meeting 2019| Nov. 10-13| San Antonio, Texas.

RESEARCH PAPERS IN REVIEW

- **Mensah, A. K.,** Marschner, B., Shaheen, S. M., and Rinklebe, J. (2021). Biochar, compost, iron oxide, manure, and inorganic fertilizer affect the bioavailability of arsenic and soil quality of an abandoned arsenic-contaminated gold mine spoil (revised manuscript re-submitted to the journal of *Ecotoxicology and Environmental Safety*).
- **Mensah**, A. K., Bansah, K. J., and Tuokuu, X. F. D. (2021). Informal artisanal mining and the military: perspectives on the use of armed security forces to 'hunt' informal miners in Ghana (under review in *Africa Geographical Reviews*).

MANUSCRIPTS IN PREPARATION

- **Mensah. A. K**, Marschner, B., Wang, J., Bundschuh, J., Shan-Li Wang, S. L., Yang, P. T., Shaheen, S.., Rinklebe (2021). Mobilisation and speciation of arsenic in an abandoned arsenic-contaminated gold mine spoil under reducing and oxidising conditions (Ready for submission in the *Journal of Hazardous Materials*).
- **Mensah, A. K.,** Marschner, B., Shaheen, S. M., and Rinklebe, J. (2021). Compost and manure

addition enhanced arsenic phytostabilization potential of ryegrass grown in a contaminated gold mining spoil

RESEARCH DISSERTATIONS AND THESES

Doctor of Philosophy (PhD):	*Arsenic contamination and remediation of active and abandoned gold mining spoils in Ghana*. Institute of Geography, Department of Soil Science and Soil Ecology, **Ruhr-Universität Bochum, Germany.** Defended on the 21 December 2021
Master of Science (M.Sc.):	*Effects of Eucalyptus sp. plantation on soil physico-chemical properties in Thiririka Sub-catchment, Kiambu County, Kenya*. Department of Geography, **Kenyatta University, Nairobi, Kenya.** February 2016.
Bachelor of Science (B.Sc.):	*Can revegetation restore fertility of degraded mined soils? A Review.* Department of Soil Science, **University of Cape Coast, Cape Coast, Ghana.** May 2011.

EVIDENCE OF RESEARCH QUALITY, IMPACT AND VISIBILITY

- **Google Scholar citation matrix since 2016** across 20 research items as of December 29, 2021:
    - *Total citations:* ***377***
    - *H-index:* ***6***
    - *i10-index:* ***6***
    - *Available at:* *https://scholar.google.de/citations?user=wJmx7UkAAAAJ&hl=en*

- **ResearchGate matrix** across 20 research items as of December 29, 2021:
    - *RG Score:* ***11.78***
    - *Total research interest:* ***455.2***
    - *Total citations:* ***323***
    - *Total recommendations:* ***85***
    - *Total reads:* ***41,732***
    - *Available at:* *https://www.researchgate.net/profile/Albert_Kobina_Mensah*

HONOURS, AWARDS AND GRANTS

- **Young Future Leadership Award as early career young scientist making outstanding contribution to agriculture** at the West African Forum on Precision Agriculture organised by the African Plant Nutrition Institute at the University of Cape Coast in Ghana. 11 - 12 February 2020.
- **GERMAN ACADEMIC EXCHANGE SERVICE (DAAD) In-Region Scholarship** for Master of Science (IWM) Studies at Kenyatta University, Nairobi, Kenya. 2013 – 2015.
- **GERMAN ACADEMIC EXCHANGE SERVICE (DAAD) – GOVERNMENT OF GHANA research scholarship grant** for PhD training at Ruhr University, Bochum, Germany. 2017-2021
- **Association of African Universities (AAU) six months graduate internship grant.** University of Cape Coast, Ghana. July 2016 – March 2017.
- **Best Graduating Student 2004.** Prestea Senior Secondary Technical School, Ghana.

