UNIVERSITY OF CAPE COAST

STUDIES ON THE MEDIATION OF CYANIDE AND HEAVY METALS IN EFFLUENT AND TAILINGS IN A MINING ENVIRONMENT IN OBUASI, GHANA

BY

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DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my own original work and that no part of it has been presented for another degree in this university or elsewhere.

Candidate's Signature: .... Date: 08-02-2013

Name: RUFAI MAHAMA AHMED

Supervisors' Declaration

We hereby declare that the preparation and presentation of the thesis were supervised in accordance with the guidelines on supervision of thesis laid down by the University of Cape Coast.

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ABSTRACT

Mining is one of the main anthropogenic sources of metal contamination in water and soil. Soil pollution with arsenic and lead due to industrial activities is a major environmental problem. The main objective of this study was to evaluate the heavy metal- and cyanide-mediation techniques for treated effluent and soil adopted by AngloGold Ashanti, Obuasi mine.

The concentrations of heavy metals and cyanide in detoxified effluent and amended capped tailings were assessed, using the completely randomized design. The bioavailability of heavy metals in mediated tailings was also determined using *Lactuca sativa* L. as a test crop. The concentrations of As, Pb, Cu, Zn, Fe and Cd in effluent, soil, plant and tailing samples were determined using the Atomic Absorption Spectrometer.

Bacterial degradation resulted in a reduction of cyanide in treated effluent. The concentrations of As and Pb in treated effluent were above the maximum permissible limit (MPL). The capping of tailings led to As concentrations that were above the MPL. Zeolite and beringite were the most effective in the mediation of Pb and As and resulted in decreases of the water soluble fraction in uncapped tailings. The bioavailability of As in beringite-amended uncapped tailings was higher than the MPL. The Pb contents of *Lactuca sativa* L. after amendment of uncapped tailings with biochar and zeolite were also above the MPL. Bacterial degradation was probably the most efficient cyanide detoxification process.

It is recommended that long term studies be conducted to evaluate the most efficient techniques of mediating effluent and tailings.

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DEDICATION

Dedicated to my mum, Hajia Amina, my dad, Alhaji Tanko

and my sons Iliasu, Yussif & Hassan

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CHAPTER ONE

INTRODUCTION

Background to the Study

The degradation of large tracts of land by the large-scale surface mines constitutes a major threat to agriculture in the communities and their economic survival (Awudi, 2002). The increased production and consumption of the earth's raw materials, coupled with the growth of the world's population over the past twenty decades, have resulted in environmental buildup of waste products, especially heavy metals (Adriano, 2001; Zaghloul & Abou-Seeda, 2005). Heavy metal pollution of soils has become a widespread problem and often possesses serious long-term risks for cultivated soils, ecosystem and human health (Kabata-Pendias, 2001; Adriano, 2001; Zaghloul & Abou-Seeda, 2005). There is the transfer of metal pollutants to ground water, into the food chain and into the human body from the soil, which acts as an important heavy metal sink (Birke & Rauch, 2000).

Soil contamination is identified by the European Soil Strategy as one of the main threats to soil quality (European Commission, 2006a). Governmental and regional institutions are increasingly giving attention to issues of soil pollution (European Commission, 2006b). Initiatives have commenced to limit and prevent further soil degradation and to examine applicable remediation measures (Poggio, Vrscaj, Schulin, Hepperle & Marsan, 2008). The Ghana Environmental Protection Agency (GEPA) has unfortunately concentrated on monitoring the levels of heavy metals and other pollutants in water to the neglect of soil pollution in mining environments.

Zeolite, beringite and other inorganic materials reduce the levels of heavy metals in contaminated soils (Lombi, Zhao, Zhang, Sun, Fitz, Zhang & McGrath, 2002; Oste, Lexmond & Van Riemsdijk, 2002). The use of biochar is an evolving sustainable technology for restoring highly degraded tropical soils (Lehmann & Rondon, 2006). The application of biochar contributes significantly to exchangeable cation sorption and retention capacity due to its high surface area, charge density and negative surface (Liang, Lehmann, Solomon, Kinyangi, Grossman, O'Neill, Skjemstad, Theis, Luizao, Peterson & Neves, 2006).

Prospecting for gold is a major activity in Ghana and modern gold mining has occurred on a large-scale since the beginning of the twentieth century (Coutsoukis, 2004; International Council on Mining & Metals [ICMM], 2006). The mineral sector has been a major recipient of foreign direct investment (FDI) in Ghana (Organization for Economic Cooperation and Development [OECD], 2002). However, the desired environmental legislation to address the inevitable environmental impacts of mining has been less than the zeal that supported policy reforms to attract foreign investments to the mining sector (Awudi, 2002).

More than thirteen large-scale gold mines that employ cyanide heap-leach processes and capital-intensive machinery with minimal labour requirement operate in Ghana (Awudi, 2002). The extensive use of cyanide compounds in the extraction of gold and their effluents is a major source of these toxic contaminants to the environment (Patil & Paknikar, 2000;

Khodadadi, Abdolahi & Teimoury, 2005). Mining operations and waste disposal methods therefore constitute major causes of pollution by cyanide, heavy metals and other environmental problems (United States Environmental Protection Agency [USEPA], 1994a). The global economic and environmental climate has progressively changed in recent years and there is increasing pressure on mining companies to clean up toxic tailings (OECD, 2002).

In Ghana, environmental pressure groups such as Wassa Association of Communities affected by Mining (WACAM), The National Coalition on Mining (NCOM) and Third World Network-Africa (TWN-Af) have expressed concerns over the magnitude of land degradation and water pollution that occur in mining environments. In some mining communities, the spent rocks from surface mining operations deposited on agricultural lands deprive the people who are predominantly farmers of their livelihoods (WACAM, 2003). The heavy metals of sediments from waste damps and deforested lands pollute rivers that serve as main sources of drinking water during heavy rainfall (National Coalition on Mining [NCOM], 2009; Wassa Association of Communities affected by Mining [WACAM], 2003).

Arsenic concentrations up to 350 $\mu g\ L^{-1}$ has been reported to occur in stream waters affected by mining pollution in the Obuasi area of southern Ghana by Smedley (1996). Surface mining operations have resulted in stream pollution from cyanide spillages, acid mine drainage (AMD) and tailings leakages (Owusu-Koranteng, 2005). These activities have serious health implications and deprive the people in these communities access to the basic human need of good quality drinking water (Owusu-Koranteng, 2005; WACAM, 2008).

Although several detoxification processes of the effluent have evolved over the years, the methods adopted by AngloGold Ashanti at Obuasi are oxidation by hydrogen peroxide (H_2O_2) and SO_2, natural degradation by ultraviolet radiation, carbon-in-solution, photo-oxidation and the use of rotating biological contractors (RBCs) that involve bacterial degradation with *Pseudomonas* sp. (USEPA, 1994a; Opong, 2008).

Biological degradation by stimulating naturally occurring indigenous microorganisms can be less expensive than chemical methods and faster than natural attenuation. This allows for less treatment time and cost for water reuse or for discharge of effluent streams to the environment (USEPA, 1994a). Thiocyanates are removed from wastewater in the through the use of excess quantities of chlorine and alkaline media (Ho, Wang & Wan, 1990; Tan, Teo & Chin, 1985) and an increase in the rate of cyanide breakdown by 30 % requires a 20 % excess of H_2O_2 (Khodadadi et al., 2005).

Statement of the Problem

The use of chlorine and H_2O_2 is expensive with regard to the quantities of these concentrated reagents required for effective degradation of hazardous products such as cyanide (USEPA, 1994a; Khodadadi et al., 2005). Substantial quantities of sludge that contain heavy metals result after the degradation of wastewater by concentrated solutions of chlorine (Khodadadi et al., 2005).

Bacterial degradation is effective and beneficial only after exponential growth of inoculated bacteria in wastewater is maximized (Opong, 2008).

This is yet to be achieved at AngloGold Ashanti, Obuasi, since the inoculation of *Pseudomonas* sp. to detoxify effluent is at the preliminary stage and bacterial growth is yet to be optimised in the exponential phase (Opong, 2008). The natural attenuation method of photo-oxidation, through use of ultraviolet radiation, involves long periods when employed to degrade toxic components (USEPA, 1994a).

The effectiveness of the different processes used for the remediation of effluent contaminated with cyanide and heavy metals are of great significance. The seepage of pollutants of water bodies and the aerial deposition of particulate matter emissions such as As_2O_3 into soils occur in mining environments (Aubynn, 1997; Birke & Rauch, 2000; Sastre, Vicente & Lobo, 2001). The efficiency of the methods used by AngloGold Ashanti, at Obuasi, for the detoxification of mine waste water therefore needs to be assessed.

Zeolite, beringite and biochar are not used as amendments at AngloGold Ashanti, Obuasi mine, and research on the application of these amendments on Ghanaian soils is limited. The main method of remediating heavy metals contained in tailings sites at AngloGold Ashanti, Obuasi mine, is capping with lateritic soil, and growing plants such as Vetiva grass (*Vetiveria zizanioides*) and *Paspalum* sp. that are tolerant to high levels of heavy metals. The capping of tailings with laterite does not remove the contaminants from the soil/tailings (Kertulis-Tartar, Ma, Tu & Chirenje, 2006). There is therefore the need to explore effective methods of mediating heavy metal polluted sites.

Objectives

General Objective

To evaluate the heavy metal- and cyanide-remediation techniques for contaminated processed gold ore effluent and soil adopted by AngloGold Ashanti at Obuasi.

Specific Objectives

The specific objectives of the research were to:

i. Determine the levels of free cyanide, As, Pb, Cd, Zn, Fe and Cu in treated effluent and soil/tailings.

ii. Establish if mining activities result in elevated levels of cyanide and heavy metals (As, Pb, Cd, Zn, Fe and Cu) in processed gold ore effluent and soil/tailings.

iii. Assess the efficiency of four processed gold ore effluent detoxification methods used by AngloGold Ashanti at Obuasi.

iv. Evaluate the effects of zeolite, beringite and poultry manure on the concentrations of Arsenic and Lead in contaminated soil.

v. Test the remediation potential of biochar in As and Pb contaminated soil.

vi. Determine if the heavy metals (As and Pb) in lettuce grown on mediated soils/tailings are within acceptable limits.

Research Questions

i. What are the concentrations of free cyanide, As, Pb, Cd, Zn, Fe and Cu in detoxified gold ore effluent?

ii. What are the concentrations of free cyanide, As, Pb, Cd, Zn, Fe and Cu in soil/capped tailings?

iii. What are the levels of free cyanide, As, Pb, Cd, Zn, Fe and Cu in soil/tailings amended with zeolite, beringite, poultry manure and biochar?

iv. What are the concentrations of free cyanide, As, Pb, Cd, Zn, Fe and Cu in *Lactuca sativa* grown on mediated soil/tailings amended with zeolite, beringite, poultry manure and biochar?

v. What are the levels of free cyanide, As, Pb, Cd, Zn, Fe and Cu in amended soil/tailings and *Lactuca sativa* grown on mediated soil/tailings in relation to permissible limits.

Hypothesis

The hypothesis that formed the basis of the study was:

Ho: The mediation of polluted tailings and the detoxification of wastewater does not result in reduced toxicity and mobility of heavy metals that are within permissible limits.

H_A: The mediation of polluted tailings and the detoxification of wastewater will result in reduced toxicity and mobility of heavy metals that are within permissible limits.

CHAPTER TWO

LITERATURE REVIEW

Methods of Gold Mining

The two main gold mining methods are surface and underground mining (USEPA, 1994b; World Gold Council [WGC], 2006). AngloGold Ashanti at Obuasi operates an underground mine (55 %) at depths up to 1500 m, although open pit (35 %), heap leach (6 %), surface mining (4 %) also take place (AngloGold Ashanti, 2007a).

In surface mining operations, the floor of the pit is lowered in approximately 9-metre benches (WGC, 2006); holes are drilled in blastholes filled with explosive and blasted. The rock fragments from the drill holes are assayed and the grade and chemistry of the bench are tested. The wastes are discarded, while the low grade and high-grade ores are processed for gold extraction (WGC, 2006).

The methods used in underground mining are more diverse than in open pit mining. This is because the approach used must be the most cost-effective one that fits in with the configuration of the ore zones, the strength of the ore zone and the rock type. The main underground gold mining methods are cut and fill, drift and fill, block caving and long hole stoping (WGC, 2006). The underground mining methods differ due to the strength of ore-containing rock, the excavation of the undermined rock, types of tunnels or drifts created and transportation of the ore (WGC, 2006).

Beneficiation of Gold

Most ores contain valuable metals such as gold contained in a matrix of less valuable rock called gangue. The aim of ore beneficiation is to separate valuable minerals from the gangue to produce materials that have a high content of the valued mineral (USEPA, 1994b). The ore is crushed and ground into fine particles containing the mineral to be recovered and gangue residue. The separation of the particles on the basis of differences in physical or chemical properties between the ore mineral and the gangue results in a high mineral concentrate and the tailings that contain low concentration values (USEPA, 1994b).

The properties that are used as a basis for separating valuable minerals from the gangue include specific gravity, magnetic permeability, conductivity, surface tension, solubility, affinity for certain chemicals and the tendency to form metal complexes. The two most common processes used in gold contained in the milled ore are flotation and leaching (USEPA, 1994b).

Mercury and cyanide compounds are used in the mining industry to extract refined gold from the ore (OECD, 2002). Cyanide compounds have however been more extensively used in the past due to its greater efficiency in the extraction of refined gold (ICMI, 2006). The process of cyanide leaching has been used since the 1970's to efficiently beneficiate a variety of low-grade gold ores (USEPA, 1994a). The process of extracting gold from the ore is termed cyanidation (ICMI, 2006) expressed by the reaction, known as Elsner's equation as follows:

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)^-{}_2 \quad + 4OH^- \ldots\ldots\ldots\ldots (1)$$

The high affinity of cyanide for gold ensures that gold is preferentially extracted. The AngloGold Ashanti mine at Obuasi operates three gold extraction treatment plants, namely, the sulphide plant that treats ore from underground, the oxide plant processes open-pit and low grade ore and the tailings plant for material from reclamation operations (AngloGold Ashanti, 2007b).

Types and Disposal of Waste Products of Gold Mining

The main by-products in the mining industry are mine water, spent or waste rock and tailings (USEPA, 1994b; WGC, 2006). The water removed from a mine to gain or facilitate access to an ore body is known as *mine water*. Mine water originates from precipitation, flows into pits or underground workings and/or groundwater aquifers that are intercepted by the mine (WGC, 2006). Waste rock consists of non-mineralized and low-grade mineralized rock removed from above or within the ore body during extraction activities (USEPA, 1994b). In metal mining operations, tailings, which consist of crushed rock and ore after most of the target metals have been removed, are often toxic and if not contained, are harmful to the environment (USEPA, 1994b; WGC, 2006).

There are varied ways of the disposal of mine water and spent rock. However, this aspect of the review of literature concentrates on the disposal of tailings, which is the by-product of mining that is of interest in this research.

Milled tailings are the by-product of mineral processing operations that require disposal (USEPA, 1994b; WGC, 2006). The disposal of slurry tailings in impoundments is the most common and economical method of disposal, because tailings produced by mills are usually in slurry form. There are four main types of slurry impoundment layouts, namely valley impoundments, ring dikes, in-pit impoundments, and specially-dug pits (Ritcey, 1989). The impoundment design choice is primarily dependent upon natural topography, site conditions, and economic factors (USEPA, 1994b).

The impounded water decanted from tailings ponds is recycled to the mill for reuse in beneficiation processes. Two methods are generally available for decanting pond water, namely decant towers and pumping. Tailings dewatered to less than 18 % moisture placed underground as backfill in underground mines (WGC, 2006). Dry disposal methods can be prohibitively expensive due to additional equipment and energy costs. However, the advantages of dry disposal include minimizing seepage volumes, land needed for an impoundment or pile and the ability to conduct simultaneous tailings deposition and reclamation (USEPA, 1994b).

Effects of Chemicals and By-products of Gold Ore Processing on Man and the Environment

Cyanide

Cyanide salts used in gold ore processing result in the production of hydrogen cyanide and cyanide ions (ICMI, 2006).

The different forms of cyanide such as hydrocyanic acid, cyanide ions, soluble cyanide salts, metal cyanide complexes, cyanates and nitriles (Ebbs, 2004) could be highly toxic even in minute quantities, depending on conditions such as pH, temperature, moisture conditions and aeration.

The effluent generated from cyanide-treated gold mining operations often contain cyanide complexes of zinc (Zn), copper (Cu) and iron (Fe), high levels of heavy metals such as arsenic (As), cadmium (Cd), mercury (Hg), lead (Pb) that are toxic and need to be treated before reuse or discharge to the environment (ICMI, 2006). Soluble salts and stable metal complexes of cyanide can dissociate into hydrocyanic acid (HCN) and cyanide ions (CN^-) that are the most labile and toxic cyanide species. The toxicity of a substance that is typically expressed as the concentration or dose that is lethal to 50 % of the exposed population (LC_{50} or LD_{50}) for HCN (g) is 0.37 to 1.11 $cmol_c\ kg^{-1}$ (ICMI, 2006).

Inhalation of gaseous HCN in this range results in death within 10 to 60 minutes, with death coming more quickly as the concentration increases (ICMI, 2006). However, initial symptoms of cyanide poisoning can occur from an exposure of 0.07 to 0.15 $cmol_c\ kg^{-1}$ of gaseous hydrogen cyanide, and may include headache, drowsiness, weak and rapid pulse, deep and rapid breathing, nausea and vomiting. Convulsions, dilated pupils, clammy skin, a weaker and more rapid pulse and slower, shallower breathing can follow these symptoms. HCN is known to cause poisoning through breathing and is easily absorbed through the skin and mucous membranes of the eyes, nose and lips. Exposure to 1.85 $cmol_c\ kg^{-1}$ of gaseous HCN immediately leads to respiratory failure while a concentration of 0.37 $cmol_c\ kg^{-1}$ is fatal for a few minutes (ICMI, 2006). Fish and aquatic invertebrates are very sensitive to cyanide exposure. The swimming performance, growth patterns, osmo-regulatory mechanisms and reproduction in many species of fish are adversely affected by the concentrations of free cyanide from 5.0 to 7.2 μg L^{-1} in aquatic environments (ICMI, 2006). Free cyanide concentrations of 20 to 76 µg L^{-1} cause the death of many aquatic species (ICMI, 2006).

Arsenic

Arsenic is the twentieth most abundant element in the earth's crust, fourteenth in sea water and is the twelfth most abundant element in the human body (Mandal and Suzuki, 2002). Arsenic is one of the most toxic elements encountered in the environment (Dermatas, Moon, Menounou, Meng and Hires, 2004; Hudson-Edwards, Houghton and Osborn, 2004). Inorganic arsenic compounds have been classified as Group I carcinogens based on human epidemiological data (International Agency for Research on Cancer [IARC], 1987).

The general symptoms of chronic arsenic poisoning include malaise, weakness, decreased appetite and substantial loss of weight and also the degeneration of the periphery of the nervous system (Mosaferi, Yunesian, Mesdaghinia, Nasseri, Mahvi and Nadim, 2005). The more specific features include the typical rain drop pigmentation of the skin and excessive thickening of the palms of the hands and soles of the feet, including the characteristic arsenic corns (Hindmarsh, 2002). Human health problems such as skin and bladder cancers and also chronic arsenic poisoning (arsenicosis) result from the drinking of arsenic-contaminated water (Choprapawon & Rodcline, 1997).

Lead

Lead affects virtually every organ and system in the body in both humans and animals. The most sensitive effects of lead are neurological, haematological and cardiovascular (Marlowe, Cossairt, Moon, Errera, MacNeel, Peak, Ray & Schroeder, 1985; Agency for Toxic Substances and Disease Registry [ATSDR], 1999a). The neurological effects include impaired cognitive ability and IQ decrements of 1to3 points in children when blood lead (PbB) increase from 10 to 20 μg dL^{-1} (Needleman & Gatsonis, 1990; Pocock, Smith & Baghurst, 1994; Schwartz, 1994; IPCS, 1995). In adult humans, slowing of conduction velocity occurs at blood lead (PbB) of ≥ 30 μg dL^{-1} while peripheral nerve function in children could be affected at a low PbB level of 3 μg dL^{-1} (ATSDR, 1999a). Lead interferes with the synthesis of heme and high levels of exposure leads to hypochromic and normacytic anaemia. Even in the absence of detectable effects on haemoglobin levels, synthesized heme adversely affects the health of children (ATSDR, 1999a). Cardiac lesions and electrocardiac abnormalities occur in humans at high levels of lead exposure. Epidemiological studies have also reported an association between increases in blood pressure and elevated PbB levels (ATSDR, 1999a). Renal damage with increased acetyl-β-D-glucosaminidase activity in urine has also been recorded in children with a mean PbB level of 34.2 μg dL^{-1} (Verberk, Willems, Verplanke & De Wolffab, 1996).

Cadmium

Cadmium is a very toxic non-essential metal that accumulates in mammalian kidneys and causes kidney dysfunction. The damage of kidneys in humans resulting from chronic exposure to cadmium is diagnosed by the presence of microglobulin proteins in urine (Alloway & Ayres, 1997). The primary route of industrial exposure is inhalation. The inhalation of fumes containing cadmium can result initially in metal fume fever but may progress to chemical pneumonitis, pulmonary edema, and death (Hayes, 2007). Studies by USEPA (1992a) and Hrudey, Chen and Rousseaux (1995) indicate that humans exposed to low levels of cadmium over time may incur kidney damage as well as lung, bone, cardiovascular system, liver, and reproductive system damage.

Communities in Japan consuming cadium-contaminated rice have been observed to develop *Itai-itai* disease and renal abnormalities, including proteinuria and glucosuria (Nogawa, Kobayashi, Okubo & Suwazono, 2004). Cadmium and several cadmium-containing compounds are known carcinogens and can induce many types of cancer (National Toxicology Program [NTP], 2008).

Chemistry of Cyanide and Heavy Metals Associated with Gold Ore Processing

The mobilisation and immobilisation of compounds is correlated to their physical and chemical properties (Adeniji, 2004). This is important in the determination of the remediation mechanisms for specific metals (Adeniji, 2004).

Cyanide

Cyanide is a singly-charged anion that has carbon and nitrogen atoms that are held by a triple bond: ($C{\equiv}N^-$). Cyanide is a strong ligand that is capable of complexing most heavy metals even if present in small concentrations (Young & Jordan, 1995). Cyanide occurs in one of three forms, namely, free cyanide in the form of Hydrocyanic acid (HCN) or Cyanide ions

(CN^-), weak acid dissociable and total cyanide (International Cyanide Management Institute [ICMI], 2006; Terry & Jack, 2007). Cyanide can be present in environmental matrices and waste streams as simple cyanides such as Hydrocyanic acid (HCN), cyanide ions (CN^-), soluble salts (NaCN, KCN, $Ca(CN)_2$), metal cyanide complexes, cyanates and nitriles (Ebbs, 2004).

Arsenic

Arsenic (As) occurs in Group V of the periodic table (ATSDR, 1999b). Arsenic exists in four oxidation states: -3, 0, +3 and +5 (ATSDR, 1999b). Arsenate (AsO_4^{3-}) and its protonation states of H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_3^- form precipitates with metal cations (Evanko and Dzombak, 1997). As (V) is the dominant form in soils under aerobic conditions (Turpeinen, Panstar-Kallio, Häggblom & Kairesalo, 2002) and is prevalent in the soil solid phase (Montperrus, Bohari, Bueno, Astrue & Astrue, 2002).

Arsenite (AsO_3^{3-}) and its protonated forms, H_3AsO_3, $H_2AsO_3^-$ and $HAsO_3^{2-}$, dominate under reducing conditions (Evanko & Dzombak, 1997). As (III) is the primary form of As that occurs in waste environments (Dermatas et al., 2004). AsO_3^{3-} can be adsorbed or co-precipitated with metal sulphides (Evanko & Dzombak, 1997). Under extreme reducing conditions, As (0) and arsine (AsH_3) may occur. Arsenic often occurs in its anionic form and does not form complexes with Cl^- and SO_4^{2-} (Evanko & Dzombak, 1997).

Arsenic (III) [H_3AsO_3] and arsenic (V) [$H_2AsO_4^-$] are strongly adsorbed to the Mn and Fe oxide-dominated soil exchange complex when pH is close to 6 and the desorption of sorbed arsenic is low even with strong pH variations (Chakravarty, Dureja, Bhattacharyya, Maity & Bhattacharjee, 2002). Inorganic As species are generally more mobile and toxic than organic forms to plants, animals and humans (Meharg & Hartley-Whitaker, 2002).

Lead

Lead (Pb) naturally exists with an oxidation state of 0 or +2. Lead (Pb^{2+}) and lead hydroxyl compounds are the stable forms of lead (Evanko & Dzombak, 1997). Lead (Pb^{2+}) is the most reactive and common form of lead and produces mononuclear and polynuclear oxides and hydroxides. Lead compounds of low solubility are formed in the presence of inorganic and organic ligands (Evanko & Dzombak, 1997). Adsorption, ion exchange, precipitation and complexation with organic matter are four mechanisms that limit the leaching of lead through surface water or groundwater (Evanko & Dzombak, 1997). Similarly, in soils, these four mechanisms are factors that lead to the high lead adsorption in soils (Evanko & Dzombak, 1997). The concentration of dissolved salts, pH and minerals affect the amounts of lead that occurs in surface and ground waters (Evanko & Dzombak, 1997).

Cadmium

Cadmium predominantly exists in the +2 oxidation state as Cd^{2+}, although rare cases of Cd^{+} may occur (Wikimedia, 2009). Relatively more stable complexes of $CdCl^{+}$ are formed when Cl^{-} combines with Cd (Alloway & Ayres, 1997). Cadmium may be precipitated as cadmium carbonate, hydroxide and phosphate or by adsorption on clay minerals, carbonates or hydrous oxides of iron and magnesium (USEPA, 1992b). According to Dudley, McLean, Furst and Jurinak (1991), adsorption mechanisms may be the main source of cadmium removal from soils. It has further been noted that the greatest amount of total cadmium in soils and sediments polluted with mine wastes are associated with the exchangeable fraction (Hickey & Kittrick, 1984).

Copper

Copper is a naturally occurring element that exists in the environment as the free metal, and in the (I) and (II) oxidation states. The copper (II) oxidation state has been of much concern because it correlates with the biological availability and toxicity of copper (ATSDR, 1990). The retention of copper in soils is through exchange and specific adsorption processes (USEPA, 1992b). In non-calcareous soil, the clay mineral exchange phase serves as a sink for Cu (Cavallaro & McBride, 1978). On the other hand, the specific adsorption of Cu onto $CaCO_3$ surfaces greatly influences the concentration of Cu in solution of calcareous soil (Dudley et al., 1991). Precipitation may be an important mechanism of the retention of copper in waste-soil systems although at concentrations found in uncontaminated soils, Cu precipitates are unstable (USEPA, 1992b).

Zinc

Zinc occurs in only one oxidation state, Zn (II), and tends to have a stabilizing role in its binding with sulphydryl groups and maintenance of protein conformation (Bremner & Beattie, 1995). Clay minerals, carbonates or hydrous oxides readily adsorb zinc (USEPA, 1992a). The greatest proportion of the total Zn in polluted soils and sediments are associated with Fe and Mn oxides (Kuo, Heilman & Baker, 1983; Hickey & Kittrick, 1984). In non-polluted soil, the retention of Zn by precipitation is low due to the relatively high solubility of Zn compounds (USEPA, 1992b).

Iron

Iron occurs in the inorganic or organic complexes, dissolved and colloidal states and also in relatively coarse suspended particles (De Anil, 2000). Iron exists in the Fe^{2+}, Fe^{3+} (De Anil, 2000) and zero-valent (Fe^{0}) states. Redox reactions have a marked influence on the concentration of soluble iron in soil solution. Insoluble Fe^{3+} dominates in oxidized or well aerated soils. On the other hand, Fe^{2+} is the most abundant species of iron under waterlogged or reducing conditions. Iron (II) forms inner sphere complexes with or is chemisorbed by organic matter that requires significant activation energy to desorb (McBride, 1989).

Interrelationships among Heavy Metals in the Mining Environment

Typical geogenic elements such as iron, manganese, chromium and nickel show highly significant mutual correlation, whereas their correlation with copper, lead and zinc is generally not significant (Romić, Romić, Dolanjski & Stricevic, 2004). Low and insignificant correlations exist amongst Zn, Cu, Pb and Fe while significant correlations occur between Cd and the metals Cu ($P < 0.01$), Fe ($P < 0.001$) and Pb ($P < 0.001$) (Romić et al., 2004).