PRESENTATIONS AT INTERNATIONAL CONFERENCES AND MEETINGS

- ASA, CSSA, SSSA International Annual Meeting conference on the theme: "*A Creative Economy for Sustainable Development*", Salt Lake City, Utah, USA. November 7 – 10, 2021.
  Oral Paper Presented: **Mensah, A. K.,** Marschner, B., Shaheen, S. M., and Rinklebe, J. (2021). Compost and manure addition improved arsenic phytostabilization potential of ryegrass grown in a contaminated gold mine spoil. Available at: https://scisoc.confex.com/scisoc/2021am/meetingapp.cgi/Paper/133911
- DAAD Scholarship Holders Meeting in Ruhr University Bochum, Germany.

  Public Lecture Delivered: From Nairobi to Deutschland: 6 Years of Being a DAAD Scholar!

- DAAD Alumni workshop in Accra- “Contemporary Healthcare Issues in Sub-Saharan Africa- Economic, Social and Cultural Perspective” held on November 25 and 26, 2019.

  Abstract accepted for oral presentation: **Mensah, A. K.**, Marschner, B., Shaheen, S. M., Wang, J., Wang, S. L., & Rinklebe, J. (2019). Arsenic in highly contaminated abandoned and active gold mine spoils in Ghana: geochemical fractionation, and assessment of potential environmental and human health risks.
- First Joint Meeting on Soil and Plant System Sciences (SPSS 2019). Natural and Human-induced Impacts on the Critical Zone and Food Production, Bari, Italy. 23-26 September 2019. Available at: https://spss2019.azuleon.org/welcome.php

  Oral Paper Presented: **Albert Kobina Mensah**, B. Marschner, S. M. Shaheen, J. Rinklebe (2019). Arsenic in an abandoned gold mine spoil in Ghana: effects of pH, geochemical fractionation, and potential mobilisation.
- British Soil Science Society Annual Meeting Conference on the theme: *“Managing soil resources to secure our future”,* Sheffield, United Kingdom. 4-5 September 2019. Available at: https://www.soils.org.uk/event/1674.

  Oral Paper Presented: **Albert Kobina Mensah**, B. Marschner, S.M. Shaheen, J. Rinklebe (2019). Arsenic in highly contaminated gold mine spoils in Ghana: geochemical fractionation, potential mobilization, and risk assessment.
- Research Day organised by Research School at the Ruhr University Bochum on “Requirements and Attitudes for a Successful Research Career”. Venue: Ruhr University Bochum, Germany. February 28, 2019.

  Poster Paper Presented: **Mensah**, **A. K.,** and Marschner, B. (2019). Arsenic contamination, binding forms and factors influencing mobility and release.
- DAAD Scholarship Holders Meeting in Cologne, Germany. 8 – 10th June 2018.

  Public Lecture Delivered: Arsenic: a silent soil and environmental health threat from gold mining in Ghana. Available on page 11 at: https://www.daad.de/medien/der-daad/presse/downloads/programmheft_stipendiatentreffen_k%C3%B6ln.pdf
- Selected as a Right Livelihood Junior Scientist. Presented and participated in the workshop “Mobilization for Change: Human Rights, Governance and the Empowerment of the Marginalised”, Bonn, Germany. September 2 – 7th 2017.

  Poster Paper Presented: **Mensah**, **A. K** (2017). Effects of biochar and compost application on soil properties, growth and yield of maize grown in acidic rainforest and coastal savannah soils in Ghana. Available at: https://rlc-blog.org/?p=1491
- An Interaction Between Iowa State University, USA and Soil Science Department of the University of Cape Coast at Academic Board Chamber, University of Cape Coast, Ghana. May 25, 2012.