The presence of competitive cations can affect metal adsorption in soils. Calcium ions (Ca^{2+}) compete effectively with cationic heavy metals for adsorption sites, and this competition seemed to be greater for Zn and Cd than for Cu and Pb (Kiekens, 1983; Pierangeli, Guilherme, Oliveira, Curi & Silvia, 2003). This occurs because the retention of Zn and Cd in the soil by exchange reactions, while Cu and Pb form inner-sphere complexes with organic matter and with Fe, Al, and Mn oxides (Kiekens, 1983; Pierangeli et al., 2003).

There is a high positive correlation between Zn and Cd in nature (De Anil, 2000). Zinc pollution with mining and Cd has been observed to always occur in ZnS and other ores. The geochemical association of Zn and Cd may mitigate the effects of Cd because of Zn-Cd antagonism (Alloway & Ayres, 1997). Cyanide can form complexes with other metals such as Cu, Fe and Zn. The formation of strongly bond complexes of cyanide and Fe or Cu, ties up the cyanide that would become unavailable to dissolve gold (ICMI, 2006).

Levels of some Heavy Metals in Water, Soil and Plants

Linsay (1979) has reported that the range and average levels of some heavy metals in soils in mg kg^{-1} are arsenic (1 - 50 and 5), lead (2 - 200 and 10), copper (2 - 100 and 30), iron (10000 - 300000 and 71000) and zinc (10 - 300 and 50), respectively. In contaminated soils of the Baia Mare region of Romania, the levels of Pb, Zn, Cd and Cu, in mg kg $^{-1}$, are 1054 - 40375, 490 - 1175, 13.2 - 24.2 and 37.6 - 409.5, respectively. In the Zlatna area, the values of these heavy metals are 50 - 2000, 1900 - 3100, 40 - 80 and 360 - 7000 mg kg^{-1} respectively (Damian and Damian, 2007). According to Chen, Tsai and Tsui (1999), the worldwide concentrations of As, Pb, Zn and Cu in soils are highly varied and are in the ranges of 15 – 75, 40 – 1000, 75 – 4000 and 40 – 1600 mg kg^{-1}.

In the Ashanti Gold belt of Ghana, Pb (0.06 – 0.57 mg L^{-1}), Hg (0.19 – 0.66 mg L^{-1}), Mn (0.42 – 0.62 mg L^{-1}), Fe (0.56 – 1.15 mg L^{-1}), Cd (0.08 – 0.9 mg L^{-1}), Ni (0.009 – 0.044 mg L^{-1}) and Cr (0.07 – 0.12 mg L^{-1}) concentrations have been observed in stream, borehole and well water (Bowel, 1993). These concentrations of trace metals are above the World Health Organization guideline values. Smedley (1996) has also reported of arsenic concentrations up to 350 µg L^{-1} in stream waters affected by mining pollution in the Obuasi area of southern Ghana. In rivers of the Tibetian Plateau of China, water soluble Pb, Zn and Cu of concentrations 318 – 781, 18.2 – 29.2 and 12.6 – 14.4 mg L^{-1}, respectively have been recorded (Huang, Sillanpaa, Duo & Gjessing, 2008).

The concentrations of Pb, Zn, Cu, Fe, Mn and Cd in edible plant parts cited from varied sources are in the ranges of 0.009 – 3.83, 0.62 – 1132, 4.54 – 39.99, 1.67 – 4272, 14.9 – 500 and 0.013 – 12.86 mg kg^{-1} (Bigdeli and Seilsepour, 2008; Khan, Cao, Zheng, Huang and Zhu, 2008; Abbas, Parveen, Iqbal, Riazuddin, Iqbal, Ahmed and Bhutto, 2010; Raphael, Eunice and Frank, 2010). Arsenic concentrations of 0.014 – 0.091 mg kg^{-1}have also been recorded by Abbas et al. (2010).

Permissible limits of some Heavy Metals in Industrial Effluent, Drinking Water, Soil and Food

The processing of gold results in the production of effluent that contains harmful pollutants such as arsenic and cyanide compounds that have human health implications. The effluent produced is subsequently released into water bodies and which may leach and subsequently contaminate soil and groundwater. Standards have severally been set to monitor the levels of contaminants in industrial effluent, drinking water and soil (Ghana Environmental Protection Agency [GEPA], 2006; International Finance

Corporation & World Bank [IFC/WB], 2007; World Health Organization [WHO], 2008).

GEPA (2006) has set the following effluent quality guidelines, measured in mg L^{-1}, for discharges into natural water bodies: free cyanide (0.2), total cyanide (1.0), dissolved arsenic (2.0), total arsenic (1.0), dissolved lead (0.1), dissolved zinc (2.0), dissolved copper (2.0), dissolved or total iron (2.0) and pH (6.0 – 9.0). The emphasis of the GEPA concentrates more on the levels of these pollutants in water bodies rather than in soils, as evidenced in their monitoring tours.

The effluent guidelines values, in mg L^{-1}, of the Environmental, Health and Safety (EHS) guidelines of the IFC/WB (2007), which is applicable to the direct discharges of treated effluent to surface water, are as follows: free cyanide (0.1), total cyanide (1.0), arsenic (0.1), lead (0.2), zinc (0.5), copper (0.3), total iron (2.0), cadmium (0.05) and pH (6.0 – 9.0).

The WHO (2008) guidelines emphasize the acceptable limits of pollutants in drinking water. This is important for the determination of the health and safety of downstream communities that utilize the water derived from treated effluent discharged upstream into water bodies. The World Health Organization guidelines for drinking water quality, in mg L^{-1}, are listed as follows: cyanazine (0.0006), total cyanide (0.07), arsenic (0.01), lead (0.01), copper (2.0), total iron (2.0) and cadmium (0.003) (WHO, 2008). Iron, zinc and pH are considered not to be of health concern at levels normally found in drinking water (WHO, 2008).

Different regions have varied standards on the tolerable limits of soil pollutants. The Canadian environmental quality criteria values, in mg kg^{-1}, are free cyanide (0.5 and 100), arsenic (20 and 50), cadmium (3 and 20), lead (375 and 1000), copper (150 and 500) and zinc (600 and 1500), respectively for agricultural and contaminated industrial sites (Canadian Council of Ministers for the Environment [CCME], 1991). The Dutch total heavy metal concentration maximum limits for uncontaminated soils and the desirable intervention values for contaminated soils , in mg kg^{-1}, are arsenic (29 and 55), lead (85 and 530), copper (36 and 190) and zinc (140 and 720), respectively (International Soil Reference and Information Centre & Food and Agricultural Organization [ISRIC & FAO], 2004).

The Food and Agricultural Organization/ World Health Organization [FAO/WHO], (1999) and [FAO/WHO] (2001) guidelines for the maximum limit (ML) of different metals in vegetables (in mg kg^{-1}) are as follows: As (0.1), Hg (0.03), Cd (0.10), Mn (500), Fe (425), Zn (100), Cu (73), Ni (67) and Co (50). The maximum limit of Pb for edible crops in China is set at 0.2 mg kg^{-1} (Chinese Department of Preventive Medicine [CDPM], 1994). According to Samara, Misaelides, Tsalev, Anousis, Koui and Tzis (1992), the permissible limits of Zn and Pb in plants are 10 – 50 and 2.0 – 2.5 mg kg^{-1}, respectively. The maximum levels of Cd, Cr, Cu, Ni, Pb and Zn permitted by the State Environmental Protection Administration [SEPA], (2005) for vegetables and fruits are 0.1 – 0.2, 0.5, 20.0, 10.0, 9.0 and 100 mg kg^{-1}, respectively.

Detoxification Measures of Effluent Produced from Gold Mining Operations

Mining companies that have recently adopted sound gold processing methods are obliged to manage carefully the tailings and effluents accumulated from the previous use of cyanide. Mining companies should use the minimum effective amounts of cyanide required to recover metals, and dispose of cyanide in a way that eliminates or reduces environmental impacts (McKinnon, 2002). The efficiency of existing cyanide effluent detoxification processes from gold ore processing need be investigated to avert any deleterious effects on the ecosystem due to the reports of cyanide spillages and water pollution by environmental non-governmental organizations such as NCOM (2009) and WACAM (2003).

The processes involved in the detoxification of cyanide include natural degradation by ultraviolet radiation, Cyanisorb process, the INCO process involving oxidation by SO_2, Acidification-Volatilisation-Recovery (AVR) process and Acidification-Volatilisation-Neutralisation (AVN) process. The others are oxidation by ozone, hydrogen peroxide (H_2O_2) and chlorination, biological treatment and conversion into stable iron cyanide precipitates (USEPA, 1994a).

Natural Degradation

Natural degradation processes involve the reduction of cyanide levels of industrial waste without human intervention. Natural degradation processes, which occur to some extent in tailings impoundments, are capable of decreasing cyanide levels. The chemical reactions involved in natural degradation, as cited by USEPA (1994a), are microbial action, volatilisation, hydrolysis, anaerobic biodegradation and complexation.

The microbial generation of cyanate and ammonia in the soil occurs via the following reactions:

$$CN^- + ½O_2 + enzyme \rightarrow CNO^- \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$CNO^- + H_2O \rightarrow NH_3 + CO_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The volatilisation of cyanide from solution occurs after the absorption of CO_2 or SO_2 from the atmosphere and subsequently the formation of hydrocyanic acid. The chemical equations of these reactions are:

$$CO_2(g) + H_2O \rightarrow H_2CO_3 \rightarrow HCO_3^- + H_3O^+ \ldots\ldots (4)$$

$$H_3O^+ + CN^- \rightarrow HCN(g) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The hydrolysis of hydrocyanic acid in soils results in the formation of acid which is represented by the chemical equation:

$$HCN + 2H_2O \rightarrow NH_4COOH \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Under anaerobic conditions, the following cyanide degradation processes take place:

$$CN^- + H_2S(aq) \rightarrow HSCN + H^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

$$HSCN + 2H_2O \rightarrow NH_3 + H_2S + CO_2 \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Cyanide ions react with metals to form relatively stable complexes that have high stability constants. The complexation of zinc and cyanide occurs via the chemical reaction:

$$Zn(CN)_2 + 2CN^- \rightarrow Zn(CN)_4 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Oxidation by Hydrogen Peroxide (H_2O_2)

Cyanide in solution is oxidized, in the presence of the copper ion as a catalyst, by hydrogen peroxide to cyanate ion which subsequently hydrolyses to form ammonia and carbonate (Khodadadi et al., 2005; USEPA, 1994a) according to the equations:

$$CN^- + H_2O_2 \xrightarrow{Cu(II)} CNO^- + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

$$CNO^{-} + 2H_2O \rightarrow CO_3^{2-} + NH_4^{+} \;\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

The H_2O_2 process can be applied to waste waters but reagent requirements increase for slurries (USEPA, 1994a). The pH of cyanide polluted waste water should be maintained between 9 and 10 (Khodadadi et al., 2005) or a pH not less than 8 (Young and Jordan, 1995) to prevent the release of HCN gas. The reaction rate of the H_2O_2 system can be increased by raising temperature, increasing catalyst dose or the addition of excess H_2O_2 (Khodadadi et al., 2005). This is one of the cyanide detoxification methods applied to decant from slurry after gold extraction by AngloGold Ashanti at Obuasi.

Photo-oxidation

Photolysis enhances reduction/oxidation (redox) reactions by utilizing energy from electromagnetic radiation to catalyze electron transfer processes (Young & Jordan, 1995). Photolytic reactions can occur directly if the absorbing compound is the species that is mediated or indirectly if that photon-energy is transferred from an absorbing compound to the species being mediated (Fox & Dulay, 1993). Photo-oxidative reactions involve the acceptance of an electron from another species by the absorbing compound to satisfy its electron vacancy (Young & Jordan, 1995). The energy required for electron transfer is provided by ultraviolet (UV) radiation and many redox reactions are catalyzed after exposure to natural sunlight (Daniels, 1968).

Photo-oxidation of cyanide by UV light is slow and the rate of cyanide degradation can be enhanced when UV light is used with H_2O_2, at an optimum dose of 35.3 mmol dm^{-3} and pH of 10.5 (Malhotra, Pandit, Kapoor & Tyagi, 2004). Photo-oxidation reactions are carried out at alkaline pH values between 10 and 11, since at acidic pH values, cyanide ions form highly toxic HCN gas which is volatile and difficult to oxidise (Malhotra et al., 2004). The rate of cyanide degradation increases with increasing UV light intensity (Malhotra et al., 2004). Photo-oxidation of cyanide is a detoxification method employed by AngloGold Ashanti, Obuasi mine.

Oxidation by Potassium Permanganate ($KMnO_4$)

Potassium permanganate ($KMnO_4$), an oxidizing agent, reacts with cyanide ions in alkaline or neutral media according to the following equation:

$$2KMnO_4 + 31CN^- + H_2O \rightarrow 2MnO_2 + CNO + 2OH^- \ldots\ldots\ldots (12)$$

For each kilogram of cyanide to be oxidized, 4.05 kg of $KMnO_4$ is required and a catalytic amount of Cu (II) salt to enhance the cyanide oxidation rate. The treatment of 100 ppm 25 L cyanide waste with 10 g $KMnO_4$ and 0.6 g $CuSO_4.5H_2O$ results in the disappearance of more than 99 % cyanide in less than two hours (University of Melbourne [UM], 2005). To ensure complete oxidation of cyanide and metal cyanide complexes, the permanganate treated waste cyanide should be left overnight prior to discharge it into sewage (UM, 2005).

Oxidation by Chlorination

Free chlorination conducted at pH more than 10 is a detoxification method used to destroy cyanide and the resulting byproducts are bicarbonate ions and nitrogen gas (Whelton, Jensen, Richards & Valdivia, 2003). Unlike chlorination used for the inactivation of pathogens where hypochlorous acid

(HOCl) is the desired chemical, hypochlorite (OCl⁻) is the desired chlorine species when destroying cyanide ions (Whelton et al., 2003). During cyanide destruction, hypochlorite reacts with the cyanide ion to form cyanate (CNO⁻) as follows:

$$CN^- + OCl^- \rightarrow CNO^- + Cl^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

The cyanate ion is reduced to nitrogen, carbon dioxide and water molecules as follows:

$$2NaCNO + 3Cl_2 + 4NaOH \rightarrow N_2 + 2CO_2 + 6NaCl + 2H_2O \ldots (14)$$

The chlorine and cyanide ion reaction rate could be increased at higher pH values and the destruction of cyanide is less effective at pH levels not greater than 10 (Whelton et al., 2003). Studies have shown that the breakdown of CNCl is dependent on both pH and time (Whelton et al., 2003).

Cyanogen chloride, which is highly toxic, could be produced (LaGrega, Buckingham, Evans & Management, 2001; Pendersen & Marinas, 1995). At higher pH, cyanogen chloride is transformed into a more desirable reaction by-product, cyanate ion (CNO⁻), as indicated by the following chemical equations:

$$NaCN + Cl^- \rightarrow CNCl + NaCl \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

$$CNCl + 2NaOH \rightarrow NaCNO + H_2O + NaCl \ldots\ldots (16)$$

The CNO⁻ ion could be sequentially reduced to harmless molecules (Whelton et al., 2003).

When cyanide is in the form of metallocomplexes, specifically iron and nickel, destruction is more difficult (APHA, 1998; LaGrega et al., 2001). Many of these metallocomplexes do not dissociate and as a result the time required for destruction is greatly increased. According to LaGrega et al.

(2001), in order to destroy nickel complexes, a 20 % excess dose of chlorine is needed. Ferrocyanide is also converted to ferricyanide during chlorination and additional destruction by chlorine is ineffective (Whelton et al., 2003).

The Acidification-Volatilization-Recovery Process

The Acidification-Volatilization-Recovery (AVR) process, which has also been used to detoxify cyanide, is generally applicable to barren solutions. However, the process has been redesigned to handle slurries (Smith & Mudder, 1991). It involves the initial formation of HCN gas after the creation of an acidic medium by addition of H_2SO_4 (USEPA, 1994a). The gas is then absorbed into a NaOH solution:

$$CN^-(aq) + H^+(aq) \rightarrow HCN(g) \ldots\ldots\ldots\ldots\ldots\ldots (17)$$

$$HCN(g) + NaOH(aq) \rightarrow NaCN(aq) \ldots\ldots\ldots\ldots\ldots (18)$$

The Acidification-Volatilization-Neutralisation Process

The system developed for the Golden Cross mine in New Zealand, Acidification-Volatilization-Neutralisation (AVN), has been used to handle slurries (Smith & Mudder, 1991). Unlike the AVR, the NaCN formed is returned to the leaching process and lime added to the detoxified wastewater to precipitate heavy metals (USEPA, 1994a).

Conversion into Stable Precipitates of Iron Cyanide

Cyanide can form complexes with metals such as iron (Fe), gold (Au), cadmium (Cd), cobalt (Co), copper (Cu) and nickel with Fe and Au being the most stable. Iron cyanides are the dominant cyanide species in groundwater and the soil (Meeussen, Keizer & Van Riemsdijk, 1992). Iron cyanide complexes occur as strong complexes such as ferricyanide, $Fe(CN)_6^{3-}$ and ferrocyanide, $Fe(CN)_6^{4-}$ or as iron cyanide precipitates like Prussian blue, $Fe_4[Fe(CN)_6]_3$ and Turnbull's blue, $Fe_3[Fe(CN)_6]_2$ (Ebbs, 2004; Meeussen et al., 1992). The formation of strong complexes between cyanide and precious minerals has been utilized in ore heap leaching operations to selectively extract gold from low grade ore (Ebbs, 2004). The complexation of Fe and cyanide occurs via the chemical reaction:

$$Fe^{3+} + 6CN^- \rightarrow Fe(CN)_6{}^{3-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (19)$$

Some metal-cyanide complexes such as those of iron-cyanide are very stable and contaminated sites have been detected forty-five years after cyanide use had ceased (McKinnon, 2002).

The INCO Process involving Oxidation by SO_2

In the INCO process, free cyanide and weakly or moderately bound metal-cyanide complexes present in the waste stream are oxidized to cyanate (CNO^-) by the addition of sulphur dioxide and oxygen. The reaction usually takes place in a well-mixed and aerated reactor. The aeration provides mixing and oxygen (Smith & Mudder, 1991). Sulphur dioxide may be supplied to the reactor in a gas or liquid state, or by the application of sodium sulphite or sodium metabisulphite. INCO has reported actual SO_2 dosages to be 3 - 5 g g^{-1} CN^-, for barren solutions and 4 - 7 g g^{-1} CN, for tailing slurries. The reagent consumption for sulphur dioxide is 2.5 mg SO_2 mg^{-1} of weak acid dissociable (WAD) cyanide and for lime, 2.2 mg CaO mg^{-1} WAD cyanide (Smith and

Mudder, 1991). Higher dosages are required to treat low concentrations of WAD forms of cyanide (Vergunst, Iamarino & Devuyst, 1991).

The INCO process is pH dependent and the optimal pH range is 8 - 10. Incomplete oxidation may occur at pH levels above 11 (USEPA, 1994a). At pH levels below 8, there is a reduction in the reaction rates. Since the oxidation reaction results in the formation of sulphuric acid, lime or caustic soda is added to maintain the optimal reaction pH (USEPA, 1994a). The presence of a copper catalyst at a concentration of about 50 mg L^{-1} is also necessary for the reaction to take place. Supplemental copper is provided by the addition of copper sulphate solution to the reactor contents, if the copper concentration naturally present in the waste stream is too low (USEPA, 1994a).

Although oxygen is also added to the reactor, the oxidation reaction has also been reported to be temperature dependent. At 25 °C, the reaction is rapid and results in a residual cyanide concentration of 0.2 mg L^{-1} whereas at 5 °C the reaction is slow and results in a residual cyanide concentration of 2.0 mg L^{-1} (McGill & Comba, 1990). The sulphide treatment plant of AngloGold Ashanti, Obuasi utilises the INCO process in the detoxification of wastewater.

Biological Treatment

Microbial action, as a cyanide detoxification technique, results in the formation of ammonia from cyanide. The metal ions released from metal cyanides are absorbed by the microbial biomass and thiocyanates are converted to sulphates (USEPA, 1994a). The chemical reactions involved are as follows:

$$Cu_2CN + 2H_2O + ½O_2 \rightarrow Cu - biofilm + HCO_3 + NH_3 \ldots.(20)$$

$$SCN + 2H_2O + 2½O_2 \rightarrow SO_4{}^{2-} + HCO_3{}^{-} + NH_3 \ldots\ldots.(21)$$

According to USEPA (1994a) and Dictor, Battaglia-Brunet-Bayyaglia, Morin, Bories and Clarens (1997), the ammonia is further converted to nitrate by further microbial action as follows:

$$NH_4{}^{+} + 1½O_2 \rightarrow NO_2{}^{-} + 2H^{+} + 2H_2O \ldots\ldots\ldots\ldots\ldots\ldots.(22)$$

$$NO_2{}^{-} + ½O_2 \rightarrow NO_3{}^{-} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(23)$$

The purpose of biological detoxification processes is to enhance the rate at which natural transformations occur (USEPA, 1994a). The Rotating Biological Contractors that utilize bacteria for the detoxification of cyanide and adopted by AngloGold Ashanti, Obuasi, is based on this principle.

Treatment of Effluent at AngloGold Ashanti, Obuasi

There has been considerable amount of experimentation with the destruction of cyanide by the use of chemical treatment methods such as ferrous sulphate, potassium hypochlorate, calcium hypochlorite, alkaline chlorination and hydrogen peroxide (Opong, 2008). These technologies have not yielded consistent residues devoid of cyanide, thiocyanate and other toxic chemicals and compounds (Hoecker & Muir, 1987; Opong, 2008). The use of calcium hypochlorite is the latest of the cyanide destruction trial technology to be put on hold.

Hydrogen peroxide is currently used for the initial treatment of decant for the degradation of cyanide from the slurry of the oxide and sulphide treatment plants. The photo-oxidation and carbon-in-solution treatments are applied for the initial degradation of cyanide and heavy metals respectively prior to the detoxification of effluent in the start-up columns, biofilters and rotating biological contractors. Since the oxidation reaction results in the formation of sulphuric acid, lime or caustic is added to maintain the optimal reaction pH (USEPA, 1994a). The INCO process is employed in the detoxification of wastewater at the sulphide treatment plant of AngloGold Ashanti, Obuasi.

Biological Detoxification of Cyanide

In view of the shortfalls of the chemical treatment methods, the biological treatment option using bacteria, tests on laboratory and pilot scales has occurred (Opong, 2008). A main plant, commissioned in collaboration with Whitlock and Associates, is to be further developed based on the Homestake Plant in the USA as a benchmark (Opong, 2008). Microbial action potentially offers the cheapest and an effective means of cyanide degradation (Whitlock & Mudder, 1985; Lien & Altringer, 1993).

The Detoxification Plant

The biological cyanide detoxification plant consists of a reservoir fed with dam return effluent, biofilter and rotating biological contractor. A one square metre reservoir is situated at a height of 4.8 m on top of the same biofilter column which contains oxide treatment plant (OTP) scats as filter material (Opong, 2008). The reservoir is continuously filled with Dam Return Effluent at an average head grade of 32.9 ppm cyanide (CN), 231.9 ppm thiocyanate (SCN), 4.3 ppm nitrate (NO_3^-), 2.8 ppm phosphate and 1,293.3 ppm of calcium hardness (Opong, 2008).

The effluent is uniformly distributed over the scats in the biofilter by gravity at an average rate of 0.057 m^3 and air blown in the counter direction from an air sparger at the base of the column. The effluent is then directed into a 20-litre reservoir at an average grade of 3.6 ppm, 35.6 ppm, 44.2 ppm 1.8 ppm and 1,345.5 ppm of CN, SCN, NO_3^-, PO_4 and calcium hardness, respectively (Opong, 2008). Temperature is one of the important environmental factors associated with biological degradation (Akcil, 2003). A low temperature of the waste water needing treatment results in an unacceptable decrease in performance and the solution temperature should be above 10 °C to support adequate biological growth and action (Akcil, 2003).

The rotating biological contractor consists of five chambers partitioned by weirs. Each chamber has an independent airline to aerate the resultant solution for optimal performance of inoculated aerobic bacteria on the disks. The disks rotate at a speed of 1.7 rev. min^{-1}. The unit is fed with biofilter effluent by positive displacement at a rate of 0.041 m^3 h^{-1} into the first chamber ahead of the rotating disks (Opong, 2008). The effluent in the first chamber overflows the weir into the next chamber. The overflow of effluent from the fifth chamber is subsequently discharged into a fish pond (Opong, 2008). The effluent finally attains an average grade of 0.2 ppm cyanide (CN), 1.3 ppm thiocyanate (SCN), 46.3 ppm nitrate (NO_3^-), 1.6 ppm phosphate and 1,330 ppm of calcium hardness (Opong, 2008).

The Biodegradation Reaction Mechanisms

Cyanide is converted into mineralisation products and other naturally occurring compounds by microorganisms (Ingvorsen, Hojer-Pederson &

Godtfredsen, 1991; Stratford, Dias & Knowles, 1994). Sodium cyanate is mineralised to carbonate and ammonia via the following chemical reaction:

$$2NaCN + 4H_2O + O_2 \xrightarrow{Pseudomonas\ sp.} 2NaHCO_3 + 2NH_3 \ldots\ldots.(24)$$

Sodium thiocyanate is converted into sodium bisulphate, sodium bicarbonate and ammonium under aerobic conditions (Whitlock & Mudder, 1985; Opong, 2008).

$$2NaSCN + 4H_2O + 2NaOH + 4O_2 \rightarrow 2NaHSO_4 + 2NaHCO_3 + NH_3..(25)$$

$$NH_3 + H_2O \rightarrow NH_4{}^+ \quad + OH^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(26)$$

The ammonium produced is detoxified by aerobic autotrophic bacteria, *Nitrosomonas* and *Nitrobacter* into nitrite and nitrate, respectively (Whitlock & Mudder, 1985) as follows:

$$2NH_4{}^+ \quad + 3O_2 \xrightarrow{Nitrosomonas} 2NO_2{}^- \quad + 2H_2O + 4H^+ \ldots\ldots.(27)$$

$$2NO_2{}^- \quad + O_2 \xrightarrow{Nitobacter} 2NO_3{}^- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(28)$$

The nitrate is further reduced to molecular nitrogen, carbon dioxide and water (Opong, 2008) as follows:

$$6NO_3{}^- \quad + 5CH_3OH \rightarrow 5CO_2 + 3N_2 + 7H_2O + \ 6OH^- \ldots..(29)$$

The growth of bacteria is yet to be optimised since the detoxification reaction mechanism is in its preliminary stages (Opong, 2008).

Remediation of Heavy Metal Contaminated Soils

The pollution of soils is a very important environmental problem that has attracted public attention over the decades (Garbisu & Alkorta, 2001). Lombi et al. (2002) have noted that the contamination of soils with heavy metals is a world-wide problem. There are vast areas of land that have become non-habitable and hazardous to humans and wildlife due to widespread pollution and its magnitude demands immediate mediation measures (Garbisu & Alkorta, 2001).

A total of over one million four hundred thousand sites in fifteen European countries are alleged by the European Topic Centre Soil [ETCS], (1998) to be contaminated with organic and inorganic pollutants. The total clean-up cost needed to mediate these sites is estimated to be over seventy-one billion Dollars (ETCS, 1998). The present state-of-the-art technology for the mediation of metal contaminated soil involves the excavation and burial of the soil at a hazardous waste site at an average cost of two and a half million dollars per hectare (Raskin, Smith & Salt, 1997). The numerous costs associated with the removal of pollutants through the use of traditional physicochemical methods have led to a disregard of the adopting measures to address the problem (Garbisu & Alkorta, 2001).

Pollution caused by inorganic sources in soils posses a higher environmental hazard compared to atmospheric and water pollution (Joubert, Lucas, Garrido, Joulian & Jauzein, 2007). The contamination of heavy metals in the environment is of great concern due to their toxicity and threat to human lives (Duker, Carranza, and Hale, 2005; Ma & Rao, 1997). The total content of an inorganic pollutant is inadequate for environmental risk assessment (Joubert et al., 2007). The total heavy metal amount in soils is partitioned into different fractions. The soluble and exchangeable fractions are the most important associated to groundwater pollution and to plant nutrition (Sastre et al., 2001). The mobility and bioavailability of metals are related to the solubility of their geochemical form. Olajire, Ayodele, Oyedirdan & Oluyemi

(2003), in their studies on four contaminated soils of Southern Nigeria, found that the apparent mobility and potential bioavailability of some metals in the soil are in the order Pb > Zn > Cu > Ni > Cd.

The evaluation of mobility and bioavailability is necessary to explain the behaviour of metals in soils and potential toxicity (Navarro, Perez-Sirvent, Martinez-Sanchez, Vidal & Marimon, 2006; Wu, Luo, Cheung & Wong, 2006). Remediation measures for heavy metal toxicity should therefore be aimed at reducing the levels of water soluble and exchangeable forms in soils.

Reclamation of Mining Sites by AngloGold Ashanti

There has been extensive reclamation of lands used for mining and the containment of heavy metals at tailings sites at AngloGold Ashanti. However, the documentation of these activities is inadequate. The scientific approach in assessing the effectiveness of the remediation methods of AngloGold Ashanti is lacking and no definite scientific conclusions have been drawn from the data collected based on daily routine work.

The use of green plants to assimilate or detoxify metals or organic chemicals, and termed as phytoremediation, (Visoottiviseth, Francesconi & Sridokchan, 2002), is employed to some extent at AngloGold Ashanti. Phytostabilization, using tree species such as *Acacia mangum*, *Senna siamea* and *Malina arborea*, is the main phytoremediation application employed to contain heavy metals and cyanide compounds in soils at AngloGold Ashanti, Obuasi mine. Phytoextraction, which is one of the main technologies in remediating heavy metals, has not been extensively practiced at AngloGold

Ashanti, Obuasi mine and only small areas of mined land are planted with phytoextracting tree species.

The cappping of contaminated soil with lateritic soil does not remove the contaminants from the soil (Kertulis-Tartar et al., 2006). This is, however, the main method of remediating heavy metals contained in tailings dam sites at AngloGold Ashanti, Obuasi mine. Plants such as Vetiva grass (*Vetiveria zizanioides*) and *Paspalum* sp. that are tolerant to high levels of heavy metals are subsequently planted.

Metal Immobilisation Using Soil Amendments

Soil amendments are capable of immobilising heavy metals and improving upon soil quality (Oste et al., 2002). *In situ* immobilisation reduces negative effects of contaminants by the addition of an immobilising agent to the soil (Oste et al., 2002). The additives must possess high binding capacity without an impairment of soil structure, fertility or ecological stability (Oste et al., 2002). The soil additives are predominantly alkaline in nature (Oste et al., 2002) and include lime (Hooda & Alloway, 1996; Singh & Myhr, 1998) apatite, zeolite (Rakovan & Reeder, 1994; Oste et al., 2002) and beringite (Zaghloul & Abou-Seeda, 2005; Mench, Vangronsveld, Beckx & Ruttens, 2006).

Zeolite

Zeolites are negatively charged (Stolz, Yang & Ambruster, 2000) crystalline alumino silicate minerals (Oste et al., 2002) and the three-dimensional structure consists of (Si, Al) O_4 tetrahedra (Stolz et al., 2000). The framework is porous and consists of channels and cavities in which cations and water molecules are located (Oste et al., 2002). The open channel structure of zeolite functions as a molecular sieve and the selective exchange of cations (Oste et al., 2002).

Natural zeolites possess high cation exchange capacity (CEC), high thermal and radiation resistance (Trgo, Perić & Vukojevic-Medvdovic, 2006). The cation exchange capacity of zeolite varies from 98 to 560 $cmol_c$ kg^{-1} depending on its source and type (Oste et al., 2002; Garau, Castaldi, Santona, Deiana & Melis, 2007; Panuccio, Sorgona, Rizzo & Cacco, 2009). The negative charge of the zeolite framework is compensated by exchangeable cations such as Na, K, Ca and Mg (Stolz et al., 2000). Zeolites have the ability to exchange most of their exchangeable cations and are also capable of hydration or dehydration without any major change in structural framework. The surface area of zeolite can be as high as 700 m^2 g^{-1} (Panuccio et al., 2009). These structural properties of zeolite ensure the exchange of cations by heavy metal ions (Perić, Trgo & Vukojevic-Medvidovic, 2004).

The addition of zeolite to the soil decreases the metal concentration in solution due to its binding capacity and alkalinity (Oste et al., 2002). Zeolites are therefore potentially useful additives to bind and immobilize heavy metals contaminated soils so as to improve their quality (Oste et al., 2002).

Studies by some authors on the use of natural zeolites as a soil amendment have shown little or no effect on the availability of metals (Mineyev, Kochetavkin & Van Bo, 1990; Baydina, 1996; Chlopecka & Adriano, 1997). The use of synthetic zeolites immobilizes more heavy metals than natural zeolites (Czupyrna & Levy, 1998). Although the binding capacity of synthetic zeolites can be very high, an increase in soil pH without a simultaneous addition of calcium can raise the dissolved organic matter (DOM) concentration in the soil (Oste et al., 2002). An increase in DOM could increase metal leaching (McCarthy & Zachara, 1989; Temminghoff, Van der Zee & De Haan, 1997).

Beringite

Beringite is a modified aluminosilicate produced by burning coal residue in a fluidized bed (Lombi et al., 2002). Generally, beringite has high Ca (24.6 $cmol_c\ kg^{-1}$) and Mg (8.9 $cmol_c\ kg^{-1}$) contents. The presence of bivalent cations aids in As sorption (Trgo et al., 2006). Beringite has been observed to decrease extractable As by 34 % (Trgo et al., 2006). The addition of 5 % (w:w) beringite to the contaminated soil reduces metal toxicity and mobility and its effects persist for many years (Lombi et al., 2002). Boisson, Ruttens, Mench and Vangronsveld (1999) noted that Pb, Cd, Cu, Ni and Zn are effectively mobilized by beringite and also by steel shoots-beringite combination.

Illites and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$ usually occur in beringite, although insoluble compounds such as calcium arsenates may also be present (Vangronsveld, Ruttens & Clijsters,1999; Mench et al., 2006). Arsenate (AsO_4^{3-}) forms both outer sphere and inner sphere complexes with ettringite, which occurs as a stable mineral above a pH of 10.7 (Myneni, Traina, Logan & Waychunas, 1997).

Organic Matter

The cation exchange capacity (CEC) of soil organic matter, which could be as high as 150 to 300 $\mathrm{cmol_c\ kg^{-1}}$, plays a significant function in sorption reactions of most soils (Alloway & Ayres, 1997). The organic matter from manures serves as a nutrient pool, enhances nutrient recycling, increases CEC and increases the buffering capacity of the soil (Stewart, Robinson & Parker, 2000). The addition of organic matter (OM), preferably with lime, to mine waste-contaminated soils improves soil fertility, structure and decreases plant-available heavy metals (Tordoff, Baker & Willis, 2000; Abbott, Essingston, Mullen & Ammons, 2001). Organic amendments added to metal-contaminated soil can have ameliorative effects as a result of increases in surface area and in the number of specific adsorption sites (Shuman, 1999). Organic amendments decrease heavy metal availability through transformation from plant-available forms that are extractable with water or solutions of neutral salts to fractions associated with OM, carbonates or metal oxides (Walker, Clemente & Bernal, 2004).

The reduction in metal bioavailability is dependent on the metal ion, soil type and the characteristics of the organic matter with respect to its extent of humification and changes in soil pH (Ross, 1994; Narwal & Singh, 1998; Almås, Singh & Salbu, 1999; Walker, Clemente, Roig & Bernal, 2003). Soil humic acids can increase adsorption, thereby reducing both metal concentration and free metal activity (Sauvé, Martinez, McBride & Hendershot, 2000). Humus and other organic compounds can chelate metals and form stable complexes. Humic fractions with lower molecular weights are more effective for complexation with metallic ions, since they contain phenolic (Ph-OH) and carboxylic (-COOH) groups in higher concentrations (Silveira, Alleoni & Guilherme, 2003). On the other hand, soil organic matter can increase dissolved organic matter and fulvic acid concentrations, and subsequently increase the total dissolved metals which results in higher metal mobility (Bruemmer, Gerth & Herms, 1986; McBride, Richards, Steenhuis, Russo & Sauvé, 1997; Sauvé, McBride & Hendershot, 1998; Silveira et al., 2003).

Composts immobilise metals through cation exchange and sorption reactions (Roman, Fortun, De Sa & Almendros, 2003). Van Herwijnen, Hutchings, Al-Tabba, Moffat, Johns and Ouki (2007) have reported that amendment with compost alone initially increases plant growth by improving the nutrient status of the soil and immobilising certain metals. However, after degradation of the organic matter of compost, the adsorbed metals may be released and become available again to plants (Van Herwijnen , Hutchings, Al-Tabba, Moffat, Johns & Ouki, 2007). Copper and lead are mobilised by dissolved organic matter through complexation, although cadmium and zinc are immobilised (Bradl, 2004). Bradl (2004) noted further that the leaching of As and Pb can be increased through complexation with dissolved organic matter. Cao, Ma and Shiralipour (2003) have noted that certain composts in combination with certain soils aid in the leaching of arsenic.

Fresh manure increases heavy metal solubility due to the provision of soluble organic compounds which form complexes with metals (Almås, Singh, & Salbu, 1999; Shuman, 1999). Conversely, humic substances which form part of OM of decomposed organic materials can reduce metal solubility by the formation of steady metal chelates (Ross, 1994). Differences in metal availability are also dependent upon the salt content and pH of the mineral fraction, cation exchange capacity and the redox conditions of the soil (Almås et al., 1999; Shuman, 1999; Walker et al., 2003).

Characteristics and Effects of Biochar as an Amendment

Biochar refers to the charcoal form of black carbon that is formed by the pyrolysis or low temperature combustion of biomass at less than 600 °C in the absence of oxygen (Shrestha, Traina & Swanston, 2010). The benefits of biochar are manifested through high pH, cation exchange capacity and surface area (Lehmann, 2007).

Biochar possesses high specific surface area, charge density and negative surface charge. These properties of biochar result in a very high cation sorption and retention capacity (Liang et al., 2006). The high cation exchange capacity (CEC) of black carbon is created by either or both of two mechanisms. The high charge density per unit surface area results in a high degree of oxidation of organic matter. Secondly, there is an increase in the cation adsorption sites due to the high surface area of black carbon (Liang et al., 2006). The high CEC exhibited by soils with high black carbon content could also be attributed to the oxidation of the aromatic carbon and formation of carboxyl groups (Glaser, Guggenberger, Zech & Ruivo, 2003). According to Lehmann, Laing, Solomon, Lerotic, Luizao, Kinyangi, Schafer, Wirich and Jacobsen (2005), the formation of carboxyl groups or other functional groups with net negative charge in the presence of black carbon could be due to two main processes. This could be either due to the surface oxidation of the black carbon particles or the adsorption of highly oxidized organic matter onto the surfaces of black carbon.

Black carbon in soil is present as small particles that are predominantly < 50 µm (Skjemstad, Clarke, Taylor, Oades & McClure, 1996) and the oxidation of such particles commences from its surfaces (Lehmann et al., 2005). Oxidation processes result in oxygenated black carbon surfaces (Boehm, 1994). This leads to the formation of carboxylic, phenolic, hydroxyl, carbonyl or quinine carbon forms that change its amphoteric characteristics (Lau, Furlong, Healy & Gieser 1986). The oxidation of black carbon does not only increase its mineralisation but also creates negative charges that subsequently lead to greater CEC and nutrient retention in the soil (Glaser, Lehmann & Zech, 2002; Liang et al., 2006). The CEC of soils amended with biochar increases rapidly after four months of incubation, even without microbial activity (Lehmann & Rondon, 2006). Black carbon can therefore be utilised to improve the fertility of highly weathered soils (Lehmann & Rondon, 2006).

Biochar may have the potential of reducing the leaching of pollutants from agricultural soils (Glaser et al., 2002; Lehmann, da Silva Jr., Steiner, Nehis, Zech & Glaser, 2003). This is attributed to the strong adsoption affinity of biochar for soluble nutrients such as nitrate and other ionic solutes (Mizuta, Matsumoto, Hatate, Nishihara & Nakanishi, 2004; Radovic, Moreno-Castilla & Rivera-Utrilla, 2001). Abiotic processes contribute more significantly than biotic processes in the initial oxidation of fresh black carbon (Cheng, Lehmann, Thies, Burton & Engelhard, 2006). This ensures that further decomposition of the recalcitrant aromatic ring structure of black carbon by microbial activity is less constrained (Cheng et al., 2006). Cheng et al. (2006) have further noted that the rapid oxidation of fresh black carbon increases cation retention and decreases the potential for off-site pollution in agricultural landscapes.

The surfaces of black carbon are porous and possess aromatic surfaces that can contribute 1–10 % of the total fraction of organic matter in soils (Gustafson & Gschwend, 1997). Extractable humic and fulvic acids with high concentrations of carboxylic functional groups are also produced from biochar after oxidative degradation with dilute nitric acid (Trompowsky, Benites, Madari, Primenta, Hockaday & Hatcher, 2005). Increased dissolved organic matter and fulvic acids can lead to increased total dissolved metals and greater metal mobility (Bruemmer et al., 1986; McBride et al., 1997; Sauvé et al., 1998; Silveira et al., 2003). On the other hand, soil humic acids derived from biochar could increase adsorption, thereby reducing both metal concentration and free metal activity (Sauvé et al., 2000).

Soil Properties Influencing the Adsorption of Heavy Metals

The capacity of a soil to sorb trace elements largely depends on its Fe and Al hydrous oxides, clay content and organic matter contents (Barry, Chudek, Best & Moody, 1995; Bolan & Duraisamy, 2003; ISRIC & FAO, 2004). The pH of the soil, cation exchange capacity (CEC) and redox potential also regulate the mobility of metals in soils (Lombi & Gerzabek, 1998). Clay minerals, oxides and organic matter have a high preference for some anions than others due to the existence of strong bonds between the surface and the specific ion (USEPA, 1992b). Oxides and soils adsorb arsenate through specific binding mechanisms or inner sphere complex phenomenon, similar to that exhibited by phosphate (USEPA, 1992b; Anderson, Ferguson & Gavis, 1976; Anderson & Malotky, 1979).

The CEC of the soil is related to its ability to adsorb heavy metals. The higher the CEC values the greater the exchange sites on soil minerals that will be available for metal retention (Barry et al., 1995). The CEC of a soil increases with increasing pH, up to pH 7.0 (Alloway, 1995). The maximum retention of cationic metals occurs at pH > 7. However, the formation of metal complexes with dissolved organic matter results in increased cationic mobility with increasing pH (USEPA, 1992b). Anion exchange, that involves the retention of anions on positively charged surface sites, is maximal at pH values below 7.0 (USEPA, 1992b). Ligand exchange also occurs in anion exchange where surface complexes form between an ion and Fe or Al hydrous oxide or a clay mineral (Alloway, 1995).

Soil pH is the single most important physico-chemical soil property regulating the adsorption and desorption of ions in soils (Alloway, 1995). The fixing capacity of a soil for most trace elements increases with increasing pH from acid to a maximum under neutral and slightly alkaline conditions (ISRIC & FAO, 2004). An increase in soil pH contributes to the immobilisation of heavy metals in the soil by increasing the reactivity of the existing exchange sites for effective metal binding due to decreased protons (Oste et al., 2002).

The presence of inorganic and organic ligands in the soil solution can affect the adsorption of trace metals. The three general characteristics affecting the adsorption of trace metals, according to Sposito (1983), are that:

1. The ligand has high affinity for the metal and they form a soluble complex with high affinity for the adsorbent.
2. The ligand has high affinity for the adsorbent and the adsorbed-ligand has a high affinity for the metal.
3. The ligand has high affinity for the metal and they form a soluble complex with low affinity for the adsorbent.

Soil redox potential can influence the solubility of heavy metals. In conditions where oxidation reactions are involved, the solubility of heavy metals increases with decreasing pH. However, under reducing conditions, the solubility of Zn, Cu, Cd, and Pb is higher in alkaline pH, due to the formation of stable soluble organomineral complexes (Kiekens, 1983; USEPA, 1992b). On the other hand, if pH ranges between 4 and 6, the solubility of these metals will be lower because of the formation of insoluble sulphides or insoluble organo-mineral complexes (Kiekens, 1983).

Additives used for the Enhancement of Extraction of Soil Pollutants

Metal interaction in the soil varies considerably with the properties of the soil type (Naidu, Oliver & McConnell, 2003). The availability of metals is determined by the nature of the metal species, their interaction with soil colloids, the soil characteristics and the duration of contact with the binding surface (Naidu et al., 2003). Soil characteristics such as pH, clay and organic matter contents determine metal availability to plants by controlling metal speciation, adsorption-desorption processes, precipitation reactions and metal availability in soil solutions (Fotovat, Naidu & Suer, 1997; Naidu et al., 2003).

Chelates or acidifying agents are used to liberate the metals into soil solution, if the metal availability is low (Huang, Chen, Berti & Cunningham, 1997). The addition of metal chelates to the soil in order to significantly increase metal accumulation in plants as a strategy of phytoremediation is termed as chelate-assisted or induced phytoextraction (Garbisu & Alkorta, 2001). The formation of metal-chelate complexes prevents the precipitation and sorption of the metals, thereby maintaining their availability for uptake by plants (Salt, Blaylock, Kumar, Dushenkov, Ensley, Chet & Raskin, 1995). A significant proportion of many metals remains sorbed to solid soil constituents (Garbisu & Alkorta, 2001). Metal chelates are therefore of great relevance since cases of low metal bioavailability could occur in the soil for certain metal ions (Garbisu & Alkorta, 2001). The efficiency of metal accumulation is directly linked to the affinity of the applied chelate for the metal (Salt, Smith & Raskin, 1998). Therefore, synthetic chelates should have a high affinity for a particular metal pollutant, if efficient phytoextraction is to occur (Blaylock, Salt, Dushenkov, Zakharova & Gussman, 1997).

The extraction of soil pollutants by plants is increased by the amendment of soils with chelating agents such as ethylene diamine tetraacetic acid (EDTA), ethylene glycol tetraacetic acid (EGTA) (Blaylock et al., 1997) and soil acidifiers such as ammonical fertilizers (Salt et al., 1995). Trace metals have also been dislodged and dissolved from solids into soil solution using citrate acid and nitrilotree acetic acid (NTA) (Papassipi, Tambouris & Kontopoulos, 1997; Zeng, Sauvé, Allen & Hendershot, 2005).

Ethylene diaminetetraacetic acid (EDTA) and ethylene glycol tetraacetic acid (EGTA) have high affinities for lead and cadmium, respectively (Blaylock et al., 1997). EDTA increases the solubility of heavy metals although it does not directly affect plant accumulation of the metals (Blaylock et al., 1997). On the contrary, EDTA as a chelating agent has been observed to increase the concentration of metal contaminants in plant tissues (Huang et al., 1997; Mitch, 2002). The application of EDTA to established plants several days after harvest is very effective in facilitating the uptake of cadmium, copper, nickel, lead and zinc by plants (Raskin et al., 1997). Although the mechanisms involved in metal-chelate induced plant uptake and translocation are not well understood (Salt et al., 1998), it is likely that lead (Pb) is transported within plants as a Pb-EDTA complex (Garbisu & Alkorta, 2001).

Harter (1983) and Salt et al. (1995) have reported that at lower soil pH, the adsorption of heavy metals decreases and thus increases their concentration in soil solution. The availability and plant uptake of heavy metals could therefore be increased by maintaining a moderately acidic soil pH through the use of ammonium containing fertilizers or soil acidifiers (Salt et al., 1995).

Ethylene Di-amineTetra-Acetic acid (EDTA) as a Chelating Agent for the Extraction of Heavy Metals

The amount of plant-available metals in soil has been determined using different solutions, including 0.5 M Na_2EDTA, for their extraction (Savin Veselinovic & Markovic, 2004). Ammonium-EDTA (NH_4-EDTA) forms strong complexes with heavy metals (Sabienė, Brazuaskiene & Rimmer, 2004). NH_4-EDTA releases heavy metals from soil exchangeable (Kabata-

Pendias, 2001) and organically complexed pools (Podlesakova, Nemecek & Vacha, 2001). Ammonium-EDTA of pH 7 and concentration of 0.05 M can extract not only heavy metals involved in exchange processes, but also from organically bond complexes and those bound to carbonates (Sabienë et al., 2004).

The NH_4-EDTA-extracted heavy metals in soils and plants have a higher correlation than that between the total heavy metal content of soils and their amount in plants (Jones, Jarvis & Cowling, 1973). In England and other countries, 0.05 M NH_4-EDTA is widely used as an extractant for the determination of plant-available heavy metals (McGarth & Loveland, 1992).

Bioavailability and Bioaccumulation of Arsenic and Lead in Plants

According to Kertulis-Tartar et al. (2006), a plant is considered as a hyperaccumulator if its bioconcentration factor (BF) and the transfer factor (TF) are each greater than one. The BF is the concentration ratio of an element in plant tissue to the soil matrix while the TF is the concentration ratio of an element in plant shoots to its roots) (Kertulis-Tartar et al., 2006). The arsenic that is absorbed by the fern is mainly translocated from its extensive root system and accumulated in the above ground biomass (Tu, Ma & Bondada, 2002). Plants that are not hyperaccumulating species accumulate arsenic in a normal range of 0.1-5 mg As kg^{-1} dry weight in their leaves (Wauchope, 1983). The Chinese brake fern (*Pteris vittata* L.) accumulates 11.8-64.0 mg As kg^{-1} dry weight when grown in non-polluted soil (Ma, Komar, Tu, Zhung, Chai & Kennelly, 2001) and as much as 1442-7526 mg As kg^{-1} dry weight in their fronds in arsenic-contaminated soil (Ma et al., 2001; Tu & Ma, 2002).

Bioavailability has been defined variously by different authors. Campbell (1995) and Morel (1983) define bioavailability as the potential for a contaminant to diffuse from a bulk solution to a biological surface, bind with a cell wall or membrane, sorb or complex with the surface of a passive binding site within the protective layer of the cell and be transported across the plasma membrane. Toxicologists define bioavailability as the ability of a contaminant that is an orally ingested compound to be transferred into the systemic circulation in an organism (Zakrzewski, 1991). Bioavailability, according to Gregorich, Turchenek, Carter and Angers (2001), is defined as the readiness of a compound or element to be taken up by a living organism. In some cases the term is restricted to the supply of nutrients to biological organisms such as plants (Barber, 1984). Chemical and biological assays are used for the quantification of bioavailability.

Chemical assays assess potential bioavailability using chelating chemical substances such as resins that sorb available metals (Zhao, Sengupta, & Stewart, 1998). In a method to measure the availability of soil metallic ions to plants, using loaded or pre-treated resin, calcium-saturated sheets are placed in polypropylene bags and exposed to soil suspensions pretreated with cadmium, copper, and lead. The amounts of metal adsorbed by the resin sheet and the total metal concentration are highly correlated in the soil containing all three metals Cd, Cu and Pb. This serves as a good indicator of the phytoavailability of a combination of the metals Cd, Cu and Pb (Zhao et al., 1998).

The measurements obtained from biological assays are the most accurate estimate of bioavailability in a system. Studies by Campbell and Tessier (1996) and Geiszinger, Goessler, Kuehnelt, Francesconi and Kosmus (1998) evaluated bioavailability by collecting contaminated field samples of organisms and sediment. Chen and Chen (1999) and Figueira, Volesky, Azarian and Ciminelli (2000) sampled *Sargassum* seaweed and grey mullet, *Liza macrolepis* and exposed the organisms to various amounts of heavy metals such as cadmium, zinc, and copper. The metal uptake in the biomass was analyzed and compared to the initial injection amount. The studies were good estimates of metal bioaccumulation (Chen & Chen, 1999; Figueira et al., 2000).

Heavy metal contamination is continuously an environmental concern as long as these metals are not mediated from the ecosystem (Chen, Lee & Lui, 2000). Heavy metals can be transferred by intake of plants and human health as well as other organisms can be adversely affected through the ingestion of both water and food that have been contaminated by the soil (Chen et al., 2000). Heavy metals interact with the soil matrix and persist in the soil for long periods of time, creating long-term hazards on the environment and human health (Khalkaliani, Mesdaghinia, Mahvi, Nouri & Vaezi, 2006).

Soil additives such as zeolite, beringite, organic matter and biochar can be used to mediate arsenic- and lead-contaminated soils (Glaser et al., 2002; Oste et al., 2002; Lehmann & Rondon, 2006; Mench et al., 2006). There is the need for the determination of the bioavailability of heavy metals in soils after remediation. The bioavailability of heavy metals in mediated soils can be readily assessed using plants such as lettuce that accumulate substantial amounts of these metals in their edible aerial parts (Nadia & Zaghloul, 2007). The bioavailability and mobility of metals is important in assessing the potential health risk to the population because of the integration of metals in the food chain (Poggio et al., 2008). These problems created demands for the application of new technologies such as *in situ* immobilisation using amendments such as beringite, zeolite, poultry manure and biochar for minimizing the hazards of these pollutants.

The forgoing literature reviewed covers the effects and chemistry of cyanide and the heavy metals of interest in the research, standards for soil, plant and water quality and detoxification measures for contaminated water. The remediation of heavy metals, with emphasis on the use of zeolite, beringite, biochar and organic manure, has also been reviewed. The reviewed literature also includes the use of chelating agents such as EDTA that enhance the extraction of heavy metals. The bioavailability of metals for the evaluation of the effectiveness of remediation measures has also been reviewed. These will form the basis of the discussions of the results obtained in the research.

CHAPTER THREE

MATERIALS AND METHODS

Site Description

The research was conducted at the Obuasi Gold Mine, located 200 km North West of Accra in Ghana (AngloGold Ashanti, 2007a). Obuasi is located on latitude 6° 12' 0'' North and longitude 1° 40' 0'' West (Maplandia, 2005) (Figure 1). The study area, Obuasi, lies within the forest zone of Ghana. The area consists of primary forest of *Triplochiton-Celtis* association. It has a bimodal rainfall pattern. The annual rainfall ranges from 1200 to 2400 mm per annum. The highest and lowest temperatures recorded at AngloGold Ashanti, Obuasi mine, are 36.5 and 16.6 °C, respectively (AngloGold Ashanti, 2008a). The average pan evapo-transpiration at 0900 hours is 4.5 and the average Barometric Pressure (Para scientific) is about 98.500 (AngloGold Ashanti, 2008a).

The Obuasi mine is mainly an underground operation that possesses a total of 42.2 million tons of ore reserves (AngloGold Ashanti, 2007b). The Obuasi gold deposits occur along a zone of intensive shearing and faulting within the Precambrian greenstones. The mineral deposits are of two types, comprising quartz veins containing high-grade free gold and the main sulphide ore in which narrow veins contain gold trapped within arsenopyrite (AngloGold Ashanti, 2007a).