  Oral Paper Presented: *Soil and Water Quality Assessment in Ghana.*

CONFERENCES/SEMINARS/WORKSHOPS

- Participant, 1st Phy2SUDOE Workshop - Phytomanagement for Soil Remediation and the Creation of Value", organized by the Faculty of Biotechnology of Universidade Católica Portuguesa - Porto, under the Interreg SUDOE project "Phy2SUDOE - Advancing in the Application of Innovative Phytomanagement Strategies in Polluted Sites in Southwest Europe". Held online on July 8, 2021, from 9.00 am to 13.00 pm CEST. Available at: https://www.youtube.com/watch?v=NPoP_XMRHAM&t=2869s
- West African Forum on Precision Agriculture organised by the African Plant Nutrition Institute at the University of Cape Coast in Ghana. 11 - 12 February 2020.
- Participant, Science College organised by Research School at the Ruhr University Bochum on “Building Trust in Research(ers)”. Venue: Ruhr University Bochum, Germany. 3rd July 2018.
- Orientation Seminar for DAAD-scholarship holders from Sub-Saharan Africa. Gustav-Stresemann-Institute (GSI), Bonn, Germany. 26 – 27th October 2017

- Participant, PhD Proposal Writing Workshop organized by the German Academic Exchange Service (DAAD) at Noguchi Memorial Centre for Medical Research Conference Centre, Legon, Accra, Ghana. 30 – 31 August 2016.
- Participant, Ghana Science Association 15th Biennial Workshop on "Efficient Waste and Sanitation Management for Sustainable Development: The Role of Science, Technology and Innovation. Erata Hotel-East Legon, Accra. August 3, 2016.
- One-day seminar on "Is Ghana Food Secure?" Seminar organized by CSIR-Science Technology Education and Policy Research Institute (STEPRI). STEPRI Auditorium, Accra, Ghana. June 21, 2016.
- Participant, seminar organized by CSIR-Water Research Institute at Ghana Academy of Arts and Sciences (GAAS) Conference room, Accra, Ghana. Topic: Sustainable Water Resources Management in Ghana. June 23, 2016.
- 2nd Africa Ecosystem Based Adaptation for Food Security Conference 2015. United Nations Headquarters, Nairobi, Kenya. 30 to 31st July 2015.
- Participant, Seminar organised by Soil Science Department of the University of Cape Coast, Ghana, on the topic: *Precision Agriculture- Tools, Challenges and Significance*. March 20, 2012.
- Participant, seminar organized by Department of Environmental Sciences, University of Cape Coast at Sasakawa conference room, Ghana. Topic: *The Oil Discovery; Environmental and Social Impacts*. February 24, 2010.

OTHER TRAINING AND CERTIFICATES

- Fundamentals of statistics, experimental designs, and introduction to R for Soil Scientists. Witzenhausen, Germany. March 27 – April 2019.
- Reviewing a scientific paper. Ruhr University Research School in Bochum, Germany. April 30, 2018.
- Writing a successful research proposal for a post-doc project". Ruhr University Research School in Bochum, Germany. June 26, 2018.
- Certificate in Statistical Package for Social Sciences (SPSS). Jomo Kenyatta University of Agriculture and Technology, Juja, Kenya. October 09, 2015 – November 2015
- Certificate in Participatory GIS and E-Learning. Institute for Geographical Sciences, University of Berlin, and Kenyatta University, Kimunye (Mount Kenya), Kenya. November 02 – 06, 2015.
- Certificate in Developing Lively E-Learning Materials for Integrated Watershed Management. University of Berlin (Germany) and Kenyatta University (Kenya). Thika, Kenya. October 27 - November 01, 2014.
- Certificate in E-Library Resources. German Academic Exchange Service (Nairobi) and Information Training and Outreach Centre for Africa (South Africa). Nairobi, Kenya. August 25 – 29, 2014

RESEARCH PROJECT EXPERIENCE

- ***PhD research project/fellowship at the Ruhr University Bochum, Germany (2017 – 2021).*** This 4-year project was funded by the Ruhr University Bochum in Germany, Government of Ghana and German Academic Exchange Service. I independently planned and successfully executed a PhD project on contamination of potentially toxic elements in gold mine polluted sites, and green and sustainable remediation options. The project resulted in publishing of six quality research papers in highly ranked journals and compiling of a 232-paged doctoral dissertation for assessment and the award of a Doctor of Philosophy.