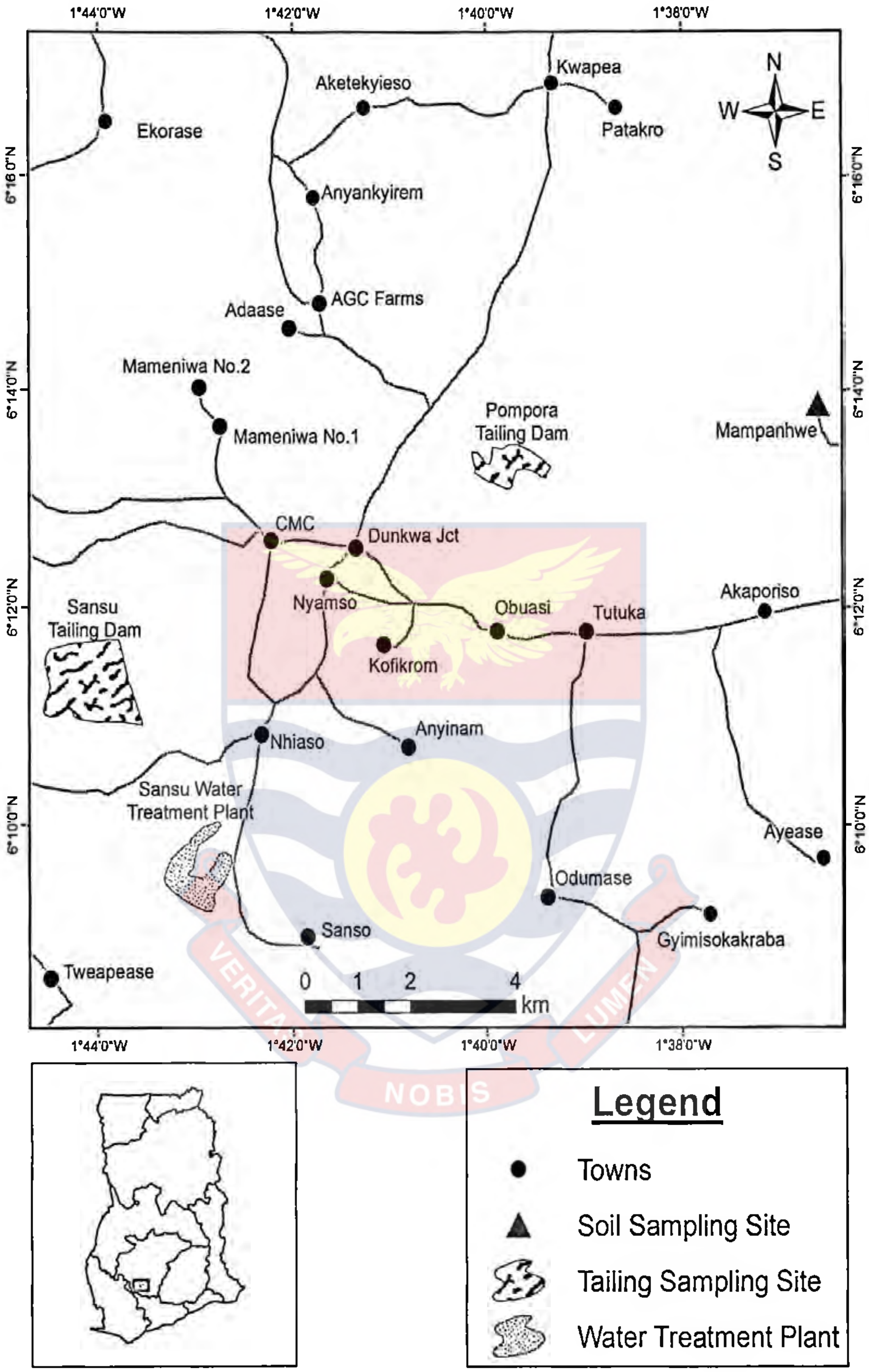


Figure 1. Location Map of the Study Area

Source: Google maps (2013)

The Obuasi mine processed up to 7 Mt yr^{-1} of gold ore until 2000 when the throughput was reduced to 5.3 Mt due to the care and maintenance of Pompora and oxide treatment plant and also the non- operation of the Heap Leach Plant (AngloGold Ashanti, 2007a). The soils of the study area are predominantly sandy clay loam and classified as Orthic-Ferric Acrisol (Adu, 1992; Food and Agricultural Organisation/International Union of Soil Sciences [FAO/IUSS], 2006). The river Jimi, which is a main tributary of the river Ankobra, flows into and out of the mining concession.

Soil Sampling

The soil samples were taken from four sites in June 2008. Three of the sites were active operational areas of AngloGold Ashanti, Obuasi mine. The control site, which constituted the fourth site, is within the concession but not yet mined. These sites were the reclaimed Pompora tailings dams I and II, Sansu tailings dam and the control which is located 12 km from Obuasi, along the Kabrakwa-Mampamhwe road (Figure 1). Soils were sampled at depths of 0 to 15 cm and 15 to 30 cm from the uncapped tailings at Sansu and the control sites. At the Pompora capped tailings sites I and II the refilled topsoil, which was predominantly made up of laterite, was sampled to a depth of 15 cm. Samples of the uncapped tailings located beneath the laterite were also taken from the 15 to 30 cm depth.

The sampling area demarcated for each of the four sites was one hectare. The zig-zag pattern of sampling was adopted and 30 soil cores were taken from each site and bulked. A composite sample of 500 g was used for subsequent analyses to establish the baseline properties of the soil.

Soil Preparation and Soil Analyses

The composite soil samples were air-dried for two weeks at the AngloGold Ashanti Environmental Section laboratory. The soil clods were crushed and pebbles and other foreign materials removed. The soils were stirred daily to hasten the drying process. The samples were then passed through a two millimetre (mm) nylon mesh. A sub-sample from the < 2 mm fraction was ground with a pestle and mortar and passed through a 0.15 mm nylon mesh for the determination of As, Pb, Cd, Fe, Zn and Cu. The initial soil properties of the study sites are presented in Tables 1 and 2.

Determination of Bulk Density

The procedure described by Anderson and Ingram (1993) was followed in the determination of the bulk density of soils from the different depths of the four sites sampled. The vegetation on the sampling spots was cleared and one centimetre of soil removed from the surface and then levelled. A cylindrical metal tube of known weight (W1) and volume (V) was driven into the soil. The volume of the soil was calculated from diameter (d) and height (h) of the cylinder using the formulae:

$$V = \pi(\frac{d}{2})^2 h \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (30)$$

The soil around the tube was evacuated and the soil beneath the tube cut. The metal tube with the soil was removed and the excess soil at the tube ends trimmed. The bulk density was taken in triplicate per soil depth. The samples were oven-dried at 105 °C for 48 hrs and the weight taken (W2). The bulk density (D_b) was calculated from the equation:

$$D_b = \frac{(W2 - W1)}{V} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (31)$$

Table 1: Some Properties of Soil/Tailings at the 0 – 15 cm depth

Soil property	Site			
	Non-mined	Capped Tailings I	Capped Tailings II	Tailings
Organic carbon (%)	2.13	0.63	0.55	1.02
Total N (%)	0.19	0.06	0.06	0.10
C: N ratio	11	11	9	10
pH (1: 2.5 - soil:water)	5.1	6.8	6.7	7.2
Extractable P - Bray I (mg kg^{-1})	6.58	16.57	4.17	1.53
Exchangeable cations (cmol$_c$ kg^{-1})				
Ca^{2+}	3.47	11.75	10.15	15.39
Mg^{2+}	1.60	8.54	3.47	9.61
K^{+}	0.21	0.42	0.41	1.40
Na^{+}	0.13	0.42	0.38	1.67
Total exchangeable bases (cmol$_c$ kg^{-1})	5.41	21.13	14.41	28.07
Exchangeable acidity (cmol$_c$ kg^{-1})	0.35	0.10	0.10	0.05
Effective cation exchange capacity (cmol$_c$ kg^{-1})	5.76	21.23	14.51	28.12
Bulk density (g cm^{-3})	1.26	1.33	1.32	1.39
Total porosity (%)	52.45	49.81	50.19	47.54
Soil texture				
Sand (%)	43.7	48.9	74	35
Silt (%)	46.3	41.1	24	61
Clay (%)	10	10	2	4

Table 2: Some Properties of Soil/Tailings at the 15 – 30 cm depth

Soil property	Site			
	Non-mined	Capped Tailings I	Capped Tailings II	Tailings
Organic carbon (%)	0.71	0.61	0.51	0.94
Total N (%)	0.08	0.06	0.05	0.08
C: N ratio	9	10	10	12
pH (1: 2.5 - soil:water)	3.8	6.8	7.0	7.2
Extractable P - Bray I (mg kg^{-1})	1.70	3.06	0.83	1.70
Exchangeable cations ($\text{cmol}_c\ \text{kg}^{-1}$)				
Ca^{2+}	1.34	5.87	10.95	15.49
Mg^{2+}	0.80	2.67	3.47	3.74
K^{+}	0.14	0.27	0.32	0.91
Na^{+}	0.07	0.10	0.17	0.96
Total exchangeable bases ($\text{cmol}_c\ \text{kg}^{-1}$)	2.35	8.91	14.91	21.10
Exchangeable acidity ($\text{cmol}_c\ \text{kg}^{-1}$)	1.10	0.10	0.05	0.05
Effective cation exchange capacity ($\text{cmol}_c\ \text{kg}^{-1}$)	3.45	9.01	14.96	21.15
Bulk density (g cm^{-3})	1.44	1.37	1.35	1.43
Total porosity (%)	45.66	48.30	49.06	46.04
Soil texture				
Sand (%)	38	40	71	33
Silt (%)	38	54	27	65
Clay (%)	24	6	2	2

Determination of Soil Water Content at Field Capacity

The procedure described by Anderson and Ingram (1993) was followed. The soil samples were taken two days after rainfall when the soil drained freely following saturation. An area of 1 m^2 was demarcated, cleared and covered with plastic sheet for 3 days so as to avoid evaporation of soil water. This was done in triplicate for the two depths of each of the four sites evaluated. Five soil cores were taken from the demarcated area and bulked. Subsamples of about 250 g of the wet soil were taken from the field. In the laboratory, 100 ± 0.005 g of the wet soil was placed in a pre-weighed petri-dish (W1) and the weight taken (W2). The samples were each oven dried at 105°C for 48 hr and weighed (W3).

The gravimetric soil water content (θg) at field capacity was calculated from the equation:

$$\theta g\ (\%) = \left[\frac{W2 - W3}{W3 - W1}\right] \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (32)$$

The volumetric soil water content (θv) at field capacity was calculated from the equation:

$$\theta v\ (\%) = \theta g \times Db \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (33)$$

Determination of Soil Water Content for Data Correction

Five grams of field fresh soil (±0.001 g) was weighed into a dry 200-mL cylinder of known weight (W1). The total weight of the cylinder and soil (W2) was recorded. The soil sample in the cylinder was oven-dried at 105 °C for two hours and reweighed until constant weight was obtained (Anderson and Ingram, 1993). The sample was cooled in a desiccator and the dry material plus the container weighed (W3). The dry mass equivalent of the moist field soil was calculated from the equations:

$$Water\ content\ (\%) = \frac{(W2 - W3)}{(W3 - W1)} \times 100 \dots\dots\dots\dots\dots (34)$$

$$Dry\ mass\ (g) = \left(\frac{100}{100 + \%\ water}\right) \times (W2 - W1) \dots. (35\ )$$

Determination of Cyanide and Heavy Metals in Effluent

Effluent Sampling and Preparation

The effluent of the AngloGold Ashanti, Obuasi mine, was sampled and analysed for free cyanide and some heavy metals in April 2008. The effluent samples were taken in black one-litre polyethylene bottles to minimize the degradation of cyanide by ultraviolet radiation. Samples were collected into the bottles after they had been initially rinsed with the effluent. Three grab samples were taken at different sampling points per effluent site. The oxidizing agent, chlorine, that can destroy cyanide in the effluent at the preservation stage, was neutralized by the addition of 5 ml of 0.06 % ascorbic acid per litre of effluent. The samples were placed in an ice chest at a temperature of about 4 ^{o}C, from the field to the laboratory. The pH of the effluent was measured with the portable Yokogawa pH metre. The pH of 50 ml of the subsamples to be analyzed for free cyanide were raised to 12 with NaOH solution to reduce losses due to volatilization of HCN and the transformation of CN^- into stable cyanide compounds at low pH (Young & Jordan, 1995). The 50 ml subsamples for the analyses of heavy metals were acidified with HNO_3 (0.1 % v/v) as a preservative (Chatterjee Das & Chakraborti, 1993).

Effluent Analyses

The concentrations of free cyanide (CN_F), As, Pb, Fe and Zn of the tailings dam, holdings pond and detoxified effluent from processed gold ore were also determined. Cadmium (Cd) and Cu, which form weak acid dissociable (WAD) metal-cyanide complexes that readily dissociate to release toxic free cyanide as well as the metal cations, were also determined. The analyses of the samples for free cyanide and heavy metal concentrations were conducted on the same day and within one week of sampling, respectively at the Analytical Laboratory of AngloGold Ashanti, Obuasi. The randomised complete block design with three replications was used. The levels of free cyanide and heavy metals were also compared with local and international standards.

The procedure adopted by AngloGold Ashanti (2006), briefly described as follows, was used for the determination of cyanide. A 10-mL test tube was filled with 6 ml of effluent sample. Effluent samples with free cyanide concentration more than the measurable maximum limit of 5 mg L^{-1}, as for the effluent of the tailings and holdings dams, were diluted and the dilution factor noted. The minimum free cyanide detection limit using the comparator was 0.03 mg L^{-1}.

The cyanide ion reacts with chlorine in chloro-T-amine to form cyanogen chloride as follows:

$$Cl_2 + CN^- \rightarrow ClCN + Cl^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (36)$$

The cyanogen chloride reacts with pyridine to form cyano-1-pyridine, via the equation:

$$ClCN + C_5H_5N \rightarrow C_5H_4NCN + Cl^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (37)$$

The cyano-1-pyridinethene reacts with dimethyl-1, 3 barbituric acid to form a complex dye with a red-blue coloration, that has an intensity that is dependent on the concentration of cyanide.

With the aid of micro-spoons provided by a cyanide determination kit, 0.04 g of each of the reagents, Chloro-T-amine powder (CN-1A) and Dimethyl-1, 3 barbituric acid (CN-2A) was added in sequence to the cyanide contaminated effluent. Three drops of the reagent Pyridine (CN-3A) was then added to the contents of the test tube and shaken for 1 min. A period of 5 min was allowed for the reactions to complete and the comparator used to determine the free cyanide level in the effluent.

The effluent samples were filtered through a 0.45 μm filter paper and the heavy metal content determined. Fifty millilitre samples of the filtrate were analyzed for As, Pb, Zn, Cu, Fe and Cd using the Atomic Absorption Spectrometer (AAS, Spectr AA 220) with an air/acetylene flame. The concentrations of As, Pb, Zn, Cu, Fe and Cd were measured at wavelengths of 193.7 nm, 283.3 nm, 213.9 nm, 324.8 nm, 248.3 nm and 228.8 nm, respectively.

Determination of Heavy Metals and Cyanide in Soils

Two heavy metal extraction procedures were used. These were the methods using DIN 38414 S4 (Din-Normen, 1984) and Ammonium ethylenediaminetetraacetic acid (EDTA). The concentration of As and Pb in Lettuce as an indicator crop of trace element bioavailability was determined using the Aqua regia digestion method.

Din-Normen Extraction

The DIN 38414 S4 (Din-Normen, 1984), a standard batch leaching test, which has been widely used for regulatory compliance and general assessment purposes in Germany and Austria was followed. Deionised water, that allows the test material to establish the pH, was added to each sample at a liquid to solid (L/S) ratio of 10:1. The soil suspension was shaken for 24 hours on a reciprocating shaker at 125 rpm. After the extraction, each of the resulting solutions was filtered through a 0.45 µm filter paper and the leacheate analyzed for soluble heavy metals.

Field moist soil samples were used for the determination of free cyanide concentration in June 2008. The moisture content of the soil was noted for data correction of dry mass determination. Although the same procedure of the DIN 38414 S4 (Din-Normen, 1984) extraction for the determination of heavy metals was followed in the determination of the free cyanide content of soils, the samples were shaken for only 30 min in air-tight black plastic bottles due to the high volatilization of the hydrocyanic acid component of free cyanide. The soil suspension was allowed to settle and immediately decanted for analyses. The same procedure adopted by AngloGold Ashanti (2006) for the determination of free cyanide in effluent was then followed.

Ethylene Di-amine Tetra-acetic Acid (EDTA) Extraction

Approximately 10.0 g of air-dried soil was weighed and then pulverized in a clean, nitric acid washed mortar and pestle, for the Ammonium tetra-sodium ethylene di-amine tetra-acetic acid (Na_4-NH_4-EDTA) extraction

(Agricultural Development & Advisory Services [ADAS], 1986; Sabienë et al., 2004). The soil was wrapped in a paper towel before being pulverized with the mortar and pestle to minimize the nitric acid washing necessary for the mortar and pestle. The soil was placed into a 100 ml conical flask and 50 ml of 0.05 M (Na_4-NH_4-EDTA) (pH 7) was added. The flask with the soil: Na_4-NH_4-EDTA mixture was shaken at room temperature on a mechanical shaker at 125 rpm for 1 hr (ADAS, 1986; Sabienë et al., 2004). The slurry was then passed through a filter paper into a sterile 100 ml conical flask. The filtrate was brought to exactly 100 ml with the extraction solution, and the filtrate was analyzed using the Atomic Absorption Spectrophotometer (AAS, Spectr AA 220). The concentrations of As, Pb, Zn and Cu were measured at wavelengths of 193.7 nm, 283.3 nm, 213.9 nm and 324.8 nm, respectively.

Aqua Regia Digestion

The aqua regia digestion procedure as adopted from Chen and Ma (2001) is briefly described as follows: A freshly prepared solution of aqua regia (HNO_3 – HCl (1:3 v/v) was used for the analysis. Well-mixed samples, each weighing of 1.0 g, were digested in 12 ml of aqua regia on a Tecator digester for 3 h at 110 °C. The samples were evaporated to near dryness and then diluted with 20 ml of 2 % (v/v with water) nitric acid and transferred into 100-ml volumetric flasks. The solutions were then filtered through Whatman no. 42 filters and diluted to the 50 ml mark for analysis.

Preparation of Plant Samples

The samples of aerial parts of lettuce were prepared using the procedure described by Dhargava and Raghupathi (1993). A brief description of sample preparation procedure is as follows: The fresh tissue was washed in sequence in detergent solution, dilute M/10 HCl (8 ml Conc. HCl/litre) and distilled water. The liquid detergent was used to remove waxy coatings on leaf surface and any soil particles while the M/10 HCl was used to remove metallic contaminants. The plant samples were then washed in distilled water to wash the previous two solutions used. The extra moisture was wiped out, then placed in new paper bags and dried in a well-ventilated oven at 70 °C to constant weight. The plant samples were homogenized using a mortar and pestle to avoid contamination of Fe from the cutting blade and Zn and Cu from the brass sieves. After grinding, the samples were placed in a desiccator before sampling for the analysis of Lead and Arsenic.

Statistical Analyses

The Genstat statistical package (Genstat, 2008) was used for the analyses of the data. The analysis of variance (ANOVA) was mainly used to determine the effects that the effluent detoxification method will have on the levels of free cyanide and the heavy metals, As, Pb, Zn, Fe, Cd and Cu. The ANOVA was also used for the analyses of the levels of As, Pb, Zn and Cu of different soils of the AngloGold mining environment and the effects of amendments (zeolite, beringite, poultry manure and biochar) on the concentrations of As and Pb in contaminated soil. The bioaccumulation of As and Pb in lettuce grown on mediated soil/tailings was also subjected to the ANOVA. The least significant difference (lsd) was used for the separation of means at the 95 % confidence level.

CHAPTER FOUR

COMPARATIVE STUDY OF CYANIDE AND ASSOCIATED HEAVY METALS IN TREATED EFFLUENT AND CAPPED TAILINGS AT THE ANGLOGOLD ASHANTI, OBUASI MINE

Introduction

The global economic and environmental climate has progressively changed in recent years and there is increasing pressure on mining companies to clean up toxic tailings (OECD, 2002). In Ghana, environmental pressure groups such as Association of Communities affected by Mining (WACAM), The National Coalition on Mining (NCOM) and Third World Network-Africa (TWN-Af) have expressed concerns over the magnitude of land degradation and water pollution that occur in mining environments. In some mining communities, the spent rocks from surface mining operations deposited on agricultural lands deprive the people who are predominantly farmers of their livelihoods (WACAM, 2003).

The heavy metals contained in the waste damps and deforested lands pollute rivers that serve as main sources of drinking water during heavy rainfall (WACAM, 2003; NCOM, 2009). Arsenic concentrations up to 350 µg L^{-1} has been reported to occur in stream waters affected by mining pollution in the Obuasi area of southern Ghana by Smedley (1996). Surface mining operations have resulted in stream pollution from cyanide spillages, acid mine drainage (AMD) and tailings leakages (Owusu-Koranteng, 2005). These activities have serious health implications and deprive the people in these communities access to the basic human need of good quality drinking water (Owusu-Koranteng, 2005; WACAM, 2008).

AngloGold Ashanti at Obuasi operates an underground mine (55 %) at depths up to 1 500 m, although open pit (35 %), heap leach (6 %) and surface mining (4 %) also take place (AngloGold Ashanti, 2007a). The mine operates three treatment plants, namely; the sulphide plant that treats ore from underground, the oxide plant processes open-pit and low grade ore and the tailings plant for material from reclamation operations (AngloGold Ashanti, 2007b). Cyanide compounds are used to extract gold at the AngloGold Ashanti, Obuasi mine. Cyanides are present in the effluent that results from the processing of gold (Khodadadi et al., 2005). Cyanide in the environment reacts with metal ions to form toxic metal cyanide complexes (Theis & West, 1986; Meeussen et al., 1992).

Many processes have been employed in the decontamination of effluent containing cyanide and associated heavy metals worldwide. These include natural degradation by ultraviolet radiation as in the tailings dam, oxidation by hydrogen peroxide (H_2O_2), oxidation by chlorination, Cyanisorb process and the INCO process involving oxidation by SO_2 (Akcil, 2003). Oxidation by ozone Acidification-Volatilisation-Recovery (AVR) process, Acidification-Volatilisation-Neutralisation (AVN) process, sulphidisation, acidification, recycling and thickening (SART), conversion into stable iron cyanide precipitates and increased solution pH by liming are the other decontamination measures (USEPA, 1994a). However, an integration of different effluent detoxification methods is used by the mine under study, until final discharge into natural water bodies. These are the use of H_2O_2, carbon-in-solution (CIS), photo-oxidation and Rotating Biological Contractors (RBCs) that involve bacterial degradation with *Pseudomonas* sp. at different points of effluent flow.

AngloGold Ashanti, Obuasi mine, has also carried out extensive reclamation of lands used for mining and the containment of heavy metals at tailings sites. However, there is no documentation of these activities. The main method of remediating heavy metals contained in tailings sites at AngloGold Ashanti, Obuasi mine, is through capping of contaminated soil with lateritic soil.

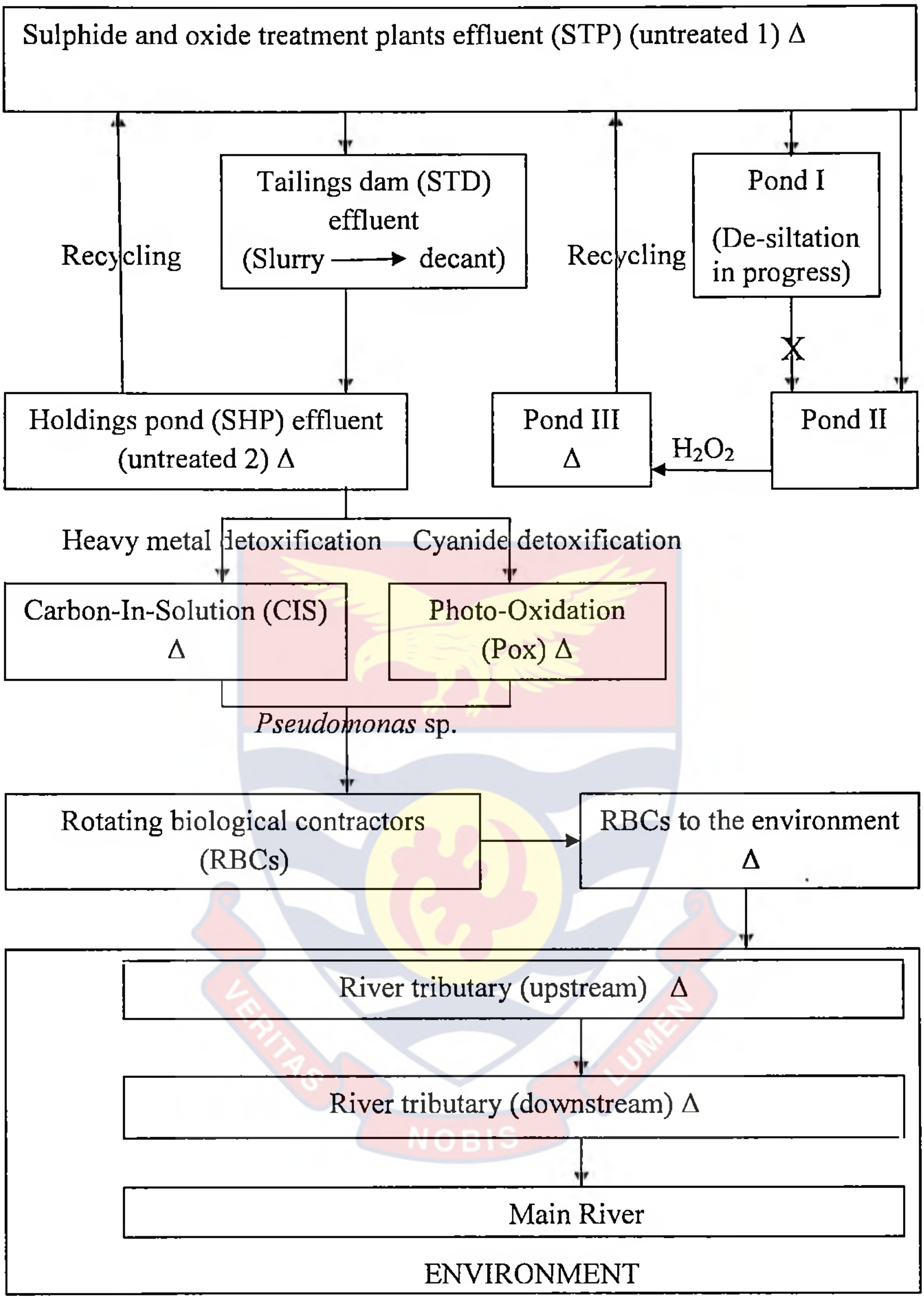
The specific objectives of this study were to:

1. Assess the effectiveness of the detoxification methods for cyanide and heavy metals in waste water.
2. Determine the effect of capping on the levels of free cyanide and heavy metals in tailings in the AngloGold Ashanti, Obuasi, concession in relation to local and international acceptable limits.

Materials and Methods

Effluent Flow and Discharge into the Environment

The flow chart process of effluent after gold extraction by the oxide and sulphide treatment plants before its discharge into the environment is illustrated in Figure 2. Briefly, the treatment of the processed gold ore effluent commences with its flow from the sulphide and oxide treatment plants. Since the oxidation reaction of the treatment plants results in the formation of sulphuric acid, $Ca(OH)_2$ is added to maintain the optimal reaction



Δ Sampling points used for data analysis

Figure 2. Flow Chart of the Detoxification Process of Milled Gold Ore Effluent

Source: Author’s construct (2008)

pH before discharge into the tailings dam and also impoundments 1 and 2 (Figure 1). Pond 1 which was designed to flow into Pond 2 was silted up so there was no flow of effluent from Pond 1 to Pond 2. The effluent in Pond 2 then flows into Pond 3 which is treated with hydrogen peroxide to detoxify cyanide. The supernatant wastewater from the tailings dam is then channelled into the holdings pond. Subsequently, the supernatant wastewaters from pond 3 and the holdings are recycled to the oxide and sulphide treatment plants for reuse.

The wastewater in the holdings pond undergoes the carbon-in-solution and photo-oxidation treatments for the detoxification of heavy metals and cyanide, respectively. The process of bacterial degradation for the detoxification of cyanide, using *Pseudomonas* sp., then takes place via the Rotating Biological Contractors (RBCs). The resultant treated wastewater produced through the processing of gold by AngloGold Ashanti, Obuasi mine, is channelled into a fish pond and subsequently released into the water course of the environment. A description of the wastewater detoxification methods is provided in Chapter Two – Literature Review.

The treated effluent flows into the environment at the upper course of the Nyame stream located near Nyamebekyere and into the lower course downstream at Apitikokoo. The water finally flows into the River Jimi which is a tributary of the river Ankobra and subsequently into larger water bodies. The decanted tailings slurry, that was previously treated with $Ca(OH)_2$, subsequently solidifies and is latter capped with lateritic soil.

Sampling and Preparation of Effluent and Soil, Chemical Analysis of Heavy Metals and Statistical Analysis of Data

The procedures that were followed in the sampling and preparation of the effluent and soil are described in detail in Chapter Three – General materials and methods. The chemical analysis of soils and effluent and also the statistical analysis of detoxification/remediation processes are similarly described in Chapter Three. The randomised complete block design with three replications was used in the experiment to determine the effect of capping on soil pH and the concentrations of free cyanide, As and Pb. However, multiplicative rather than additive effects were observed in the EDTA-extractable metal contents for the capped tailings, tailings and non-mined soil. The data on non-normally distributed variables (EDTA-extractable heavy metals) were log transformed to ensure the normality of residuals. The least significant difference (lsd) was used for the separation of means at the 95 % confidence level.

Results and Discussion

Temperature, pH and Free Cyanide of Untreated and Treated Effluent of the AngloGold Ashanti, Obuasi Mine

The results of the temperature, pH and free cyanide of the effluent produced by AngloGold Ashanti in April 2008 are presented in Table 3.