- ***Artisanal and small-scale mining (ASM) sustainability/use of the military and armed security men against informal miners in Ghana (2018 – 2021).***

This project investigated the contributions of the informal mining sector in Ghana to gold mining revenues in Ghana as well as sustainable options for ensuring a cleaner ASM. The project was personally funded, and it was a collaboration between Dr. Obed Owusu (University of Dalhousie, Canada), Dr. Kenneth Bansah (Missouri University of Mines and Technology, USA) and me. Additionally, we also appraised the sustainability of the military interventions and mining enactments instituted by Governments of Ghana since 1980 to 2021 against informal miners. Parts of results were published in 2019 in the *Journal of Sustainable Mining*.

- ***Impacts of biochar and compost applications on soil properties, growth, and yield of maize in acidic rainforest and coastal savannah soils in Ghana (2016 – 2017).***
  This project was funded by the Association of African Universities (AAU) six months graduate internship grant. This six-month project was executed at the department of soil sciences and technology village at the University of Cape Coast, Ghana. The project was executed successfully, and the results were published in 2018 in the *International Journal of Agronomy*.

COURSE DEVELOPED

- **Course 170077: Mining and Water Resources/Environmental Protection in Africa (Summer Semesters 2019 and 2020).** Institute of Geography, Ruhr University Bochum, Germany. Available at: https://moodle.ruhr-uni-bochum.de/course/view.php?id=27126**.** The course exposed students to the concepts of environmental sustainability in Africa. Specifically, it focused on introducing to students, issues of mining and environmental protection in Africa. It also discussed with students the various options available for solving environmental problems from mining activities in Africa and improving livelihoods of people in mining communities. Teaching modes involved lecture, short assignments, tutorials, videos, short films, and presentations.

PEER REVIEW AND EDITORIAL ACTIVITIES

- Journal: *Science of The Total Environment* (Article ID: STOTEN-D-21-19164)
  Article type: Research Paper
  Article title: Accumulation risk of potentially toxic elements through the soil-tobacco-human pathway: Causative factors, novel probabilistic models, and soil thresholds
  Date invited: August 20, 2021
  Date due for review submission: September 10, 2021
  Review submitted: September 12, 2021

- Journal: *Agronomy* (Article ID: Agronomy-1363188)
  Article type: Research Paper
  Article title: Presence of metals and metalloids in the environment of east Croatia as possible post-war consequence
  Date due for review submission: September 3, 2021
  Date invited: August 20, 2021
  Date summitted: September 4, 2021

- Journal: *African Geographical Review* (Article ID: RAFG-2020-0088)
  Article type: Commentary
  Article title: Risk-based Contaminated Land Management Policy mindset: A way out for Ghana’s Environmental Challenges
  Date due for review submission: 24-Nov-2020; 2nd round review due on 04-Jan-2021
  Date invited: October 25, 2020; 2nd invite on the 05-Dec-2020
  Date summitted: November 23, 2020; 2nd round submission on 30-Dec-2020

- Journal: *Ecological Engineering* (Article ID: ECOLENG-D-18-01069)

Article type: Research paper
Article title: Biological traits beneficial for restoration on soils with elevated concentrations of copper- a study of native trees on mine tailings in Zambia
Date due for review submission: Oct 10, 2018; 2nd round review due on March 23, 2019.
Date invited: Sep 19, 2018; 2nd invite on the March 2, 2019
Date summitted: 9th October 2018; 2nd round revision submitted on the March 23, 2019.