The pH of the treated effluent discharged ranged from 6.1 and 7.5. The raw effluent, with pH values between 7.6 and 7.7, were significantly higher than those of the treated effluent ($P < 0.05$) (Table 3). Free cyanide, in the form of hydrocyanic gas, is released at pH values less than 8 from mine waste

Table 3: Temperature, pH and Free Cyanide of Effluent of the AngloGold Ashanti, Obuasi mine

Treatment	Effluent		
	pH	Temperature (^{o}C)	Free cyanide (mg L^{-1})
Sulphide treatment plant effluent (untreated 1)	7.7	30.6	5.67
Hydrogen peroxide	7.2	30.3	0.23
Tailings decant (untreated 2)	7.6	31.1	31.67
Photo-oxidation	6.8	31.7	1
Carbon-In-Solution	7.5	30.5	10.67
Rotating Biological Contractors (Bacterial degradation)	6.1	30.6	0.43
Environment (upstream)	7	29.9	0.001
Environment (downstream)	6.8	29.8	0.001
lsd (0.05)	0.05	0.26	2.53
GEPA effluent discharge permissible maximum limit	6 – 9	29-30	0.2
IFC/ World Bank effluent guidelines	6 – 9	< 3° C differential	0.1
WHO guidelines for drinking water quality (2008)	n.h.c.[1]	n.l.[2]	0.07[3]

[1] Not of health concern at concentrations normally occurring in drinking water
[2] Not listed
[3] Total cyanide

which occurs in the form of tailings slurry or decant of wastewater (Young & Jordan, 1995). Cyanide volatilization rates increase further with decreasing pH (Young & Jordan, 1995). The pH of the untreated mine waste after gold extraction is therefore raised through the addition of calcium oxide, before its release. This could account for the higher pH of the untreated waste water in contrast to the treated effluent. It is worth to note that the pH of the feed of untreated wastewater need be sufficiently increased to ensure a higher pH of the discharged wastewater into the tailings dam. The pH values could be adjusted to value of 11 or higher so that the free cyanide will be hydrolyzed to produce aqueous hydrogen cyanide and not released as hydrocyanic acid (Young & Jordan, 1995).

The effluent pH of 6.1 after bacterial degradation was less than the values obtained for photo-oxidation, carbon-in-solution and hydrogen peroxide treatments ($P < 0.05$). A pH of less than 7 and a temperature of 25 °C are favourable conditions for hydrolysis of cyanate (OCN^-) produced after bio-oxidation into HCO_3^-, NH_4^+ and OH^- ions (Goldstein, 1976). This might explain why the lowest effluent pH condition was created after the metabolism of cyanide by thin films of the bacteria *Pseudomonas* sp. on rotating biological contractors (RBCs).

The operating effluent pH of 7.2 for the hydrogen peroxide treatment might not have been optimal to yield the desired reaction rate for an efficient reduction of the total cyanide, and subsequently the free cyanide levels in the effluent. This is because the formation of HCN and its volatilization into the atmosphere is optimal at pH less than 9.7 (Khodadadi et al., 2005). The pH value of 7.0 of the effluent discharged into the upstream water course was greater ($P < 0.05$) than the downstream pH of 6.8. Fluctuations occur in the water quality parameters of the rotating biological contractors (RBCs) and subsequently the composition of effluent discharged from the into the environment (AngloGold Ashanti, 2008b). The variations in the amounts of $Ca(OH)_2$ added to regulate effluent pH over time could have contributed to the higher pH of the water upstream. The soil of the AngloGold, Obuasi mining area at the 0 – 15 cm depth is acidic (pH of 5.1 ± 0.1) (Table 1). The soil solution that seeps from the acidic soil of the study area into the water course could have led to increased hydrogen ion activity at the lower course.

The pH of drinking water is considered by the World Health Organization guidelines to be of no health concern at levels normally found in drinking water (WHO, 2008). Nonetheless, compliance with the effluent discharge limits of 6.0 to 9.0 set by the Ghana Environmental Protection Agency (GEPA) is of great relevance. This could ensure that neither highly acidic nor too alkaline wastewaters are released into the environment. The pH of the discharged effluent is within the GEPA standards and the survival of the organisms that occur in the stream, into which it flows, may not be adversely affected.

Generally, the temperatures of both the treated and untreated effluent ranged from 30.3 ^{o}C to 31.7 ^{o}C. The temperature of the treated wastewater was significantly lower than that of the untreated effluent ($P < 0.05$). The hot tailings slurry, from which the untreated effluent is obtained, could account for its significantly lower temperature compared to the treated effluent. The slightly higher effluent temperature of the photo-oxidation treatment compared to the untreated effluent (+ 0.6 ^{o}C) could be ascribed to the greater exposure and absorption of energy from ultraviolet light to degrade the cyanide in the effluent enclosed in a relatively smaller reservoir (Malhotra et al., 2004). The upstream and downstream temperatures of the discharged effluent were not significantly different ($P > 0.05$).

The free cyanide levels of the untreated effluents (5.6 – 31.67 mg L^{-1}) were significantly higher than the levels in the treated effluent (0.23 – 10.67 mg L^{-1}) ($P < 0.05$) (Table 3). The mean concentration of free cyanide in treated wastewater ranged from 0.23 mg L^{-1} for the hydrogen peroxide treatment to 10.67 mg L^{-1} for the carbon-in solution (CIS) treatment. The free cyanide concentration of the effluent of the RBCs discharged into the environment was 0.23 mg L^{-1} above the effluent discharge limits set by the GEPA.

The efficiencies of the free cyanide remediation technologies (% decrease of the concentration of free cyanide) of the wastewater were in the following decreasing order: bacterial degradation (98.6 %) > photo-oxidation (96.8 %) > hydrogen peroxide (H_2O_2) (95.9 %) > CIS (66.3 %). The least efficient remediation technology was that of the CIS and bacterial degradation was the most efficient.

The % efficiency of free cyanide remediation attained using the H_2O_2 could be improved. If the optimal H_2O_2 concentration, temperature and an effluent pH above 7.2 are maintained to yield a residual effluent cyanide of zero for the H_2O_2 treatment, a 100 % decrease in free cyanide levels could be achieved. A zero residual effluent has been attained at a pH of 9.7, H_2O_2 concentration of 6.65 mg L^{-1} and a temperature of 35 °C by Khodadadi et al. (2005). The CIS treatment was mainly designed to reduce the levels of dissolved As, Pb, Cd, Zn, Fe and Cu in wastewater before final discharge into the environment. Thiocyanate (SCN^-) is adsorbed on the activated carbon that is utilized in the CIS treatment (Dictor et al., 1997). The thiocyanate, which is a weak acid dissociable species, is degraded into NH_4^+, which is later converted into NO_2^- and subsequently transformed into NO_3^- (Dictor et al., 1997). This could have accounted for the reduction in the concentration of free cyanide for the CIS treatment. Bacterial degradation potentially provides a relatively cheaper and more efficient means of cyanide degradation than chemical methods (Akcil, 2003). The highest efficiency of the effluent detoxification after passing through the RBCs confirms it.

Water Soluble As, Cd, Pb Cu, Zn and Fe Concentrations in Untreated and Detoxified Effluents

The data in Table 4 shows the concentrations of dissolved heavy metals, As, Pb, Cd Cu, Zn and Fe, in untreated and treated effluents. Significant differences were observed between treated and untreated effluents (Table 4).

Detoxification of Hazardous Heavy Metals (As, Pb and Cd)

The levels of dissolved As, Pb and Cd in the treated wastewater were significantly lower ($P < 0.05$) than those of the untreated wastewater (Table 4). The concentrations of the untreated effluent of the sulphide/oxide treatment plants (3.33 mg L^{-1}) and the tailings decant (5.04 mg L^{-1}) after the different detoxification treatments were in the ranges of As (1.7 to 4.35 mg L^{-1}), Pb (0.1 to 0.11 mg L^{-1}) and Cd (0.02 to 0.03 mg L^{-1}) (Table 4). Subsequently, this yielded effluent that was discharged from the RBCs into the environment with levels of As and Pb that were 21.78 and 1.06 fold the effluent discharge limits set by the GEPA. On the other hand, using the Environmental, Health and Safety (EHS) effluent guideline of the International Finance Corporation/

Table 4: Heavy Metal Concentrations in Effluent of the Study Area

	Dissolved metals (mg L^{-1})					
Treatment	As	Pb	Cd	Cu	Zn	Fe
Sulphide treatment plant effluent (untreated 1)	3.33	0.14	0.034	0.83	0.09	0.25
Hydrogen peroxide	1.70	0.10	0.029	0.35	0.05	0.21
Tailings decant (untreated 2)	5.04	0.18	0.034	2.05	0.12	0.18
Photo-oxidation	3.70	0.10	0.029	0.79	0.05	0.13
Carbon-In-Solution	4.23	0.11	0.018	0.44	0.04	0.13
Bacterial degradation	4.35	0.11	0.032	0.35	0.07	0.15
Environment (upstream)	0.95	0.04	0.020	0.03	0.05	0.16
Environment (downstream)	0.92	0.03	0.018	0.02	0.04	0.15
lsd (0.05)	0.086	0.008	0.002	0.047	0.01	0.012
GEPA maximum permissible limit	0.20	0.10	-	2.0	2.0	2.0
IFC/WB effluent guidelines (2007)	0.10	0.20	0.05	0.30	0.50	2.0
WHO guidelines for drinking water quality (2008)	0.01	0.01	0.003	2.0	n.h.c*	n.h.c*

*Not of health concern at concentrations normally occurring in drinking water

World Bank (IFC/WB, 2007), an assessment of the quality of the discharged wastewater, indicated that As, Pb and Cd concentrations differed respectively by factors of 43.54, 0.53 and 0.64. The guideline values are more stringent for As than Pb using the IFC/WB (2007) standards and vice versa for the GEPA (2006) limits.

Generally, except for As, the effluent concentrations of the metals under consideration were within acceptable limits. However, the trend of the toxicity of the effluent discharged into the environment based on these two standards decreased in the order As > Cd > Pb. An As concentration of 4.35 mg L^{-1} in the discharged wastewater possess a potential risk to the surrounding environment. This could be through the contamination of groundwater and downstream water bodies used for irrigation (Liu et al., 2010). The seepage of As, Pb and Cd into soil from the point of discharge could aggravate the environmental risks of farmers in the nearby communities.

The As, Pb and Cd concentrations in the water upstream were 78.2 %, 58.5 % and 37.5 %, respectively less than that of the effluent concentration discharged into the environment after bacterial degradation. The concentrations of As, Pb and Cd in lower course of the stream were 79.4 %, 72.7 % and 43.8 %, respectively greater than that of the treated wastewater discharged after bacterial degradation. These significantly lower levels of the dissolved metals with distance along the water course could be partly ascribed to the dilution effect as has similarly been observed by Huang et al. (2008). A consideration of the WHO (2008) guidelines for drinking water quality implies that the natural water body into which the effluent is discharged could be considered as contaminated with As, Pb and Cd if taken by inhabitants of the surrounding communities.

However, it is worth noting that although the typical natural levels of As in fresh water are less than 0.01 mg L^{-1} (Smedley & Kinniburgh, 2002) the levels of As in the water bodies, that flowed through upstream and downstream farming communities, were 0.95 mg L^{-1} and 0.92 mg L^{-1}, respectively. These values are also as much as 91.5 % to 94.9 % greater than the WHO (2008) guidelines for drinking water quality and could have harmful effects on human health if used as drinking water (Bhattachartya et al., 2002). Of greater concern, is the fact that, the soluble and exchangeable fractions of toxic metals in soils are the most important forms in relation to groundwater pollution and plant nutrition (Sastre et al., 2001).

Detoxification of Trace Metals (Zn, Cu and Fe)

Each of the different detoxification methods decreased the levels of Zn, Cu and Fe, but to varied extents (Table 4). The % decrease of the levels of the Zn, Cu and Fe for the different wastewater remediation technologies were hydrogen peroxide (H_2O_2) (44.4 %, 57.8 % and 16.0 %), CIS (66.7 %, 78.5 % and 27.8 %), photo-oxidation (58.3 %, 61.5 % and 27.8 %) and bacterial degradation (41.7 %, 82.9 % and 16.7 %) respectively (Table 5).

The % reduction in the level of Cu was least for the H_2O_2 treatment. This was possibly due to the use of Cu^{2+} as a catalyst in the oxidation of cyanide solution by H_2O_2 into CNO^- which is subsequently hydrolyzed into CO_3^{2-} and NH_4^+ (Akcil, 2003). The CIS process, which is mainly designed for the detoxification of heavy metals in wastewater, was the most effective treatment in reducing the levels of Cd, Zn and Fe. The CIS was also efficient in reducing the concentration of Cu in the wastewater. Moderate amounts of cyanide complexes of Cu and Zn are bio-degraded or bio-absorbed during bacterial treatment. In bacterial degradation, metal complexes of cyanides are converted into HCO_3^- and NH_3, while the freed metals are either precipitated from solutions or adsorbed by the bio-film (Akcil, 2003). The reduction in the

Table 5: Efficiency of Effluent Detoxification Methods in the Remediation of Heavy Metals

Treatment	As	Pb	Cu	Zn	Fe	Cd
	------------	------------	Concentration (mg L^{-1})	------------	------------	------------
Sulphide treatment plant effluent (control 1)	3.33	0.14	0.83	0.09	0.25	0.034
Hydrogen peroxide	1.70 (48.9)	0.10 (28.6)	0.35 (57.8)	0.05 (44.4)	0.21 (16.0)	0.029 (14.7)
Tailings dam effluent (control 2)	5.04	0.18	2.05	0.12	0.18	0.034
Photo-oxidation	3.70 (26.6)	0.10 (44.4)	0.79 (61.5)	0.05 (58.3)	0.13 (27.8)	0.029 (14.7)
Carbon-in solution	4.23 (16.1)	0.11 (38.9)	0.44 (78.5)	0.04 (66.7)	0.13 (27.8)	0.018 (47.1)
Bacterial degradation	4.35 (13.7)	0.11 (38.9)	0.35 (82.9)	0.07 (41.7)	0.15 (16.7)	0.032 (5.9)

Notes: Values in parenthesis represent the % reduction in heavy metals after detoxification. The % decrease for H_2O_2 was related to control 1 and those of the other detoxification methods to control 2.

effluent concentration of Cu and Zn might therefore have been due to degradation, precipitation or adsorption onto the bio-film of the rotating biological contractors.

The levels of the dissolved Zn and Fe in untreated and treated effluents were less than the GEPA (2006) standards. The level of dissolved Cu in the untreated processed gold ore tailings decant was 0.049 mg L^{-1}above the GEPA maximum permissible level of 2.0 mg L^{-1}. However, after treatment the Cu level in the effluent from the rotating biological contractors (RBCs) was decreased by 82.9 % to comply with the GEPA set limits before discharge into the environment (Table 5). In compliance to the set standard, a concentration of 0.35 mg L^{-1} was achieved at the point of discharge of the treated waste water into the environment (Table 4). The order of magnitude in the occurrence of dissolved metals was Cu > Fe > Zn in both the treated and untreated effluent. Generally, the levels of Zn, Cu and Fe in the treated effluent were below the WHO (2008) drinking water quality guidelines. Hence, with respect to Zn, Cu and Fe toxicity, the mining activities in the area do not pose a threat to the environment and human health.

Capping with Lateritic Soil for the Reclamation of a Closed Tailings Dam Site

The capping of tailings with lateritic soil is the main method of remediating heavy metal contamination in tailings sites at AngloGold Ashanti, Obuasi mine. Tables 6 and 7 present data on the effects of reclamation measures on the levels of water soluble heavy metals, pH, free cyanide and

EDTA-extractable As, Pb, Cu, Zn, Fe, Cd of soils, respectively in the AngloGold Ashanti mining environment at Obuasi.

Table 6: The content of EDTA-extractable heavy metals of soil/tailing in the AngloGold mining environment at Obuasi

	EDTA-extractable metals (mg kg^{-1})			
Soil	As	Pb	Cu	Zn
Non-mined (0-15 cm)	20.3 g	1.63 e	2.71 f	5.71 g
Non-mined (15-30 cm)	9.1 h	1.06 f	2.53 e	6.44 f
Capped tailings (site 1) (0-15 cm)	28.5 f	2.9 g	4.42 d	12.67 de
Capped tailings (site 1) (15-30 cm)	107.1 e	4.63 b	2.77 g	14.40 b
Capped tailings (site 2) (0-15 cm)	198.1 d	4.23 c	6.54 a	11.87 e
Capped tailings (site 2) (15-30 cm)	515.5 b	4.93 a	4.87 d	13.10 c
Uncapped tailings (0-15 cm)	725.6 a	4.01 d	6.01 b	12.77 d
Uncapped tailings (15-30 cm)	371.9 c	4.04 d	5.43 c	21.33 a
Canadian limits for Contaminated industrial (agricultural) sites (1991)	50 (20)	1000 (375)	500 (150)	1500 (600)

Table 7: **Levels of Water Soluble Heavy Metals, Free Cyanide and pH of Soil/Tailings in the AngloGold Ashanti Mining Environment at Obuasi**

Soil	Water soluble metals (mg L^{-1})						pH	Free cyanide (mg kg^{-1})
	As	Pb	Cu	Zn	Fe	Cd		
Non-mined (0-15 cm)	0.177e	0.023f	0.002c	0.007d	1.043a	0.002b	5.5d	0.01f
Non-mined (15-30 cm)	0.047e	0.019f	0.008b	0.009d	0.540b	0.001b	5.4e	0.01f
Capped tailings (site 1) (0-15 cm)	0.322d	0.054c	0.004c	0.020cd	0.124c	0.013b	6.5b	0.40d
Capped tailings (site 1) (15-30cm)	0.641 c	0.045d	0.008b	0.037bc	0.084cd	0.015ab	6.4c	0.47c
Capped tailings (site 2) (0-15 cm)	0.444d	0.048d	0.002c	0.043ab	0.094c	0.008b	6.5b	0.43cd
Capped tailings (site 2) (15-30cm)	0.932b	0.035e	0.010b	0.047ab	0.021d	0.037a	6.4c	0.20e
Uncapped tailings (0-15 cm)	2.672 a	0.135a	0.008b	0.037bc	0.136c	0.029a	7.3a	1.30a
Uncapped tailings (15-30 cm)	0.817bc	0.092b	0.023a	0.056a	0.117c	0.021a	7.3a	0.73b
lsd (0.05)	0.192	0.008	0.005	0.018	0.082	0.028	0.097	0.06

Note: Means with the same letters in a column are not significantly different from one another at the 95 % level of significance

Effects of Capping with Laterite on the Concentrations of EDTA-extractable Heavy Metals of Soils and Tailings in the AngloGold Ashanti Mining Environment at Obuasi

The effects of reclamation measures on the concentrations of EDTA-extractable heavy metals (As, Pb, Cu, Zn, Fe, Cd) of soils and tailings are presented in Table 6. The mean EDTA-extractable As levels of the non-mined soil at the 0 to 15 cm and 15 to 30 cm depths, which were 20.27 (± 0.5) and 9.1 (± 0.06) mg kg^{-1}, respectively, were within the Canadian limits for agricultural sites. The Canadian standards were used because there are no Ghana Environmental protection Agency (GEPA) set limits for soils.

The levels of As in non-mined soil were generally lower than those of the capped tailings and uncapped tailings at the 0 - 15 cm and 15 -30 cm depths ($P < 0.05$) (Table 6). At the 0 - 15 cm depth, the concentration of As in the capped tailings was significantly less than that of the uncapped tailings ($P < 0.05$). There might have been the capillary flow of AsO_4^{3-} from the uncapped tailings at the 15 - 30 cm depth to the previously unpolluted lateritic soil. Laterite predominantly consists of Fe oxides that strongly adsorb arsenate (AsO_4^{3-}) (Chakravarty et al., 2002). This could also have contributed to the significantly lower ($P < 0.05$) levels of EDTA-extractable As in the capped tailings compared to the uncapped tailings. Although the levels of EDTA-extractable As in the capped tailings (28.5 – 198.1 mg kg^{-1}) were significantly reduced ($P < 0.05$) compared to the uncapped tailings (725.6 mg kg^{-1}) at the 0 – 15 cm depth (Table 6), they were above the Canadian standards set for agricultural sites. These capped tailings would therefore not be suitable for agricultural purposes unless further remediation measures are adopted to reduce As to an acceptable level.

The levels of EDTA-extractable Pb, Cu and Zn in the non-mined soil, capped and uncapped tailings were significantly different from one another ($P < 0.05$). However, they were generally lower than the Canadian standards for both agricultural and contaminated soils (Table 6). The levels of these three metals in non-mined soil, capped and uncapped tailings of the AngloGold mining could therefore be considered safe to humans and other organisms.

Effects of Capping with Laterite on the Levels of Water Soluble Heavy Metals, pH and Free Cyanide in the AngloGold Ashanti Mining Environment at Obuasi

The results of the effects of the capping of tailings with laterite on the levels of water soluble heavy metals, pH, free cyanide is presented in Table 7. The separation of means indicated that the levels of free cyanide, water soluble As, Pb and Zn in the 0 -15 cm and 15 – 30 cm depths of non-mined soil were significantly lower ($P < 0.05$) than those of capped and uncapped tailings (Table 7). These higher levels of As and Pb, that are hazardous heavy metals, are of concern since the levels of water soluble As and Pb in the treated effluent discharged into the environment after bacterial degradation (Table 4) were higher than the GEPA (2006) standards for effluent discharge and the WHO (2008) guidelines for drinking water quality. The seepage of As and Pb from the capped and uncapped tailings could further increase their concentrations in water bodies.

The water soluble Pb contents of the capped tailings were also significantly lower than those of the uncapped tailings at the 0 – 15 cm and 15 – 30 cm depths ($P < 0.05$) (Table 7). The concentrations of dissolved Fe in non-mined soil, at the 0 – 15 cm and 15 – 30 cm depths, were significantly greater than those of the capped and uncapped tailings ($P < 0.05$) (Table 7). Except at the 0 – 15 cm depth of capped tailings (Site 1), the levels of Zn in soil solution were significantly lower in non- mined soil compared to the other treatments. These results are contrary to the finding of Salt et al. (1995) who reported that at lower soil pH, the adsorption of heavy metals decreases and thus increases their concentration in soil solution. Other factors that affect metal solubility/availability such as CEC, soil characteristics and the concentration of metal ions in the soil matrix (Table 6) might explain the results obtained.

The difference between the levels of Cd in the 0 – 15 cm depth of the capped and uncapped tailings was significant ($P < 0.05$). This indicated that the capping of tailings could be used to contain and reduce the level of exposure of Cd in tailings. The trend of the results for Cu in solution indicated that there were significantly higher levels at 0 – 15 cm than at 15 – 30 cm in non-mined soil, capped and uncapped and. The reverse of this pattern was observed for water soluble Pb (Table 7). The higher levels of copper in the lower soil horizons might be due to its attraction to soluble organic ligands that form complexes which increases the mobility of Cu in soils (USEPA, 1992b). On the other hand, Pb compounds of low solubility are formed in the presence of organic and inorganic ligands (Evanko & Dzombak, 1997). This coupled with the reaction of soluble Pb in soil with carbonates, clays, sulphates and hydroxides that lead to its retention of Pb (USEPA, 1992b), could be the reason for the significantly lower Pb in the 0 – 15 cm depth compared to the 15 – 30 cm depth.

The concentrations of free cyanide in the capped (0.2 - 0.47 mg kg^{-1}) and uncapped tailings (0.73 - 1.3 mg kg^{-1}) were significantly greater than that of the control (0.01 mg kg^{-1}) ($P < 0.05$) (Table 7). The levels of free cyanide in the capped soil at the 0 – 15 cm depth varied from 0.4 -0.43 mg kg^{-1} and were significantly lower than that of the uncapped tailings ($P < 0.05$). This might be explained by the formation of strong complexes of ferricyanide [$Fe(CN)_6^{3-}$] and ferrocyanide [$Fe(CN)_6^{4-}$] (Ebbs, 2004). The capping of tailings with lateritic soil could therefore be an effective method of reducing the levels of free cyanide in contaminated soil.

The mean pH of the non-mined soil at the 0 – 15 cm and 15 – 30 cm depths were 5.5 and 5.4, respectively (Table 7). These results show that the general pH of the non-mined part study area is highly acidic (Table 7). This is partly a reflection of the low total Ca (3.47 $cmol_c\,kg^{-1}$) and Mg (1.6 $cmol_c\,kg^{-1}$) content in the soil (Tables 1 and 2) and a higher H^+ ion activity for the 15 – 30 cm depth. Tailings generally exhibit acidic characteristics due to the oxidation of arsenopyritic (FeAsS) gold bearing rock to produce H_2SO_4 (Alloway &and Ayres, 1997). The pH of uncapped tailings (7.3) was, however, neutral at the 0 - 15 cm and 15 – 30cm depths (Table 7). This could be attributed to the addition of liming material [$Ca(OH)_2$] to increase the pH of the tailings slurry discharged into the tailings dam as observed by Gonzaléz and Gonzaléz-Chavéz (2006). An elevated amount of Ca^{2+} ions therefore occured in the uncapped tailings (Tables 1 and 2) that resulted in an increased pH and lower acidity. Gonzaléz and Gonzaléz-Chavéz (2006) similarly recorded neutral to slightly alkaline pH values of 7.1 – 8.4 for mine tailings and attributed it to the reaction of mine tailings with carbonates. The capping of tailing led to significantly less alkaline conditions than that of the uncapped tailings ($P < 0.05$) (Table 6) possibly due to inherently acidic pH (5.4 ± 0.04) of the laterite layer of soil.

Conclusions

The concentrations of free cyanide in the tailings mill effluents after treatment decreased by more than 90 % for the photo-oxidation, hydrogen peroxide and bacterial treatments. However, the levels of free cyanide released into the environment were 0.03 mg L^{-1} and 0.13 mg L^{-1} greater than the local (GEPA, 2006) and international (IFC/WB, 2007) effluent discharge limits, respectively. The efficiency of free cyanide detoxification of the different remediation processes could be improved by attaining an effluent pH of 9 – 10 and a copper catalyst concentration of 50 mg L^{-1}.

The carbon-in-solution (use of activated carbon), which is solely incorporated into the multiple detoxification chain to precipitate dissolved gold and heavy metals was the most efficient in the reduction of the levels of Fe, Zn and Cd. It is necessary to increase the number of absorbent columns containing the activated carbon to ensure a higher % decrease in the levels of As, Cu and Pb. The beneficiation of gold in the study area is from arseno-pyrite rock ores which result in the release of high amounts of As contained in the feed of tailings effluent. The high levels of As in the effluent discharges could be partly due to the low efficiency (14 - 49 %) of As remediation processes employed. However, the concentrations of Cu, Zn and Fe attained after the integration of the four tailings effluent detoxification processes were lower than the local and international set limits for effluent discharges. The levels of Cd and Pb released into the environment were also in compliance with the IFC/WB (2007) guidelines for effluent discharges although the water soluble Pb concentration was 0.01 and 0.1 mg L^{-1} higher than the GEPA (2006) and WHO (2008) standards, respectively. The incorporation of both chemical and biological processes could therefore have the potential to reduce the toxicity of gold mill effluent, if optimal conditions are created.

The levels of Zn, Cu, free cyanide in capped and uncapped tailings were within internationally set standards for soils. The concentrations of As (EDTA-extractable and water soluble) were not only significantly higher in capped and uncapped tailings compared to non-mined soil but also above maximum permissible limits for soil. Although the concentrations of EDTA-extractable Pb in capped and uncapped tailings were within the maximum permissible limits, these values were significantly greater than that of non-mined soil. The seepage of Pb from treated effluent, that has concentrations higher than the GEPA (2006) and WHO (2008) standards, into the surrounding water bodies and soil could further aggravate its levels. Lead (Pb) and arsenic (As) are non-essential elements recognized as health hazardous and all have resulted in major health problems as a result of environmental pollution (Berglund, Davis & L'Hermite, 1984).

CHAPTER FIVE

REMEDIATION AND BIOAVAILABILITY OF ARSENIC AND LEAD IN SOIL/TAILINGS AND CHANGES IN pH THROUGH THE USE OF INORGANIC (ZEOLITE AND BERINGITE) AND ORGANIC (POULTRY MANURE) AMENDMENTS

Introduction

The capacity of soils to retain and release metals can be an important factor to predict environmental impact of anthropogenic sources of these elements (Silveira et al., 2003). In Chapter Four, the concentrations of Pb and As in capped tailings in the AngloGold Ashanti, Obuasi mine were above the maximum permissible limits. There was therefore the need for the introduction of other supplementary remediation measures such as the application of zeolite, beringite and poultry manure to reduce the levels of As and Pb. These formed the basis of the study in this Chapter.

Pollution of soils by heavy metals such as Pb and As is of great global concern due to its adverse effects on the health of man and the environment (Ma & Rao, 1997). Heavy metals, unlike contaminants of organic origin, are generally non-degradable and persist in the soil for long periods of time (Adriano, Wenzel, Vangronsveld & Bolan, 2004). They also interact with the soil matrix and persist in the soil for long periods of time, creating long-term hazards on the environment (Khalkaliani et al., 2006). Heavy metals can therefore be transferred by intake of plants and human health as well as other organisms can be adversely affected through the ingestion of both water and food that have been contaminated by the soil (Chen et al., 2000).

Soil contamination has been identified as one of the main threats to soil quality (European Commission, 2006a). Governmental and regional institutions are increasingly giving attention to issues of soil pollution (European Commission, 2006b). Subsequently, initiatives have commenced to limit and prevent further soil degradation and to examine applicable remediation measures (Poggio et al., 2008). There has been extensive reclamation of lands used for mining and the containment of heavy metals at tailings site at AngloGold Ashanti, Obuasi mine. However, the documentation of these activities is inadequate. The scientific approach in assessing the effectiveness of the different soil/tailings decontamination methods is lacking.

Conventional soil remediation technologies, although suitable for relatively small and heavily contaminated areas, are financially and physically inefficient in extensive and moderately contaminated sites (Oste et al., 2002). The new techniques of treating contaminated soils emphasize among others immobilisation and stabilisation of potentially toxic elements (PTEs) (Vangronsveld & Cunningham, 1998). The capping of contaminated tailings with lateritic soil does not remove the contaminants from the soil (Kertulis-Tartar et al., 2006). This is, however, the main method of remediating heavy metals contained in tailings sites at AngloGold Ashanti, Obuasi mine.

Many soil amendments that have been screened for their potential to immobilize heavy metals in soils are alkaline materials such as beringite and zeolite (Edwards Rebedea, Lepp & Lovell, 1999; Oste et al., 2002; Mench et al., 2006). Organic amendments also affect heavy metal availability depending on the degree of humification, stability and solubility of metal chelates, pH and the redox condition of the soil (Ross, 1994; Shuman, 1999; Walker et al., 2003). The formation of metal complexes with soluble organic compounds can increase metal solubility (Almås et al., 1999; Shuman, 1999) while the formation of stable metal chelates can reduce metal solubility (Ross, 1994; Walker et al., 2003).

Metals such as arsenic and lead are highly toxic and pose a threat to human health (Dermatas et al., 2004; ATSDR, 1999a, b). Heavy metals can be transferred by plant intake and human health can be adversely affected through the ingestion of water and food that have been contaminated by the soil (Chen et al., 2000). Vegetables absorb heavy metals from contaminated soils and as aerial deposits from polluted environments (Zurera-Cosano, Moreno-Rojas, Salmeron-Egea & Pozo-Lora, 1984). Vegetables are suitable pollution indicators and used as test crops to assess the effectiveness of mediation of heavy metals in soil/tailings. The bioavailability of heavy metals in mediated soils can be readily assessed by growing plants such as lettuce that accumulate substantial amounts of these metals in their edible aerial parts (Nadia & Zaghloul, 2007).

The objectives of this study were therefore to:

i. Assess the extent of alkalisation or acidification of non-mined agricultural soil, tailings capping and uncapped tailings through the use of organic (poultry manure) and inorganic amendments (zeolite, beringite).

ii. Achieve specific objective iv. that was set in Chapter One – Introduction.

iii. Determine the most efficient amendment in reducing the bioavailability of arsenic and lead after mediation of non-mined soil, capped and uncapped tailings using *Lactuca sativa* as the test crop.

Materials and Methods

The soils were sampled from four sites of the AngloGold Ashanti, Obuasi, mining concession. These sites were the reclaimed Pompora tailings I, II, Sansu decanted tailings and non-mined agricultural soil (control). Top soils (0 – 15 cm) of the four sites were sampled.

One hectare of each of the four sites was sampled in a zig-zag pattern. Forty soil cores were taken from each site, bulked into four composite samples and transported to the AngloGold Ashanti Environmental Section laboratory. The soil samples were then prepared by air drying, crushing, discarding of foreign material, crushing and sieving through a 2-mm nylon mesh.

Five hundred grams (500 g) air dry soil from each of the four sites was placed in 0.5 L plastic containers. The soils/tailings were amended with zeolite and beringite at the rates of 0, 30 and 60 kg ha^{-1} (w/w) and poultry manure at the rates of 0, 3 and 6 t ha^{-1} (w/w). The soil/tailings samples were mixed thoroughly with the amendments and then moistened to field capacity. There were three replications of the imposed treatments. The completely randomised design was used. The samples were incubated at a mean room temperature of 25 ^{o}C in the laboratory and moistened weekly to maintain the soil at field capacity. The soils/tailings were sampled at 0, 4, 8 and 12 weekly intervals, mixing thoroughly before sampling. Five random sub-samples were taken with a spatula and bulked for analysis from each container at these time intervals. The pH, water-soluble and EDTA-extractable As and Pb concentrations were determined using the procedures described in Chapter Three (Materials and methods).

The bioavailability of As and Pb in the mediated soils/tailings was subsequently determined after the use of amendments zeolite, beringite and poultry manure. Lettuce (*Lactuca sativa*) was chosen as the plant indicator of the bioavailability of As and Pb due to the high accumulation of heavy metals in the edible leafy aerial parts (Nadia & Zaghloul, 2007).

The field practices for the cultivation of lettuce as described by Grubben (2004), although slightly modified, were followed. The lettuce seeds were planted in a seedbed that was shaded with oil palm fronds. The seedlings were pricked out three weeks after germination and planted at a spacing of 4 cm × 4 cm. The seedlings were nursed for another three weeks and subsequently transplanted into the containers/pots containing the mediated non-mined soil/tailings. The soil/tailings samples were then moistened to field capacity and then moistened weekly to maintain the soil/tailings at field capacity. Fertilizer was incorporated into the soil/tailings samples at the rates of 50 kg N ha^{-1}, 45 kg P $ha^{-1}$and 65 kg K ha^{-1}at the time of transplanting. At three-weeks after transplanting, 50 kg N $ha^{-1}$was applied as recommended by Grubben (2004). The aerial parts of the lettuce plants were harvested and prepared for the analysis of the concentrations of Arsenic and Lead following the procedure described in Chapter Three (General Materials and Methods).

The analysis of variance (ANOVA) was used to determine the effects of the amendments on pH, water-soluble and EDTA-extractable As and Pb in the non-mined soil, capped and uncapped tailings. The percentage change was used to explain the differences in the effects of the amendments. The percentage change in treatment effect on the value of the variable (arsenic, lead or pH) was extrapolated from the relationship:

$$\%\,\Delta\,Variable = 100\left(\frac{V_{x\,Rate} - V_0}{V_0}\right)$$

The percentage change in value of variable at any given rate of application of amendment is represented by $\%\,\Delta\,Variable$, the value of the variable at a specific rate of application is given by $V_{X\,Rate}$ and the value of the variable at 0 kg ha^{-1} rate of application is represented by V_0.

Results and Discussion

The results of the influence of different rates of application of the amendments zeolite, beringite and poultry manure on the pH, EDTA-extractable As and Pb and also water soluble As and Pb of non-mined agricultural soil, capped and uncapped tailings are presented and discussed in this section. Treatment effects were observed from the results on the different types, rates of application of amendments and incubation periods on the pH, EDTA-extractable and water soluble As and Pb of non-mined soil, capped and uncapped tailings ($P < 0.05$)(Tables 8 – 22). Generally, there were no significant differences in the concentrations of arsenic and lead ($P > 0.05$) at the zero kg ha^{-1} rate of applied amendments (Tables 11 – 22) for non-mined soil, capped and uncapped tailings.

Soil pH, Arsenic and Lead as Influenced by Type and Rate of Application and Type of Amendment at Different Incubation Periods in Different Soil/Tailings

The effects of different rates of application of the amendments (zeolite, beringite and poultry manure) on the pH of non-mined agricultural soil, capped and uncapped tailings are presented in Tables 8 – 10.

Table 8: Effects of Rate of Application and Type of Amendment on the pH of Non-Mined soil as Affected by Incubation Period

Amendment	Rate of application (kg ha^{-1})	Weeks after incubation		
		4	8	12
		------------------ Soil pH	------------------	------------------
Zeolite	0	5.3 d	5.3 e	5.3 d
	30	5.5 c	5.6 cd	5.6 c
	60	5.8 b	5.9 b	5.9 b
Beringite	0	5.3 d	5.3 e	5.3 d
	30	5.7 b	5.8 b	5.8 b
	60	6.2 a	6.3 a	6.4 a
Poultry manure	0	5.3 d	5.3 e	5.3 d
	30	5.5 c	5.5 d	5.6 c
	60	5.7 b	5.7 c	5.8 b

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

Table 9: Effects of Rate of Application and Type of Amendment on the pH of Capped Tailings as Affected by Incubation Period

Amendment	Rate of application ($kg\ ha^{-1}$)	Weeks after incubation 4	8	12
		----------------- Soil pH	----------------------	
Zeolite	0	6.5 cd	6.4 ef	6.4 ef
	30	6.6 bc	6.6 cd	6.6 cd
	60	6.7 ab	6.8 a	6.9 b
Beringite	0	6.5 cd	6.5 d	6.5 d
	30	6.7 ab	6.7 bc	6.7 c
	60	6.8 a	6.8 a	7.1 a
Poultry manure	0	6.4 d	6.5 de	6.5 de
	30	6.6 bc	6.3 f	6.3 f
	60	6.8 a	6.1 g	6.1 g

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

Effects of Amendments on the pH of Non-mined Soil, Capped and Uncapped Tailings

At 4, 8 and 12 weeks after incubation (WAI), there were significant differences ($P < 0.05$) in soil/tailings pH among the amendments at the different rates of application (Tables 8, 9 and 10). The application of beringite to non-mined soil, from 4 to 12 WAI, yielded the highest percentage change in soil pH of 20.7 % at application rate of 60 $kg\ ha^{-1}$. The addition of 60 $kg\ ha^{-1}$

Table 10: Effects of Rate of Application and Type of Amendment on the pH of Uncapped Tailings as Affected by Incubation Period

Amendment	Rate of application (kg ha^{-1})	Weeks after incubation		
		4	8	12
		---------------- Soil pH----------------------		
Zeolite	0	7.2 c	7.2 d	7.2 d
	30	7.3 bc	7.3 cd	7.3 cd
	60	7.4 ab	7.5 ab	7.5 b
Beringite	0	7.2 c	7.2 d	7.2 d
	30	7.4 ab	7.4 bc	7.4 bc
	60	7.5 a	7.6 a	7.7 a
Poultry manure	0	7.2 c	7.2 d	7.2 d
	30	7.4 ab	7.0 e	6.8 e
	60	7.5 a	6.8 f	6.5 f

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

beringite to uncapped tailings also resulted in a slight but significant increase in pH of 6.9 % compared to the un-amended samples between 4 WAI and 12 WAI ($P < 0.05$). Generally, the soil/tailings pH of non-mined soil, capped and uncapped tailings after the application of beringite at the rate of 60 kg ha^{-1} was significantly greater than un-amended samples (Tables 8, 9 and 10). At 12 WAI the application of 60 kg ha^{-1} of beringite to non-mined soil, capped and uncapped tailings resulted in significantly higher soil/tailings pH compared to the other amendments (zeolite and poultry manure) and non-amended soil ($P < 0.05$) (Tables 8, 9 and 10).

The pH of beringite varies between 8.0 and 11.0 depending on its origin (Lombi et al., 2002; Mench et al., 2006). Beringite-amended tailings produced a pH of 7.7 when applied at 60 kg ha^{-1}. The OH^- ions of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$, that is a constituent of beringite, could have neutralised the H^+ ions on the exchange complex (Vangronsveld et al., 1999). This possibly led to increased hydroxyl ions (OH^-) in soil solution and subsequently, increased the pH of beringite-amended soil/tailings. Basic cations such as Mg^{2+} and Ca^{2+}, derived from MgO and CaO, respectively, are constituents of beringite (Mench et al., 2006) also contributed to increased alkalinity of beringite –amended soil/tailings. The significantly higher pH of beringite-amended soils could thus be attributed to the high contents of the basic cations, Ca^{2+} and Mg^{2+} ions in beringite (Trgo et al., 2006) within the exchange complex after H^+ ions have been neutralised and Al^{3+} and Fe^{3+} ions precipitated.

The addition 60 kg ha^{-1} zeolite yielded soil/tailings pH values that were significantly greater than those of the control (0 kg ha^{-1}) at 4, 8 and 12 WAI ($P < 0.05$) for non-mined soil capped and uncapped tailings (Tables 8, 9 and 10). This could be accounted for not only by the exchange of H^+ ions in soil solution with Na^+ ions of zeolite, which has the general formula $Na_2O.Al_2O_3.xSiO_2.yH_2O$, but also the alkalisation of amended soils by zeolite that has a pH in the range of 7.0 to 9.2 (Edwards et al., 1999; Van Herwijnen et al., 2007; Panuccio et al., 2009).

Zeolites are alkaline alumino-silicates (Glisic, Glisic & Milosevic, 2009; Oste et al., 2002) and provide alkalinity to acid polluted soils (Shi, Shao, Li, Shao & Du, 2009). This possibly accounted to some extent to the increase in pH of the non-mined soil and uncapped tailings. Zeolites also have high cation exchange capacity due to the negative charges that are created by the substitution of Si^{4+} by Al^{3+} in the tetrahedral framework (Mohammed, 2002). A substantial exchange of the Na^{+} ions of zeolite for H^{+} ions in soil solution (Edwards et al., 1999; Trgo et al., 2006; Garau et al., 2007) might have also contributed to the increase in pH of the different soil/tailings.

At 4 WAI the percentage increases in the pH of non-mined soil amended with 30 kg ha^{-1} and 60 kg ha^{-1} poultry manure, extrapolated from the pH values (Table 8), were 3.8 % and 7.5 %, respectively compared to the pH of non-amended soil (0 kg ha^{-1}). Generally, the pH of poultry-amended non-mined soil, capped and uncapped tailings was significantly higher ($P < 0.05$) than un-amended soil /tailings at 4 WAI (Tables 8, 9 and 10). The pH value of the poultry manure amendment that was 8.6 (± 0.1) might have contributed to the rise in the pH of non-mined soil and capped tailings through the neutralisation of ions H^{+} by OH^{-} ions with these amendments compared to un-amended soils/tailings. Walker et al. (2004), similarly observed an increase in the pH of an acidic soil (pH = 5.29) amended with manure of a pH value of 9.09. Manures contain as much as 583 mg kg^{-1} of NH_4^{+}-N, 12.8 g kg^{-1} and 46.6 g kg^{-1} of phosphorus and potassium, respectively (Walker et al., 2004). The increase in soil /tailings pH could therefore be partly due to the replacement of H^{+} ions from soil solution by basic cations, especially K^{+} ions, which are a constituent of poultry manures. The significantly higher pH observed might also be attributed, in part, to the decomposition of poultry manures that could have led to the release NH_3 from NH_4^+-N and the adsorption of H^+ onto the exchange sites of the soil as explained by Pocknee & Summer (1997).

Thereafter, between 8 and 12 WAI, the pH values increased marginally with percentage changes of 3.7 % to 5.7 % and 7.5 % to 9.4% with the application of 30 kg ha^{-1} and 60 kg ha^{-1}, respectively of poultry manure compared to non-amended non-mined soil. According to Schwab, Zhu and Banks (2007), soil solution pH of aged cattle manure amended soil increased and reached a steady state within 12 days, after which minimal increases in pH occurred up to 30 days when compared to that of the control soil. A steady soil solution pH possibly occurred 4 weeks after the application of poultry manure with resultant minimal increases in soil solution pH at 8 and 12 WAI.

However, between 8 and 12 WAI, there were significantly lower pH values after the initial increase at 4 WAI in poultry manure-amended capped and uncapped tailings compared to un-amended tailings (Tables 9 and 10). The decomposition of aged manure could result in organic matter with an initially high concentration of fulvic acids that decreases with time. On the other hand, the concentration of humic acids of organic matter increases with time and more fulvic acids are produced by aged manure than compost (Chefetz, Hatcher, Hadar & Chen, 1996; Aoyama, 1996). These organic acids decrease the soil pH as noted by Schwab et al. (2007). The decrease in pH of poultry manure-amended capped and uncapped tailings from 8WAI to 12 WAI might have been due to the dominance of fulvic acids produced during the mineralisation of cattle and poultry. The initial increase and a subsequent decrease in pH of organic amendments is corroborated further by Garcia, Hernandez and Costa (1991) who reported of a decrease in pH of composted organic manure after an initial increase for the first 40 days.

At the end of the 12 weeks incubation period, significant differences in pH ($P < 0.05$) were also observed among the amendments applied at the rates of 30 and 60 kg ha^{-1} for non-mined soil, capped and uncapped tailings. Subsequently, the magnitude of soil/tailings pH, in decreasing order, was beringite > zeolite > poultry for the application of amendments at the rate of 60 kg ha^{-1} in non – mined soil, capped and uncapped tailings.

These trends in pH values by the different amendments could have an influence on the remediation of heavy metals and the subsequent suitability of tailings capping for agricultural purposes. The highest pH value attained through the use of beringite could have significant effects on the immobilisation of heavy metal ions in contaminated soil because of the decreased protons and increased reactivity of existing exchange sites for effective metal binding (Oste et al., 2002).

Effects of Amendments on EDTA-extractable Arsenic in Non-mined Soil, Capped and Uncapped Tailings

At 4 weeks after incubation (WAI), there were significant differences in EDTA-As ($P < 0.05$) between the amendments (beringite and poultry manure) applied at the rates of either 30 or 60 kg $ha^{-1}$and the control (0 kg ha^{-1}) in non – mined, capped and uncapped tailings (Tables 11, 12 and 13).

The concentration of EDTA-As was significantly lower when beringite was applied at 60 kg ha^{-1} (15.46 mg kg^{-1}) than at 30 kg ha^{-1} (17.02 mg kg^{-1})

Table 11: Effects of Rate of Application and Type of Amendment on EDTA- Extractable Arsenic of Non-Mined Soil as Affected by Incubation Period

Amendment	Rate of application (kg ha^{-1})	Weeks after incubation 4	8	12
		-- EDTA-extractable Arsenic (mg kg^{-1}) --		
Zeolite	0	20.01 c	19.95 c	20.04 c
	30	19.73 c	19.62 cd	19.55 d
	60	19.65 c	19.48 d	19.41 d
Beringite	0	19.76 c	19.79 cd	20.20 c
	30	17.02 d	16.35 e	16.18 e
	60	15.46 e	14.72 f	14.34 f
Poultry manure	0	19.75 c	19.79 cd	20.07 c
	30	25.83 b	28.41 b	29.16 b
	60	27.49 a	33.54 a	34.74 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

and decreased by 21.8 % and 13.9 %, respectively compared to the non-amended non-mined soil at 4 WAI (Table 11). The concentration of EDTA-As, when beringite was applied to capped tailings at 60 kg ha^{-1} (135.3 mg kg^{-1}) and 30 kg ha^{-1} (160.7 mg kg^{-1}) decreased by 24.5% and 10.3 %, respectively compared to the non-amended soil at 4 WAI (Table 12). A similar trend was observed for beringite-amended uncapped tailings at 4 WAI (Table 13). Generally, the concentrations of EDTA-As beringite applied at the rates of 30

Table 12: Effects of Rate of Application and Type of Amendment on EDTA- Extractable Arsenic of Capped Tailings as Affected by Incubation Period

Amendment	Rate of application (kg ha^{-1})	Weeks after incubation 4	8	12
		-- EDTA-extractable Arsenic (mg kg^{-1}) --		
Zeolite	0	178.6 c	177.9 cd	177.5 cd
	30	178.0 c	176.9 cd	176.4 cd
	60	177.1 c	175.1 d	174.6 d
Beringite	0	179.2 c	178.8 c	179.2 c
	30	160.7 d	156.6 e	153.6 e
	60	135.3 e	129.8 f	123.5 f
Poultry manure	0	178.2 c	178.4 c	179.0 c
	30	217.4 b	229.4 b	232.2 b
	60	234.0 a	257.9 a	262.3 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

and 60 kg ha^{-1} were significantly lower than ($P < 0.05$) that of non-amended non-mined soil, capped and uncapped tailings from 8 WAI to 12 WAI (Tables 11, 12 and 13). These results indicate that the exchangeable and strongly bonded fractions of arsenic in non-mined soil , capped and uncapped tailings that were extracted with 0.05 M EDTA buffered at pH 7 (Sabienë et al., 2004; Garau et al., 2007) decreased with the application of beringite at 4, 8 and 12 WAI. The extracting solution, Ammonium-EDTA (0.05 M, pH 7) extracted

Table 13: Effects of Rate of Application and Type of Amendment on EDTA- Extractable Arsenic of Uncapped Tailings as Affected by Incubation Period

Amendment	Rate of application (kg ha^{-1})	Weeks after incubation 4	8	12
		-- EDTA-extractable Arsenic (mg kg^{-1}) --		
Zeolite	0	789.0 c	789.7 c	790.3 c
	30	787.4 cd	785.8 de	784.7 d
	60	786.1 d	784.5 e	783.5 d
Beringite	0	789.8 c	789.3 c	790.4 c
	30	744.8 e	743.1 f	738.7 e
	60	725.9 f	722.5 g	716.2 f
Poultry manure	0	787.7 cd	787.9 cd	789.5 c
	30	851.0 b	868.1 b	874.8 b
	60	875.9 a	903.1 a	916.0 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

significantly lower concentrations of As compared to un-amended non-mined soil capped and uncapped tailings due to the formation of As complexes that are strongly bonded in the inner sphere of beringite (Sabienë et al., 2004; Mench et al., 2006; Garau et al., 2007). The complexation of As to form calcium arsenate occurs in the inner sphere of ettringite that is a constituent of beringite (Mench et al., 2006). Furthermore, the adsorption of As due to the presence of Ca^{2+} and Mg^{2+} ions in beringite contributes to a decrease in extractable As in contaminated soil (Trgo et al., 2006). The presence of bivalent cations, in ettringite that is a constituent of beringite, aids in the adsorption of As which is not easily desorbed (Chakravarty et al., 2002; Mench et al., 2006). The adsorption and complexation of As through the application of beringite could therefore be the major factors contributing to the concentration of As-EDTA compared to the control. A decrease of 34 % in extractable arsenic in contaminated soil has similarly been obtained and attributed to the presence of bivalent cations (Ca^{2+} and Mg^{2+}) in beringite that aid in the adsorption of arsenic (Trgo et al., 2006).

The rate of application of zeolite resulted in an insignificant ($P > 0.05$) concentration of EDTA-extractable arsenic compared to un-amended non-mined soil when applied at 4 WAI (Table 11). Also, at 8 and 12 WAI, the concentrations of EDTA-As were similar ($P > 0.05$) in zeolite-amended non-mined soil at rates 30 and 60 kg ha^{-1} with values in the ranges of 19.55 mg kg^{-1} to 19.62 mg kg^{-1} and 19.41 mg kg^{-1} to 19.48 mg kg^{-1}, respectively but significantly lower ($P < 0.05$) than non-amended soil (Table 12). Similarly, the uncapped tailings amended with 30 kg ha^{-1}zeolite gave the same effect as 60 kg ha^{-1} zeolite amended uncapped tailings, in terms of the concentration of As-EDTA, at all the time-points of the incubation period ($P > 0.05$) (Table 12). There were relatively higher percentage decreases in the concentrations of As-EDTA of zeolite amended tailings capping from zero WAI to 4 WAI and subsequently lesser decreases from 4 WAI to 8 WAI and 8 WAI to 12 WAI (Table 12).

At 8 and 12 WAI, the concentration of EDTA-extractable As was significantly lower ($P < 0.05$) in zeolite-amended non-mined soil and uncapped tailings than in non-amended (Tables 11 and 13). The chemisorption of As in the zeolite framework (Edwards et al., 1999) that possess both acidic and basic sites (Trgo et al., 2006) might have led to the significantly lower concentration of available As extracted with 0.05 M EDTA compared to un-amended non-mined soil and uncapped tailings at 12 WAI (Tables 11 and 13).

At 4, 8 and 12 WAI, there was no significant difference in As-EDTA between the 30 kg ha^{-1} and 60 kg ha^{-1} rates of application of zeolite ($P > 0.05$) at all the time points of the incubation experiment. At 4, 8 and 12 WAI, the concentration of As-EDTA of capped tailings amended with either 30 kg ha^{-1} or 60 kg ha^{-1}of zeolite was not significantly different to that of un-amended capped tailings (0 kg ha^{-1}) ($P > 0.05$)(Table 12). Zeolite has a high surface area (700 m^2 g^{-1}) and CEC of 98 – 560 cmol kg^{-1} depending on its source (Oste et al., 2002; Garau et al., 2007; Panuccio et al., 2009). The low affinity of negatively charged component of zeolite particles for anionic metals such as AsO_4^{3-} and AsO_2^- might have resulted in the insignificantly different levels of As-EDTA compared to un-amended tailings capping (Table 12). Therefore, zeolite may not be effective in the immobilisation of arsenic since at 12 WAI it showed no effects on the levels of As- EDTA when applied to capped tailings irrespective of the rate of application compared to un-amended tailings capping at similar rates ($P < 0.05$) (Table 12).

The application of 60 kg ha^{-1} of poultry manure in non-mined soil, capped and uncapped tailings gave significantly higher levels of As-EDTA (P

< 0.05) compared to the 30 kg ha^{-1} rate of application from 4 to 12 WAI (Tables 11, 12 and 13). Generally, the application of either 30 kg ha^{-1} or 60 kg ha^{-1} poultry manure gave significantly greater levels of As-EDTA compared to un-amended non-mined soil capped and uncapped tailings at all the time-points (4, 8 and 12 WAI) of the incubation experiment ($P < 0.05$) (Tables 11, 12 and 13). The fulvic acid component of the organic matter, that dominates during the initial stages of the decomposition of aged cattle manure, form unstable complexes while the humic substances form stable chelates with heavy metals in the soil (Almås et al., 1999; Shuman, 1999; Walker et al., 2003; Walker et al., 2004). The significantly higher concentrations of EDTA-As might have resulted from the chelation of arsenic with the fulvic substances of organic matter contained in the applied poultry manure.

The redox transformation, toxicity and fate of arsenic in soils is affected by a high organic matter that results in a reaction sequence that is driven towards methylation and volatilization (Woolson, 1977). Arsenic (V) [$H_2AsO_4^-$] which dominates under oxidizing conditions is reduced to Arsenic (III) [H_3AsO_3] with a substantial increase in organic matter (Evanko & Dzombak, 1997; Turpeinen et al., 2002). The As (III) [H_3AsO_3] formed more soluble complexes and was more mobile than the As (V) [$H_2AsO_4^-$] (Panstar-Kallio & Manninen, 1997; Stronach, Walker, Macphee & Glaser, 1997) of the amended samples. Subsequently, formation of weakly bond As (III) organic complexes that was easily extracted with 0.05 M EDTA might explain the significantly higher concentrations of As-EDTA in poultry manure-amended non-mined soil, capped and uncapped tailings than un-amended samples.

The concentrations of EDTA-As, 4 WAI of amendments at rates of 30 and 60 kg ha^{-1} were in the following increasing order: beringite < zeolite < poultry manure in the non-mined soil , capped and uncapped tailings (Tables 11, 12 and 13). At 8 WAI and the end of the incubation experiment (12 WAI), the concentrations of soil EDTA-extractable arsenic, in decreasing order of magnitude, was beringite < zeolite < poultry manure at both the 30 kg ha^{-1} and 60 kg ha^{-1} rates of application in the soil/tailings (Tables 11, 12 and 13). Beringite was the most effective amendment for the adsorption and immobilisation of arsenic in non-mined soil, capped and uncapped tailings at the end of the incubation experiment.