MEDIA ENGAGEMENTS/APPEARANCE/COMMUNITY OUREACH

- **Guest Speaker** at the joint Centre for Better Society Advocacy and Research Africa (CEBSAR-AFRICA) and Migrant Media Network (MMN) Virtual Seminar on sustainable alternatives to irregular migration. August 28, 2021. Topic delivered: Sustainable artisanal mining as a possible panacea to irregular migration.
- **E.TV Fact Sheet with Samuel Eshun** on Tuesday June 1, 2021, at 8pm GMT. Discussion: Galamsey fight: operation halt II; burning of excavators; the law and way forward.
- **Homebase TV Evening News with RSM Kofi Doe Lawson** on Friday February 7, 2020, at 5.30 – 7.00pm GMT. Discussion: Building a prosperous society for all in Ghana.
- **Guest Panel on Star Radio UK Faith Talk** on Sunday May 02, 2021, at 5pm GMT. Discussion: The church, national politics, and the community: focus on Ghana.
- **Guest Panel on CEBSAR TALK** with Evans Appiah Kissi on Saturday May 1, 2021, at 4pm GMT. Discussion: Is small-scale mining in Ghana a right call?
- **Guest Panel** on TEEN leadership and entrepreneurial development foundation talk sessions on our environment our life on May 29, 2021, at 2pm GMT. Discussion: How safe is our environment in Ghana?
- **Guest Panel** on Teen leadership and entrepreneurial development foundation talk sessions on STEM careers on the March 27, 2021, at 5pm GMT. Discussion: Career opportunities in soil and environmental sciences.
- **Guest Panel on CEBSAR TALK** with Dr. Evans Appiah Kissi on Saturday January 16, 2021, at 4pm GMT. Discussion: One on one with the founding president of CEBSAR-AFRICA.
- **Institute for Liberty and Policy Innovation Ghana 20 minutes with AK Mensah** on Friday May 8, 2020, at 19.00 GMT. Theme delivered: Covid-19 pandemic: galamsey on the rise, military taskforce not the solution.
- **Guest Speaker at CEBSAR-AFRICA 1st Public Lecture with Dr. Abu Sakara Foster** at the University of Cape Coast Sasakawa conference room, Saturday February 15, 2020. Theme: Building a prosperous society for all, not few.
- **Guest Panel on CEBSAR TALK** with Dr. Evans Appiah Kissi on Saturday December 5, 2020, at 4pm GMT. Discussion: Ghana Elections 2020.
- **Guest Panel on CEBSAR TALK** with Dr. Evans Appiah Kissi on Saturday September 12, 2020, at 3pm GMT. Discussion: Could artisanal and small-scale mining be the future of Ghana's mining sector?
- **Guest Panel on CEBSAR TALK** with Dr. Evans Appiah Kissi on Saturday September 5, 2020, at 3 pm GMT. Discussion: Is mineral mining in Africa a blessing or a curse?
- **Guest Speaker**, 3-day African Journalists for Economic Opportunity Training organised by Institute for Liberty and Policy Innovation Ghana (ILAPI-GHANA). July 12 – 15, 2019. Topic delivered: Sustainability in the mining sector in Africa
- **Main Speaker,** Centre for Better Society Advocacy and Research Africa 1st Public Lecture at the J. N. Aryeetey Auditorium-South Campus University of Education Winneba, Ghana. Date: Saturday March 17, 2018, 10am. Theme: Building a better society in Ghana: need for paradigm shifts.
- **Association of African Universities TV Talks with Paa Kwesi Acquah** on Thursday June 21, 2018, at 11am GMT. Discussion: Biochar and compost application for improve crop yield.

PROFESSIONAL ORGANISATIONS/GROUPS

- DAAD Scholars Ghana Alumni
- DAAD Scholars IWM Alumni

- Ecosystem Based Adaptation Approaches to Food Security (EBAFOSA) – GHANA
- American Soil Science Society (SSSA)
- Soil Science Society of Ghana (SSSG)
- Centre for Better Society Advocacy and Research Africa (CEBSAR-AFRICA)
- Institute for Liberty and Policy Innovation Ghana (ILAPI-GHANA)

POSITIONS HELD

- **Founding President,** Centre for Better Society Advocacy and Research Africa (CEBSAR-AFRICA) (2018 – date)
- **Second Vice President,** Institute for Liberty and Policy Innovation Ghana (ILAPI-GHANA) (2017 – date)

LANGUAGES SPOKEN

- English (native speaker)
- Deutsch (medium proficiency)
- Twi (Akan) (mother tongue)

REFEREES

- Prof. Dr. Bernd Marschner
  Ruhr-Universität Bochum Germany
  Head of Soil Science/Soil Ecology Dept.
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- Prof. Dr. Joerg Rinklebe
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