Effects of Amendments on Water-soluble Arsenic in Non-mined Soil, Capped and Uncapped Tailings

Tables 14, 15 and 16 show the results of the effects of the application of different rates the four amendments (zeolite, beringite and poultry manure), at the different incubation periods, on water soluble arsenic in non-mined soil, capped and uncapped tailings. The levels of water soluble arsenic (As-H_2O) after the application of either 30 kg ha^{-1}or 60 kg ha^{-1} beringite to non-mined soil, capped and uncapped tailings resulted in significant successive decreases in As-H_2O at 4, 8 and 12 WAI compared to un-amended soil (0 kg ha^{-1})($P < 0.05$)(Tables 14, 15 and 16). The decrease in extractable arsenic in contaminated soil/tailings (Tables 11, 12 and 13) occurred possibly due to the presence of bivalent cations (Ca^{2+} and Mg^{2+}) in beringite that aid in the adsorption of arsenic (Trgo et al., 2006). This could have resulted in the significantly lower concentration of As-H_2O of beringite-amended soil/tailings

Table 14: Effects of Rate of Application and Type of Amendment on Water Soluble Arsenic of Non-Mined Soil as Affected by Incubation Period

Amendment	Rate of application (kg ha^{-1})	Weeks after incubation 4	8	12
		----- Water soluble Arsenic (mg L^{-1}) -----		
Zeolite	0	0.229 c	0.229 c	0.228 c
	30	0.238 c	0.236 c	0.237 c
	60	0.234 c	0.233 c	0.233 c
Beringite	0	0.229 c	0.229 c	0.228 c
	30	0.095 d	0.088 d	0.089 d
	60	0.045 e	0.036 e	0.035 e
Poultry manure	0	0.229 c	0.229 c	0.229 c
	30	0.324 b	0.341 b	0.345 b
	60	0.416 a	0.438 a	0.461 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

compared to un-amended samples. The reduction in extractable As-EDTA (Tables 11, 12 and 13) as a result of the complexation of arsenic to form calcium arsenate in the inner sphere of ettringite that is a constituent of the beringite structure and the sorption of As in beringite (Mench et al., 2006) could also be assigned to the significantly lower ($P < 0.05$) concentration of water soluble As in beringite-amended samples compared to un-amended samples in non-mined, capped and uncapped tailings (Tables 14, 15 and 16).

Table 15: Effects of Rate of Application and Type of Amendment on Water Soluble Arsenic of Capped Tailings as Affected by Incubation Period

Amendment	Rate of application ($kg\ ha^{-1}$)	Weeks after incubation 4	8	12
		----- Water soluble Arsenic ($mg\ L^{-1}$) -----		
Zeolite	0	0.446 cd	0.445 c	0.446 cd
	30	0.438 d	0.446 c	0.450 c
	60	0.438 d	0.441 c	0.442 d
Beringite	0	0.446 cd	0.447 c	0.446 cd
	30	0.316 e	0.304 d	0.299 e
	60	0.289 f	0.222 e	0.201 f
Poultry manure	0	0.452 c	0.446 c	0.446 cd
	30	0.539 b	0.588 b	0.606 b
	60	0.674 c	0.728 a	0.799 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

There was no significant difference in the level of As-H_2O between zeolite applied at either 30 kg ha^{-1} or 60 kg ha^{-1} and un-amended uncapped tailings at 4 WAI ($P > 0.05$). At 8 and 12 WAI, the application of 60 kg ha^{-1} zeolite gave the same effects as un-amended uncapped tailings ($P > 0.05$) (Table 16). The insignificantly different concentrations of water soluble As compared to un-amended samples at the 60 kg ha^{-1} rate of application (Table 16) indicates that zeolite is ineffective in remediating/immobilizing arsenic in uncapped tailings.

Table 16: Effects of Rate of Application and Type of Amendment on Water Soluble Arsenic of Uncapped Tailings as Affected by Incubation Period

Amendment	Rate of application (kg ha^{-1})	Weeks after incubation 4	8	12
		----- Water soluble Arsenic (mg L^{-1}) -----		
Zeolite	0	3.11 c	3.11 d	3.11 d
	30	3.15 c	3.22 c	3.24 c
	60	3.12 c	3.13 cd	3.14 d
Beringite	0	3.11 c	3.11 d	3.11 d
	30	2.20 d	1.81 e	1.60 e
	60	1.99 e	1.14 f	0.87 f
Poultry manure	0	3.11 c	3.11 d	3.11 d
	30	3.33 b	3.53 b	3.60 b
	60	3.89 a	4.05 a	4.11 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

The high pH of zeolite (7.0 – 9.2) and the resultant neutral to slightly alkaline pH of zeolite-amended uncapped tailings (7.3 – 7.5) could lead to a decrease in the sorption of As. Arsenic solubility increases with increasing pH (Farrel and Jones, 2010). These might have contributed to the insignificantly lower concentration of As-H_2O of 60 kg ha^{-1} ($P > 0.05$) and significantly higher level of As-H_2O in 30 kg ha^{-1} ($P < 0.05$) zeolite-amended uncapped tailings compared to un-amended samples.

The concentration of As-H_2O was not significantly different between un-amended samples (0 kg ha^{-1}) and non-mined soil/capped tailings amended with either 30 kg ha^{-1} or 60 kg ha^{-1} zeolite throughout the incubation periods at 4, 8 and 12 WAI ($P > 0.05$) (Tables 14 and 15). The concentration of As-EDTA adsorbed onto the soil/tailings was not significantly different with the application of either 30 kg ha^{-1} or 60 kg ha^{-1} zeolite compared to un-amended capped tailings at the end of the incubation experiment (Table 14). This implies that there were slight and insignificant changes ($P > 0.05$) in the adsorption of extractable and available arsenic within the soil matrix. Hence the insignificantly different ($P > 0.05$) levels of water soluble arsenic extracted from zeolite and un-amended capped tailings.

On the contrary, the application of, either 30 kg ha^{-1} or 60 kg $ha^{-1}$of poultry manure produced significantly higher levels of As-H_2O compared to non-amended soils at 4, 8 and 12 WAI ($P < 0.05$) in non-mined soil, capped and uncapped tailings (Tables 14 – 16). An increase in the pH of soils has been noted to be positively correlated with the increased concentration of potentially toxic elements in soil solution and also decreased adsorption of arsenic (Cao et al., 2003; Farrell & Jones, 2010). The increased pH that occurred with the application of poultry manure to non-mined soil (Table 8) possibly contributed to the significantly high concentrations of arsenic in soil solution compared to un-amended soil.

The reduction of As (V) to As (III) in poultry and organic manure amended capped tailings may could lead to the formation of As (III)-organic complexes that are highly mobile (Panstar-Kallio & Manninen, 1997; Stronach et al., 1997). Therefore, the redox state of As might have partially accounted for the significantly higher levels of water soluble arsenic in poultry manure-amended capped tailings compared to the un-amended samples (Table 9).

The pH of poultry manure-amended uncapped tailing (6.5 – 6.8) were significantly lower than that of un-amended samples (Table 10). Fulvic acids produced from the decomposition of manure increases metal solubility (Shumann, 1999). The dominance of fulvic acids over humic acids might have resulted in the significantly higher concentrations of As-H_2O ($P < 0.05$) in poultry manure-amended uncapped tailings compared to un-amended samples.

The concentration of As-H_2O, in decreasing order, when either 30 kg ha^{-1} or 60 kg ha^{-1} rate of application and type of amendment at the end of the incubation experiment was as follows: poultry manure > zeolite > beringite. Beringite was thus the most effective in reducing the concentration of water soluble arsenic in non-mined soil, capped tailings and uncapped tailings.

Effects of Amendments on EDTA-extractable Pb in Non-mined Soil, Capped and Uncapped Tailings

The results of the effects of type and rate of application and type of amendment on the concentration of EDTA-extractable lead (Pb-EDTA) in non-mined soil, capped and uncapped tailings at the different incubation periods are presented in Tables 17, 18 and 19. The general trend after the application of all the amendments in non-mined soil, capped and uncapped tailings was an initial high percentage change in Pb-EDTA from zero WAI to 4 WAI (Tables 17, 18 and 19). This was subsequently followed by successively lower decreases in the concentration of Pb-EDTA between 4 and

Table 17: Effects of Rate of Application and Type of Amendment on EDTA-Extractable Lead of Non-Mined Soil as Affected by Incubation Period

Amendment	Rate of application ($kg\ ha^{-1}$)	Weeks after incubation 4	8	12
		-- EDTA-extractable Lead ($mg\ kg^{-1}$) --		
Zeolite	0	1.707 c	1.7 c	1.71 c
	30	1.557 d	1.503 d	1.477 d
	60	1.297 f	1.167 f	1.143 f
Beringite	0	1.703 c	1.703 c	1.7 c
	30	1.577 d	1.523 d	1.5 d
	60	1.507 e	1.447 e	1.397 e
Poultry manure	0	1.693 c	1.703 c	1.707 c
	30	1.94 b	2.043 b	2.103 b
	60	2.297 a	2.577 a	2.703 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

8 WAI and from 8 WAI to 12 WAI (Tables 17, 18 and 19).

In non-mined soil, the application of 60 kg ha^{-1} of zeolite gave significantly lower concentrations of Pb-EDTA than those of un-amended soil and soils amended with berigite at 4, 8 and 12 WAI ($P < 0.05$) (Table 17). However, the application either 30 kg ha^{-1} or 60 kg ha^{-1} of zeolite gave the lowest concentrations of Pb-EDTA in capped and uncapped tailings ($P < 0.05$) from 4 to 12 WAI (Tables 18 and 19). The significantly lower levels of Pb-

Table 18: Effects of Rate of Application and Type of Amendment on EDTA-Extractable Lead of Capped Tailings as Affected by Incubation Period

Amendment	Rate of application (kg ha^{-1})	Weeks after incubation 4	8	12
		-- EDTA-extractable Lead (mg kg^{-1}) --		
Zeolite	0	3.99 c	4.01 c	4.01 c
	30	3.76 e	3.63 e	3.57 f
	60	3.48 g	3.33 f	3.25 g
Beringite	0	4.01 c	4.01 c	4.01 c
	30	3.87 d	3.75 d	3.65 d
	60	3.72 f	3.62 e	3.60 e
Poultry manure	0	4.01 c	4.02 c	4.01 c
	30	4.35 b	4.50 b	4.53 b
	60	4.77 a	5.17 a	5.33 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

EDTA of zeolite amended soil/ tailings could be partly due to the resistance of zeolite to degradation, chemisorption of Pb in the cavities of the porous zeolite framework and the precipitation as insoluble lead oxides with increased pH (Edwards et al., 1999). Metal retention and immobilisation by zeolite may also be attributed to an increased cation exchange and the formation of stable complexes of cationic metals with the negative charges of the high specific

Table 19: Effects of Rate of Application and Type of Amendment on EDTA-Extractable Lead of Uncapped Tailings as Affected by Incubation Period

Amendment	Rate of application ($kg\ ha^{-1}$)	Weeks after incubation 4	8	12
		-- EDTA-extractable Lead ($mg\ kg^{-1}$) --		
Zeolite	0	5.01 c	4.98 c	5.00 c
	30	3.77 f	3.68 f	2.93 f
	60	3.61 g	3.46 g	2.60 g
Beringite	0	4.99 c	4.99 c	5.01 c
	30	4.84 d	4.80 d	4.77 d
	60	4.78 e	4.69 e	4.62 e
Poultry manure	0	4.99 c	4.99 c	5.00 c
	30	5.37 b	5.42 b	5.46 b
	60	5.70 a	5.90 a	5.97 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

surface area exhibited by zeolite (Shi et al., 2009; Perić et al., 2004; Panuccio et al., 2009).

At the 30 kg ha^{-1} rate of application of zeolite the level of EDTA-Pb was not different from similar rates of application of berigite in non-mined soil at 4, 8 and 12 WAI ($P > 0.05$) (Table 17). However, the same rate of application resulted in significantly lower levels of Pb-EDTA in zeolite- than beringite- amended contaminated capped and uncapped tailings (Tables 18 and 19). Garau et al. (2007) similarly reported of significantly higher concentrations of residual Pb fraction and lower Pb fractions extracted with EDTA in un-polluted acid soil than that recovered from acid contaminated soil amended with zeolite and lime.

Non-mined soil, capped and uncapped tailings amended with either 30 kg ha^{-1} or 60 kg ha^{-1} beringite produced significantly lower concentrations of Pb-EDTA than un-amended soil/tailings at 4, 8 and 12 WAI ($P < 0.05$) (Tables 17, 18 and 19). Lead minerals are highly insoluble and exhibit low mobility in natural environments (Adriano, 2001; Kabata-Pendias, 2001). The fixation of lead increases and solubility decreases with increasing pH (Lombi et al., 2002; Farrell & Jones, 2010). An increase in the pH of beringite amended non-mined, capped and uncapped tailings (Tables 8, 9 and 10) could have resulted in an increased residual Pb fraction and decreased Pb-EDTA concentrations in beringite-amended non-mined soil, capped and uncapped tailings compared to un-amended samples (Tables 17, 18 and 19).

The concentrations of Pb-EDTA of either 30 kg ha^{-1} or 60 kg ha^{-1} poultry manure-amended non-mined soil, capped and uncapped tailings were significantly greater than those of non-amended soil/tailings at 4, 8 and 12 WAI ($P < 0.05$) (Tables 17, 18 and 19). The decomposition of poultry manures could produce fulvic acids that form complexes with Pb than other metals such as Zn and Cd (Schwab et al., 2007). Fulvic acids produced as a result of the breakdown of organic materials decreases while the humic fraction increases with time (Aoyama, 1996; Chefetz et al., 1996). The complexation of Pb with both the initially high fulvic fraction and the low humic fraction may have resulted in the dominance of unstable Pb compounds and significantly higher concentration of Pb-EDTA extracted from manure-amended soil/tailings compared to un-amended samples ($P < 0.05$) (Tables 17, 18 and 19). This implies that the use of poultry manure as an organic amendment to mediate lead in soils would be inappropriate due to its effect in increasing EDTA-extractable and water soluble lead. However, poultry manure could be used as a precursor in the phyto-remediation of heavy metals. This is because the availability of the heavy metals is increased for subsequent absorption of the hyper-accumulating plants which would be disposed off later.

At the 60 kg ha^{-1}rate of application of amendments, the concentration of Pb-EDTA in amended non-mined soil, capped and uncapped tailings at 4, 8 and 12 WAI, in increasing order of magnitude, was as follows: zeolite < beringite < poultry manure. Zeolite seemed to be the most effective amendment for significantly reducing the concentration of lead in soil/tailings.

Effects of Amendments on Water-soluble Lead in Non-mined Soil, Capped and Uncapped Tailings

Tables 20, 21 and 22 show the data on the levels of water soluble lead (Pb-H_2O) after the application of different rates of zeolite, beringite and poultry manure in non-mined soil, capped and uncapped tailings. The trend in the concentration of Pb-H_2O of amended soil/tailings showed higher percentage changes between amended and un-amended soil/tailings at 4 WAI. The percentage changes in the levels of Pb-H_2O of amended samples were lower from 4 WAI to 8 WAI and 8 WAI to 12 WAI when compared to that of the control without amendment (Tables 20, 21 and 22).

Table 20: Effects of Rate of Application and Type of Amendment on Water Soluble Lead of Non-Mined Soil as Affected by Incubation Period

Amendment	Rate of application (kg ha^{-1})	Weeks after incubation 4	8	12
		----- Water soluble Lead (mg L^{-1}) -----		
Zeolite	0	0.027 cd	0.027 cd	0.028 c
	30	0.026 cd	0.025 d	0.024 d
	60	0.023 e	0.022 e	0.019 e
Beringite	0	0.028 c	0.027 cd	0.028 c
	30	0.026 cd	0.026 cd	0.026 cd
	60	0.025 de	0.025 d	0.024 d
Poultry manure	0	0.027 cd	0.028 c	0.028 c
	30	0.032 b	0.033 b	0.035 b
	60	0.042 a	0.044 a	0.044 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

Soil/tailings amended with zeolite at the rate of 60 kg ha^{-1}produced significantly lower levels of Pb-H_2O compared to un-amended soil/tailings at 4, 8 and 12 WAI ($P < 0.05$) (Tables 20, 21 and 22). The application of zeolite at 60 kg ha^{-1} also yielded lower concentrations of Pb-H_2O than the other amendments(beringite and poultry manure) in non-mined soil, capped and uncapped tailings from 4 WAI to 12 WAI ($P < 0.05$) (Tables 20, 21 and 22).

Table 21: Effects of Rate of Application and Type of Amendment on Water Soluble Lead of Capped Tailings as Affected by Incubation Period

Amendment	Rate of application (kg ha^{-1})	Weeks after incubation 4	8	12
		----- Water soluble Lead (mg L^{-1}) -----		
Zeolite	0	0.043 b	0.043 c	0.043 b
	30	0.038 c	0.037 de	0.034 d
	60	0.029 d	0.026 f	0.024 e
Beringite	0	0.042 b	0.043 c	0.043 b
	30	0.042 b	0.038 d	0.037 c
	60	0.036 c	0.035 e	0.033 d
Poultry manure	0	0.043 b	0.042 c	0.043 b
	30	0.064 a	0.066 b	0.068 a
	60	0.066 a	0.069 a	0.069 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

Zeolite-amended soil/tailings resulted in increased pH values of 5.5 – 5.9, 6.6 – 6.9 and 7.3 -7.5 compared to pH values of 5.3, 6.4 and 7.2 for un-amended non-mined soil, capped and uncapped tailings, respectively (Tables 8, 9 and 10). Generally, an increase in pH results in the reduction of the water soluble fraction of lead (USEPA, 1992b; McBride, 1994; Farrell & Jones, 2010). The significantly higher pH values ($P < 0.05$) (Tables 8, 9 and10) and the lower concentrations of the available Pb-EDTA fraction (Tables 17, 18 and

Table 22: Effects of Rate of Application and Type of Amendment on Water Soluble Lead of Uncapped Tailings as Affected by Incubation Period

Amendment	Rate of application (kg ha^{-1})	Weeks after incubation		
		4	8	12
		----- Water soluble Lead (mg L^{-1}) -----		
Zeolite	0	0.155 c	1.555 c	0.155 c
	30	0.116 f	0.097 f	0.105 e
	60	0.108 g	0.083 g	0.076 f
Beringite	0	0.154 c	0.154 c	0.155 c
	30	0.133 d	0.141 d	0.137 d
	60	0.128 e	0.115 e	0.108 e
Poultry manure	0	0.154 c	0.155 c	0.155 c
	30	0.161 b	0.166 b	0.169 b
	60	0.172 a	0.184 a	0.189 a

*Means followed by the same letters in a column are not significantly different ($P < 0.05$).

19) of zeolite-amended soil/tailings ($P < 0.05$) might partly account for the significantly lower levels of water soluble Pb compared to un-amended samples ($P < 0.05$) (Tables 20, 21 and 22).

Furthermore, ion exchange and the sorption of metal ions (chemisorption) occurs within the channels and cavities of the porous lattice structure of zeolite that results in a decrease in the concentration of water soluble and exchangeable fractions in soil solution as observed by Oste et al. (2002), Castaldi, Santona and Melis (2005) and Garau et al. (2007). At 4

WAI, there was no significant difference in Pb-H_2O between the 30 kg ha^{-1} and 60 kg ha^{-1} ($P > 0.05$) rate of application of beringite. There was also no significant difference between 30 kg ha^{-1} beringite amended soils and un-amended soils at all the time-points of the incubation period from 0 WAI to 12 WAI ($P > 0.05$). The concentration of Pb-H_2O after the application of either 30 kg ha^{-1} or 60 kg ha^{-1} of beringite was the same as that of 30 kg ha^{-1} zeolite amended soils ($P > 0.05$) (Table 12). However, the application of 60 kg ha^{-1} beringite to non-mined soil resulted in significantly lower concentrations of Pb-H_2O ($P < 0.05$) compared to un-amended soil at 4 and 12 WAI (Table 12). Increased soil solution pH may have led to reduced mobility of Pb in beringite amended soil (Lombi et al., 2002) and could have accounted for the significantly lower concentrations of water soluble Pb compared to un-amended soil.

The significantly lower levels of Pb-H_2O extracted from zeolite-amended non-mined soil, capped and uncapped tailings compared to un-amended samples ($P < 0.05$) at 4, 8 and 12 WAI application could be also ascribed to the high cation exchange of zeolite (Castaldi et al., 2005). This is supported by Nissen, Lepp and Edwards (2000) who have stated that metal retention by zeolite due to cation exchange takes place irrespective of the value of pH. However, Edwards et al. (1999) report that the mechanism of action of zeolite in the immobilisation and reduction in the water soluble fraction of metal contaminants is due to a combination of the ion exchange properties of zeolite and its ability to increase alkalinity. This explanation is buttressed by Panuccio et al. (2009) and Oste et al. (2002) who note that the specific surface area, binding capacity and alkalinity of zeolite results in the immobilisation, precipitation of insoluble phases and reduction in metal levels in soil solution.

Similarly, the application of beringite at the rate of 60 kg ha^{-1} to non-mined soil, capped and uncapped tailings resulted in significantly lower concentrations Pb-H_2O than un-amended samples, at all the time-points of the incubation period ($P < 0.05$) (Tables 20, 21 and 22), possibly due to a pH effect, increased fixation, precipitation or co-precipitation of Pb with Fe, Al and Mn oxides in presence of beringite (Lombi et al., 2002; Mench et al., 2006). Subsequently, reduced mobility of Pb could have led to the decreased water soluble fraction in beringite-amended samples.

The application of both 30 kg ha^{-1} or 60 kg ha^{-1} poultry manure to soil/tailings each resulted in significantly higher levels of Pb-H_2O than the control (un-amended soil) at 4, 8 and 12 WAI ($P < 0.05$) (Tables 20 – 23). Organic matter amendments decrease metal solubility through the transformation of water soluble and exchangeable fractions into stable fractions associated with organic matter (Walker et al., 2004). However, the reduction in metal mobility is dependent on the metal ion, soil type and the characteristics of organic matter with respect to the degree of humification (Almås et al., 1999; Narwal & Singh, 1998; Ross, 1994; Walker et al., 2003).

The high concentrations of carboxyl and phenolic reactive groups of the humic fraction of soil organic matter form complexes with metal ions, increase metal adsorption and reduce free metal activity (Alloway, 1995; Sauvé et al., 2000; Silveira et al., 2003). On the other hand, fulvic acids as major constituents of the soluble fraction and humic acids as minor components of the stable fraction of dissolved organic carbon of organic matter, that are produced during the decomposition of cattle and poultry manures contain significant proportions of non-degraded material (Schwab et al., 2007). Lead solubility, in particular and metal mobility in general, increases with increasing levels of dissolved organic matter (Bruemmer et al., 1986; McBride et al., 1997; Sauvé et al., 1998; Silveira et al., 2003; Schwab et al., 2007). The levels of fulvic acid that could have been derived from poultry manures might have increased the formation of Pb-complexes in amended soil that easily dissolved in soil solution.

Lead has a strong affinity for organic matter and accumulates in the surface layers of the soil profile (Adriano, 2001). According to Puls, Powell, Clark and Eldred (1991) and Kotuby-Amacher and Gambrell (1988), the high affinity of Pb for organic ligands lead to the formation of soluble complexes that increase the mobility of Pb in the soil. An increase in the levels of dissolved organic carbon of manure results in increased complexation of potentially toxic elements (PTEs) and a higher mobility of Pb (Schwab et al., 2007). These explanations could partly account for the increased levels of water soluble lead in poultry-amended soil/tailings in contrast to un-amended samples (Tables 20, 21 and 22). Schwab et al. (2007) similarly reported of increased lead concentrations in leachate from tailings amended with cattle manure compared to the control.

At 12 WAI, the concentration of Pb-H_2O of amended non-mined soil, capped and uncapped tailings at the 60 kg ha^{-1} rate of application was, in decreasing order: poultry manure > beringite > zeolite (Tables 20, 21 and 22).

Generally, the application of zeolite and beringite led to higher increases in pH than cattle and poutry manure. Beringite was the most effective in decreasing As mobility in non-mined soil, tailings capping and uncapped tailing. This could have been due to the complexation of As in the inner sphere of beringite. The organic amendment (poultry manure) led to the mobilisation of As in non-mined soil and uncapped tailings possibly due to the increased alkalinity effects. The increase in alkalinity, sorption/trapping of Pb within the channels and cavities of the porous lattice structure of zeolite (Oste et al., 2002; Castaldi et al., 2005; Garau et al., 2007) led not only to an increase in the concentrations of available and weakly adsorbed Pb extracted with Ammonium-EDTA but also the highest increase in water soluble Pb.

Concentration of Arsenic and Lead in Mediated Soil/Tailings

Edible plants grown on polluted soil can accumulate potentially toxic elements at high concentrations that pose a threat to human health (Vousta Graminas & Samara, 1996; Sharma, Bangar, Rajesh-Jain & Sharma, 2004). Ultimately, lettuce was cropped on mediated soil/tailings so as to assess the uptake and toxicity levels of As and Pb. Figures 3 – 5 show the results of the concentration of Arsenic and Lead in lettuce harvested from non-mined soil, capped and uncapped tailings after mediation with beringite, zeolite and poultry manure. The concentration of either As or Pb accumulated in the aerial part of the lettuce plant has been used as an index of bioavailability for the purpose of this study. Generally, the concentration of As and Pb in zeolite- and beringite-amended soil/tailings were significantly lower than those of un-amended samples ($P < 0.005$) (Figures 3 – 5).

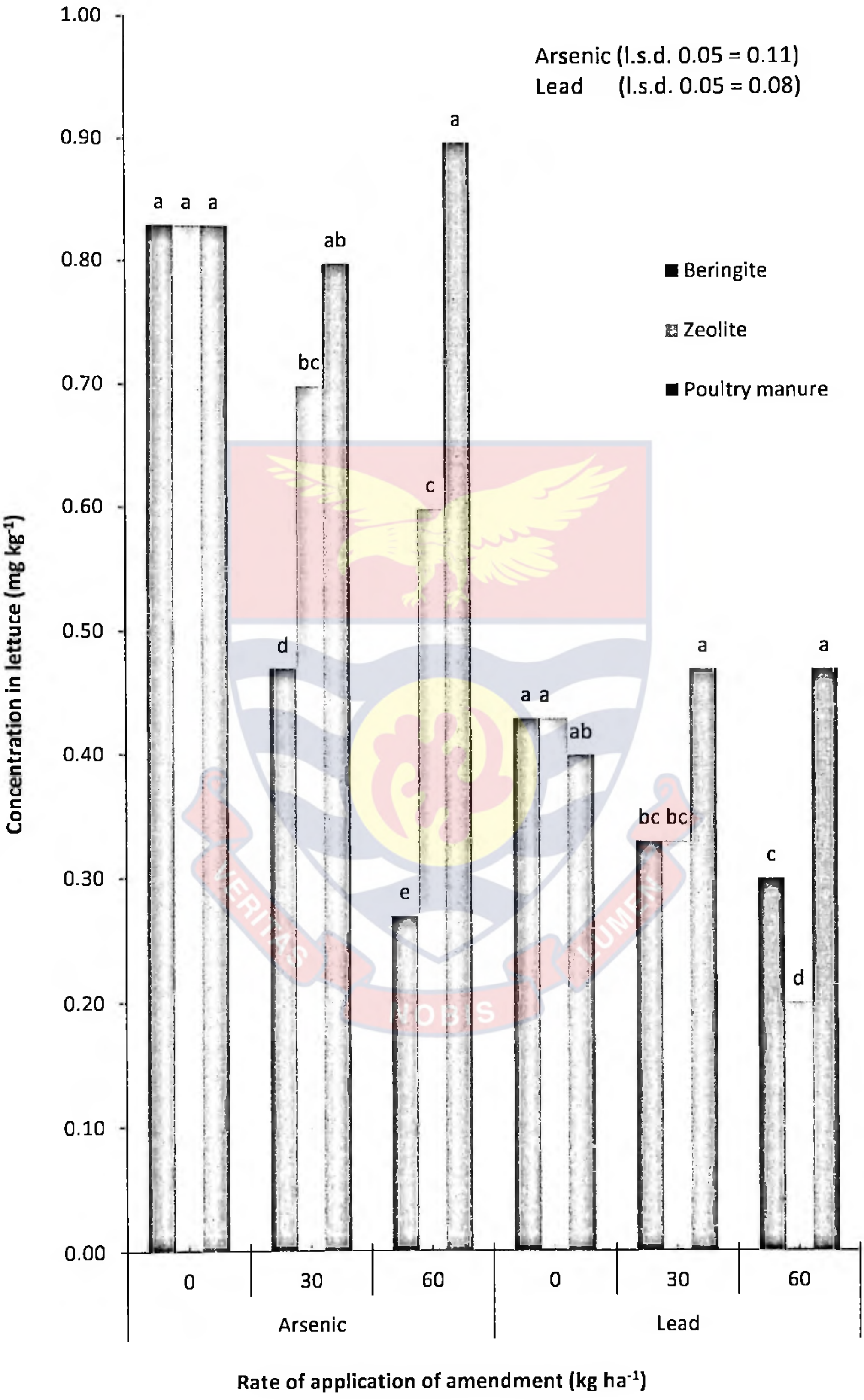


Figure 3. Bioavailability of Arsenic and Lead in *Lactuca sativa* L. Grown on Mediated Non-mined Soil

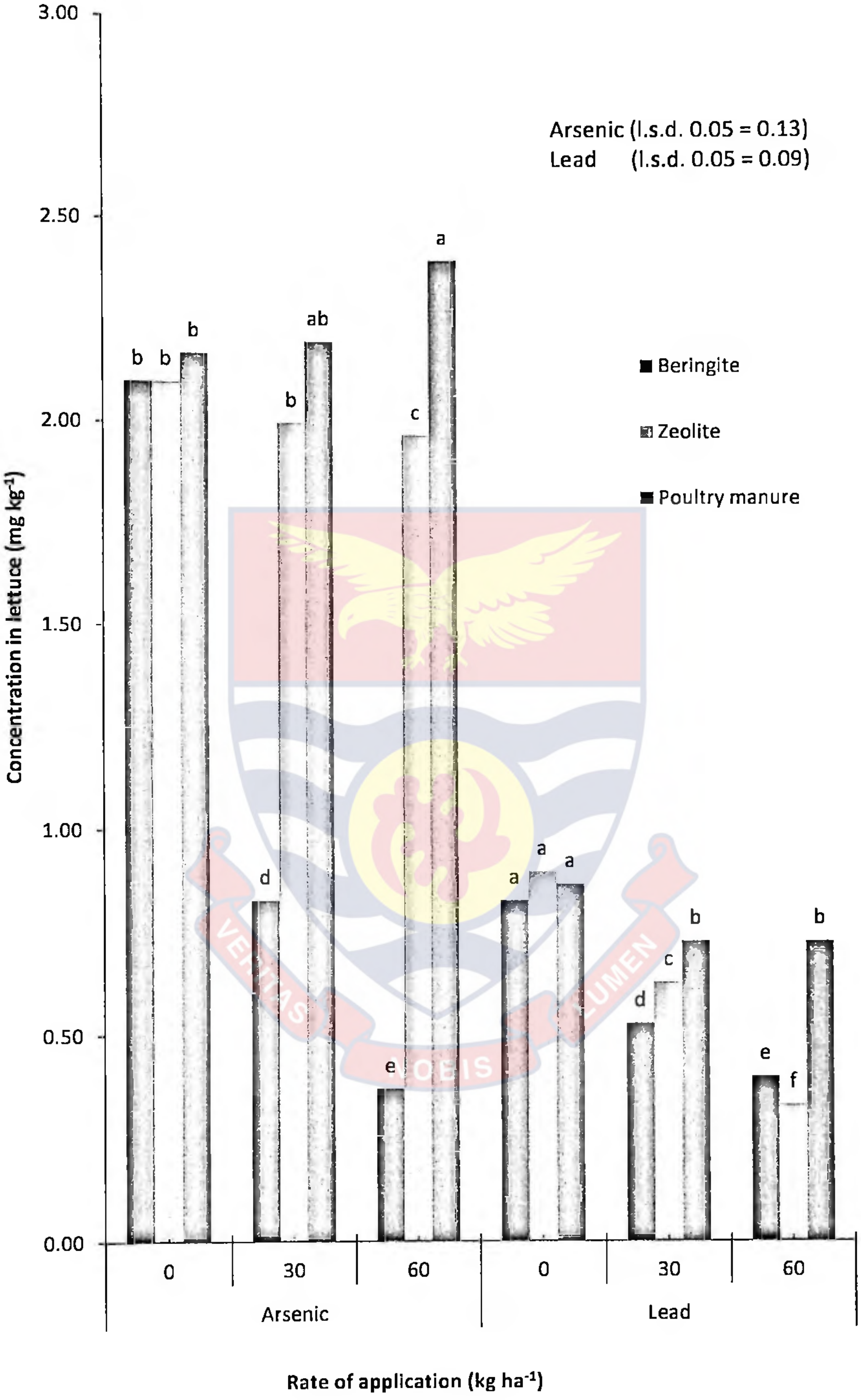


Figure 4. Bioavailability of Arsenic and Lead in *Lactuca sativa* L. Grown on Mediated Capped Tailings

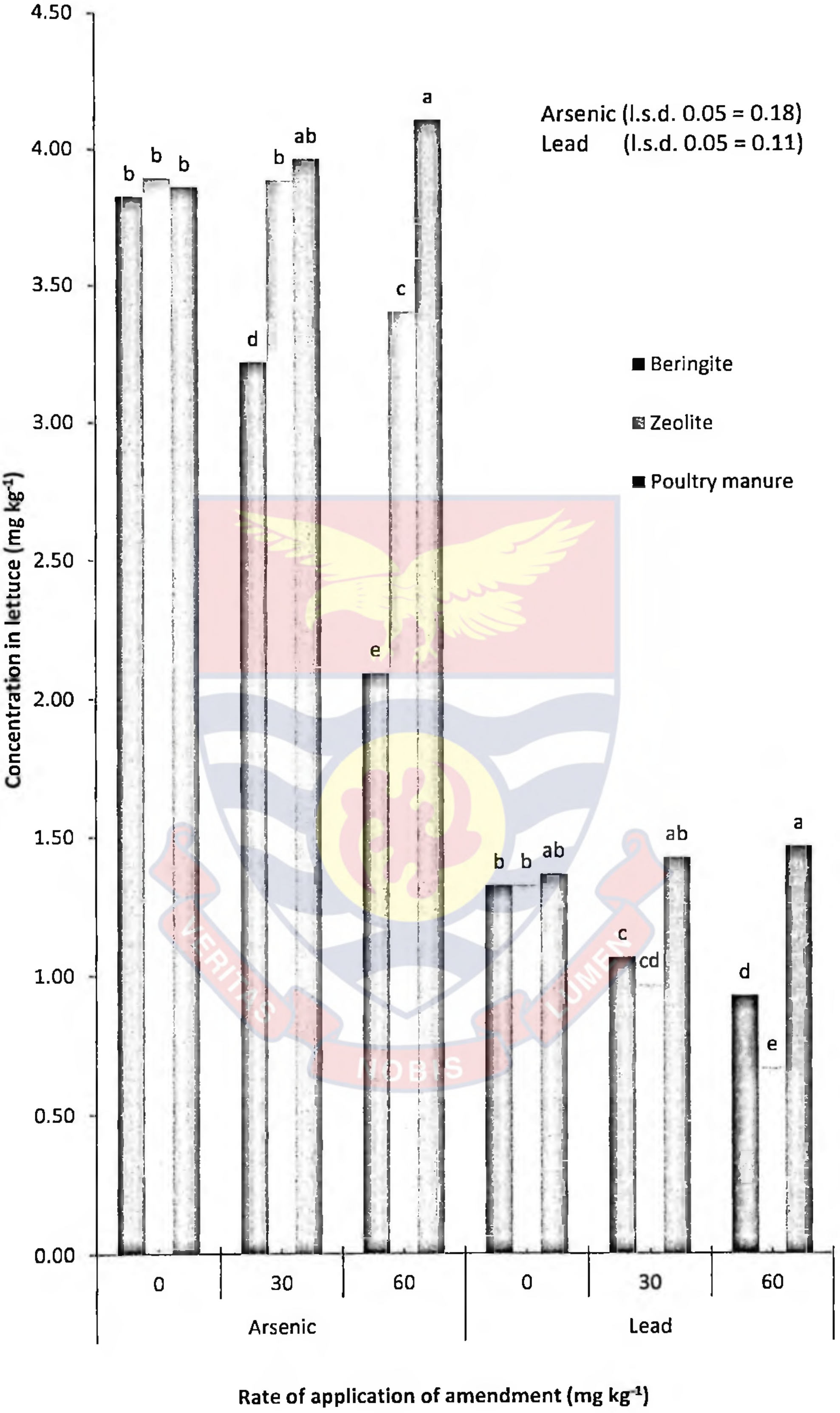


Figure 5. Bioavailability of Arsenic and Lead in *Lactuca sativa* L. Grown on Mediated Uncapped Tailings

Bioavailability of Arsenic in Lettuce Grown on Soil/Tailings Amended with Zeolite, Beringite and Poultry Manure

The concentration of arsenic accumulated in lettuce ranged from 0.27 – 4.13 mg kg^{-1}. This concentration of arsenic is within the limits given by Wauchope (1983) who states that plants that are not hyper-accumulating species accumulate arsenic in a normal range of 0.1-5 mg As kg^{-1} dry weight in their leaves. Except for non-mined soil, there were no significant differences in the concentration of arsenic ($P > 0.05$) in lettuce grown in either 30 kg ha^{-1} or 60 kg ha^{-1} zeolite amended soil/tailings (Figures 3 – 5). However, the application of zeolite at 60 kg ha^{-1} resulted in a significantly lower concentration of arsenic in lettuce compared to un-amended soil/tailings ($P < 0.05$). This trend was observed due to minimal effects of zeolite on As-EDTA (Tables 11 – 13) and water soluble Arsenic (Tables 14 – 16) in non-mined soil, capped and uncapped tailings. Non-mined soil mediated with zeolite resulted in a lower content of As in lettuce aerial biomass. The concentration of arsenic in un-amended non-mined soil (Figure 3) was lower than the UK standard of 1.0 mg As kg^{-1} dry mass (Food Standards Agency [FSA], 2007).

On the other hand, capped and uncapped tailings amended with zeolite resulted in the concentrations of arsenic in lettuce plants (Figures 4 and 5) that were above the UK acceptable limits for food (FSA, 2007). The cause of arsenic contamination may not necessarily be geologic in origin but anthropogenic. This is because the concentration of arsenic in lettuce grown on non-mined soil was within acceptable limits despite the underlying arseno-pyritic rocks. The beneficiation of gold in the study area is from arseno-pyrite rock ores which result in the release of high amounts of As during gold ore processing into the feed of tailings effluent, capped and uncapped tailings (Tables 4 – 6). The effects of mining activities in arsenic contamination were manifested through the concentrations of arsenic in lettuce that were above the UK acceptable limits for food (FSA, 2007).

The application of beringite to soil/tailings resulted in the least content of arsenic in lettuce plants. The concentrations of arsenic in lettuce plants grown in un-amended non-mined soil, capped and uncapped tailings were 0.83 (± 0.00), 2.13 (± 0.04) and 3.87 (± 0.04), respectively (Figures 3 – 5). These were in contrast to the lower arsenic values of 0.27 – 0.47 mg kg^{-1}, 0.37 – 0.83 mg kg^{-1} and 2.1 – 3.23 mg kg^{-1} in lettuce cultivated on beringite-mediated non-mined soil, capped and uncapped tailings, respectively (Figures 3 – 5). The significantly lower concentration of arsenic in lettuce could be attributed to the significantly immobilized arsenic by beringite and lower concentrations of EDTA-extractable (Tables 11 – 13) and water soluble arsenic (Tables 14 – 16) in beringite-amended soil/tailings.

The concentration of arsenic in lettuce grown in beringite-mediated capped tailings was therefore lower than the United Kingdom (UK) limit of 1.0 mg As kg^{-1} in food (FSA, 2007). However, the concentrations of arsenic in lettuce cultivated on un-amended capped tailings (2.13 ± 0.04) mg kg^{-1} (Figure 3) and amended uncapped tailings (2.1 – 3.23) mg kg^{-1} (Figure 4) was higher than the UK acceptable limit of 1.0 mg As kg^{-1} (FSA, 2007). Heavy metals in the soil can be absorbed by plants. The health of humans and other organisms can be adversely affected through the ingestion of both water and plants that have been contaminated by the soil (Chen et al., 2000). According to FAO (2006), arsenic toxicity usually occurs through contaminated food and drinking water. This implies that it would be safe to crop only on beringite-mediated capped tailings but not on either un-amended capped tailings or beringite-amended uncapped tailings.

The content of arsenic in lettuce cropped on poultry manure-amended non-mined soil, capped and uncapped were significantly greater than those of un-amended samples ($P < 0.05$) (Figures 3, 4 and 5) and above the UK set limit for arsenic in food. Poultry-manure amended soil/tailings resulted in significantly higher concentrations of EDTA-extractable arsenic (Tables 11 – 13) and water soluble arsenic (Tables 14 – 16). Hence, the mobilisation of arsenic in poultry manure-amended soil/tailings possibly resulted in the significantly greater arsenic content in lettuce compared to un-amended soil/tailings samples ($P < 0.05$) (Figures 3 – 5). Although poultry manure was not effective in immobilizing arsenic it could be a useful amendment for increasing the availability of arsenic prior to phytoremediation as observed by Garbisu and Alkorta (2001). The concentration of arsenic in lettuce grown on amended soil/tailings, in decreasing order, when 30 kg ha^{-1} of the amendment was applied to soil/tailings at the end of the incubation experiment was as follows: poultry manure = zeolite > beringite. At the 60 kg ha^{-1} the amendments applied to soil/tailings could be arranged in ascending order according to the concentrations/bioavailability of lead in lettuce as follows: zeolite < beringite < zeolite.

Bioavailability of Lead in Lettuce Grown on Soil/Tailings Amended with Zeolite, Beringite and Poultry Manure

The permissible limits of lead in vegetables cultivated for human consumption, cited from different sources are 2.0 – 2.5 mg kg^{-1} (Samara et al. 1992), 2.0 mg kg^{-1} (Malaysian Food Act [MFA], 1983) and 0.3 mg kg^{-1} (FAO/WHO, 1999). Generally, the concentration of Lead in lettuce was within the cited maximum limits. However, the concentration of lead in lettuce harvested from capped and uncapped tailings were 0.03 and 0.1 mg kg^{-1}, respectively above the maximum limits set by FAO/WHO (1999). The bioavailability of Lead in non-mined soil, capped and uncapped tailings exhibited similar trends as that observed for Arsenic (Figures 3 – 5). However, the application of 60 kg ha^{-1} zeolite resulted in the lowest concentration of Lead in aerial parts of lettuce in non-mined soil, capped and capped tailings (Figures 3 – 5). Lettuce grown on zeolite- and beringite-amended soil/tailings had significantly lower concentrations of Lead than un-amended samples. This could be partly attributed to the significantly lower concentrations of EDTA-extractable (Tables 17, 18 and 19) and water soluble (Tables 20, 21 and 22) fractions of Lead in zeolite-amended soil/tailings compared to un-amended soil/tailings.

The non-specific adsorption of Pb through cation exchange of Ca^{2+} and Mg^{2+} ions that occur within negatively charged zeolite framework, as observed by Stolz et al. (2000) and Perić et al. (2004), could explain further the reduced mobility of Lead in zeolite-amended soil/tailings. Beringite, on the other hand, exerted its influence on the immobilisation and reduced bioavailability of Lead in lettuce through cation exchange and replacement of the high calcium and magnesium constituents of beringite (Boisson et al., 1999; Mench et al., 2006).

The concentration of lead grown on poultry manure-mediated non-mined soil and uncapped tailings were similar to that of un-amended samples ($P > 0.05$) (Figures 3 and 5). However, lettuce grown on poultry manure-mediated soil/cappings had significantly higher concentrations of lead compared to un-amended capped tailings samples ($P > 0.05$) (Figure 3). The significantly higher contents of Pb in lettuce grown on poultry manure-mediated capped tailings might be related to the significantly higher concentrations of EDTA-extractable lead (Tables 17 – 19) and water soluble lead (Tables 20 – 22) that resulted from increased exchangeable and plant available lead. The amendments applied at the rate of 60 kg ha^{-1} to soil/tailings could be arranged, in descending order, according to the concentrations of lead in lettuce as follows: poultry > beringite > zeolite.

Conclusions

The study revealed that beringite-amended non-mined, capped and uncapped tailings resulted in the most significant degree of alkalisation. On the other hand, there was an increase in the alkalisation of poultry manure amended non-mined soil but an increase in the acidity of capped and uncapped tailings. The most effective amendment in mediating arsenic in soil/tailings was beringite. The application of beringite to soil/tailings resulted in the least concentrations of EDTA-extractable and water soluble arsenic. Zeolite was the most effective amendment in immobilizing Pb in soil/tailings. An increase in pH with the application of zeolite to soil/tailings resulted in reduced concentrations of EDTA-exchangeable Pb and water soluble Pb and contributed significantly to the immobilisation of lead. The study also showed that beringite was the most efficient with respect to the immobilisation of Arsenic and the mediation of arsenic contaminated soil/tailings. The application of poultry manure to non-mined soil, capped and uncapped tailings led to the immobilisation of arsenic and lead. This implies that although poultry manure would be ineffective in the mediation of Pb and As, it could be an important precursor in the mobilisation of these trace elements prior to phyto-remediation.

The least concentration of lead occurred in lettuce harvested from zeolite-amended soil/tailings. The minimal content of arsenic occurred in lettuce plants cropped on beringite-amended samples. Soil/tailings that yielded the least concentrations of As and Pb after amelioration with beringite and zeolite, respectively also produced the lowest contents of these trace elements in lettuce harvested from these soil/tailings. However, although lettuce cultivated on uncapped tailings mediated with beringite produced the least content of arsenic (2.1 – 3.23 mg kg^{-1}); the UK maximum permissible limit of 1.0 mg kg^{-1} in food (FSA, 2007) was exceeded. This implies that food crops would be safe for human consumption only on beringite-mediated capped tailings but not on either un-amended capped tailings or beringite-amended uncapped tailings.

CHAPTER SIX

BIOCHAR AS AN AMENDMENT FOR THE REMEDIATION OF ARSENIC AND LEAD IN CAPPED AND UNCAPPED TAILINGS

Introduction

Mining is one of the main anthropogenic sources of metal contamination in water and soil (Duker et al., 2005; Lee, Lee, Chon & Kim, 2008). Soil pollution of trace elements such as Arsenic and Lead in soils is a major environmental problem that could be caused by waste dumping, abandoned industrial activities and incidental accumulation (Alloway & Ayres, 1997; Joubert et al., 2007). Several industrial sites have metal concentrations that exceed acceptable levels and are therefore a potential health risk for humans, animals and plants (De Sousa, 2003; Environment Agency, 2004). Arsenic and lead pollution due to industrial activities can result in toxic effects such as skin and bladder cancers and also renal damage, respectively (Verberk et al., 1996; Dermatas et al., 2004).

Several research findings have been published on the use of zeolite, beringite and organic matter to immobilise metals through cation exchange, sorption, complexation and precipitation (Mench et al., 2006; Oste et al., 2002: Walker et al., 2004). In recent times, the application of biochar is increasingly becoming a sustainable technology that leads to the improvement of highly weathered and degraded tropical soils (Lehmann & Rondon, 2006). The application of black carbon, which exists in its charcoal form as biochar

(Shrestha et al., 2010), improves soil physico-chemical characteristics such as bulk density, water holding capacity, permeability, nutrient retention and availability (Glaser et al., 2002; Lehmann & Rondon, 2006). The hazards of heavy metals to the environment can be reduced by fixation in the soil, thereby decreasing bioavailability and further mobility (Van Herwijnen et al., 2007).

Beesley, Moreno-Jimenez, Gomez-Eyles, Harris, Robinson and Sizmur (2011) have reported that the application of biochar to contaminated soil increases the sorption of both organic and inorganic pollutants and reduces their mobility. On the other hand, the liming effects of biochar amendment and the release of carbon into soil solution could lead to an increase in arsenic mobility (Beesley et al, 2011; Glaser et al., 2002). The large surface area and high cation exchange capacity of biochar enhances the adsorption of metal pollutants (Beesley et al, 2011; Liang et al., 2006).

The lettuce plant accumulates heavy metals in its aerial parts and could be used to assess the bioavailability of heavy metals in mediated soils (Nadia & Zaghloul, 2007). The bioavailability and mobility of metals is important in assessing the potential health risk to the population because of the integration of metals in the food chain (Poggio et al., 2008). There is the need for the determination of the bioavailability of heavy metals in soils after remediation with biochar. The specific objectives of this study were therefore to:

i. Assess the effect of biochar on the extent of alkalisation or acidification of non-mined agricultural soil, capped and uncapped tailings through the use of biochar.

ii. Achieve specific objectives v. and vi. that were set in Chapter One.

Materials and Methods

Fractions of the composite samples prepared for the remediation .experiment in Chapter Five were used for this experiment. The sampling procedure and sample preparation were as described in the Materials and Methods section of Chapter Five.

Five hundred grams (500 g) air dried non-mined agricultural soil, capped and uncapped tailings of the sampled sites were placed in plastic containers (Plate 1). The soil/tailings were amended with biochar that was obtained from a Lucia biomass pyrolytic stove, at a temperature between 300 – 350 °C, under low oxygen conditions. The feed stock used to obtain the biochar was corn cob. The biochar was ground, added to the soil/tailings samples at at the rates of 0, 2, 4 and 8t ha^{-1} (w/w) and then moistened to field capacity. The completely randomised design with three replications was used.

Plate 1. Arsenic and Lead Polluted Soil/Tailings Amended with Biochar

The samples were placed in the laboratory at a mean room temperature of 25 °C and moistened weekly to maintain the soil at field capacity. The soils were taken from each container and bulked for analysis at each time interval. The pH, water-soluble and EDTA-extractable As and Pb concentrations were determined using the procedures described in Chapter Three (Materials and methods).

The bioaccumulation of As and Pb in the mediated soils/tailings was subsequently determined after amendment with biochar at the rates of 0, 2, 4 and 8 t ha^{-1} (w/w). Lettuce (*Lactuca sativa*) was used as the plant indicator of the bioavailability of As and Pb (Plates 2 and 3) due to the high accumulation of heavy metals in the edible leafy aerial parts (Nadia & Zaghloul, 2007).

Plate 2: Onset of Experiment on the Bioavailability of Arsenic and Lead of Biochar Amended Soil/Tailings

Plate 3: Experiment on the Bioavailability of Arsenic and Lead of Biochar Amended Soil/Talings Three Weeks After Transplanting

The field practices for the cultivation of lettuce as described by Grubben (2004), although slightly modified, were followed. A brief description of these field practices is stated in the Materials and Methods section of Chapter Five. The aerial parts of the lettuce plants were harvested and prepared for the analysis of the concentrations of Arsenic and Lead. Plants were harvested at 3 weeks after transplanting for analysis when the lettuce in amended and un-amended uncapped tailings showed signs of wilting possibly due to the accumulation of phytotoxic levels of arsenic.

The procedure described in the Section, Plant Preparation, in Chapter Three (Materials and Methods) was followed. A quantity of 1.0 g of the prepared plant material was digested in freshly prepared mixture of HNO_3 – HCl (1:3 v/v) on a digestor a 110 °C for 3 h to determine the concentrations of As and Pb (Chen & Ma, 2001). The detailed procedure has been described in Chapter Three. The analysis of variance (ANOVA) was used to determine the effects of the different rates of application of biochar on pH, water-soluble and EDTA-extractable As and Pb in the non-mined soil, capped and uncapped tailings. The effects of the different rates of application of biochar on the bioavailability of As and Pb were also established using the ANOVA.

Results and Discussion

The results of the effects of biochar on soil/tailings pH, EDTA-extractable and water soluble Pb are presented in Figures 6 – 14.

Effects of Biochar on the pH of Non-mined Soil, Capped and Uncapped Tailings

The pH ranged from 5.3 to 7.2 in un-amended soil/tailings (Figures 6 – 8). The pH of amended soil/tailings increased with increasing rate of biochar application at 4 WAI. Thereafter, at 8 and 12 WAI, the increases in pH were successively lower with increasing rate of biochar application. Generally, at the end of the incubation period the increase in pH in amended soil/tailings ranged from + 0.2 to + 0.4 at the 8 t ha^{-1} rate of application of biochar. Kolb et al. (2009) similarly obtained a pH increase of + 0.4 in soil amended with 10 % char.

The different rates of application of biochar at 2, 4 and 8 t ha^{-1} each resulted in significantly greater soil/ tailings pH compared to the control (0 t ha^{-1}) ($P < 0.05$) at all the time-points of the incubation period (Figures 6, 7 and 8). The highest soil pH was produced when 8 t ha^{-1}of biochar was applied to the soil /tailings ($P < 0.05$). However, the 4 and 8 t ha^{-1} rates of application of

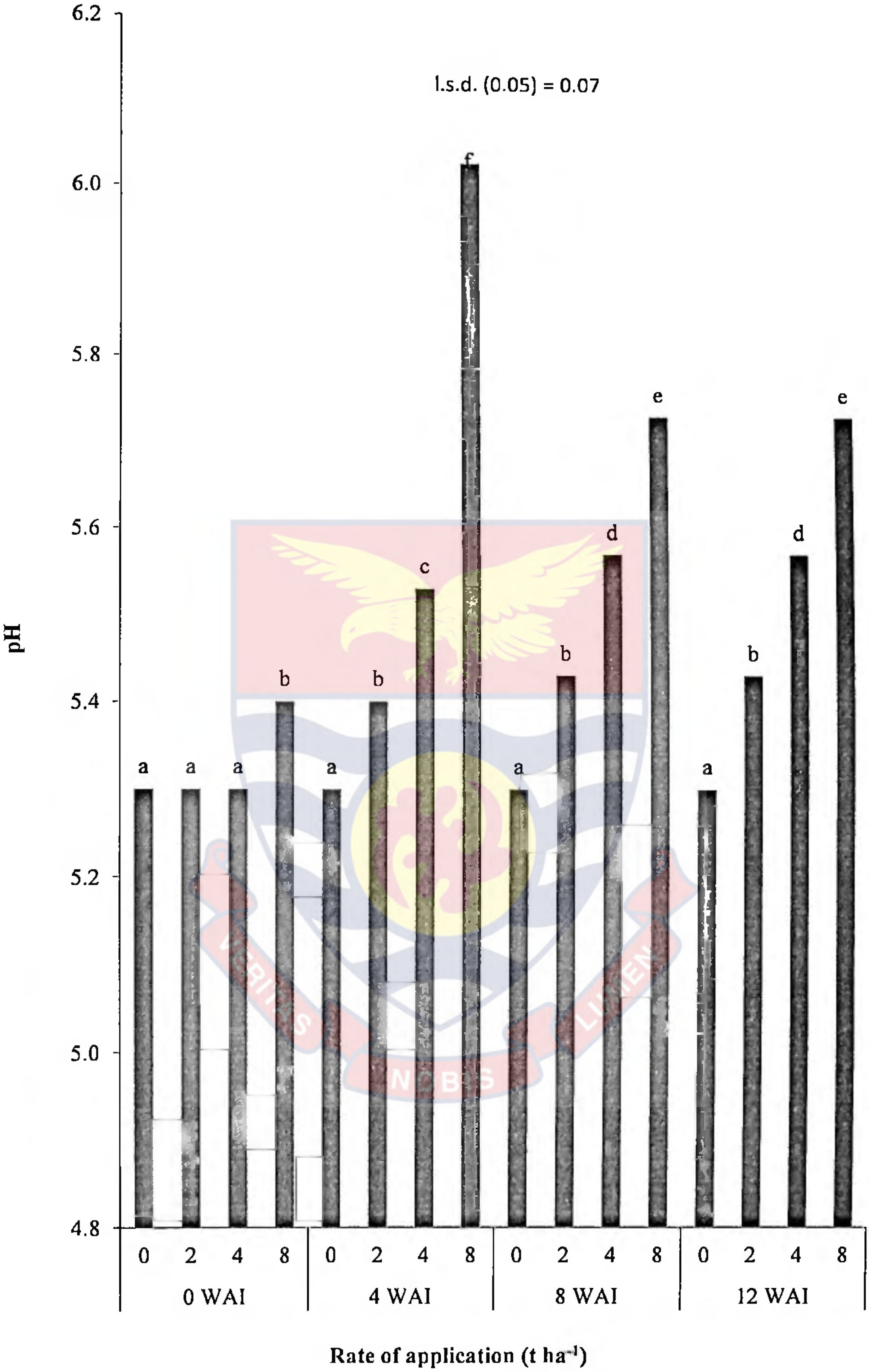


Figure 6. Effects of Biochar on the pH of Non-mined Soil

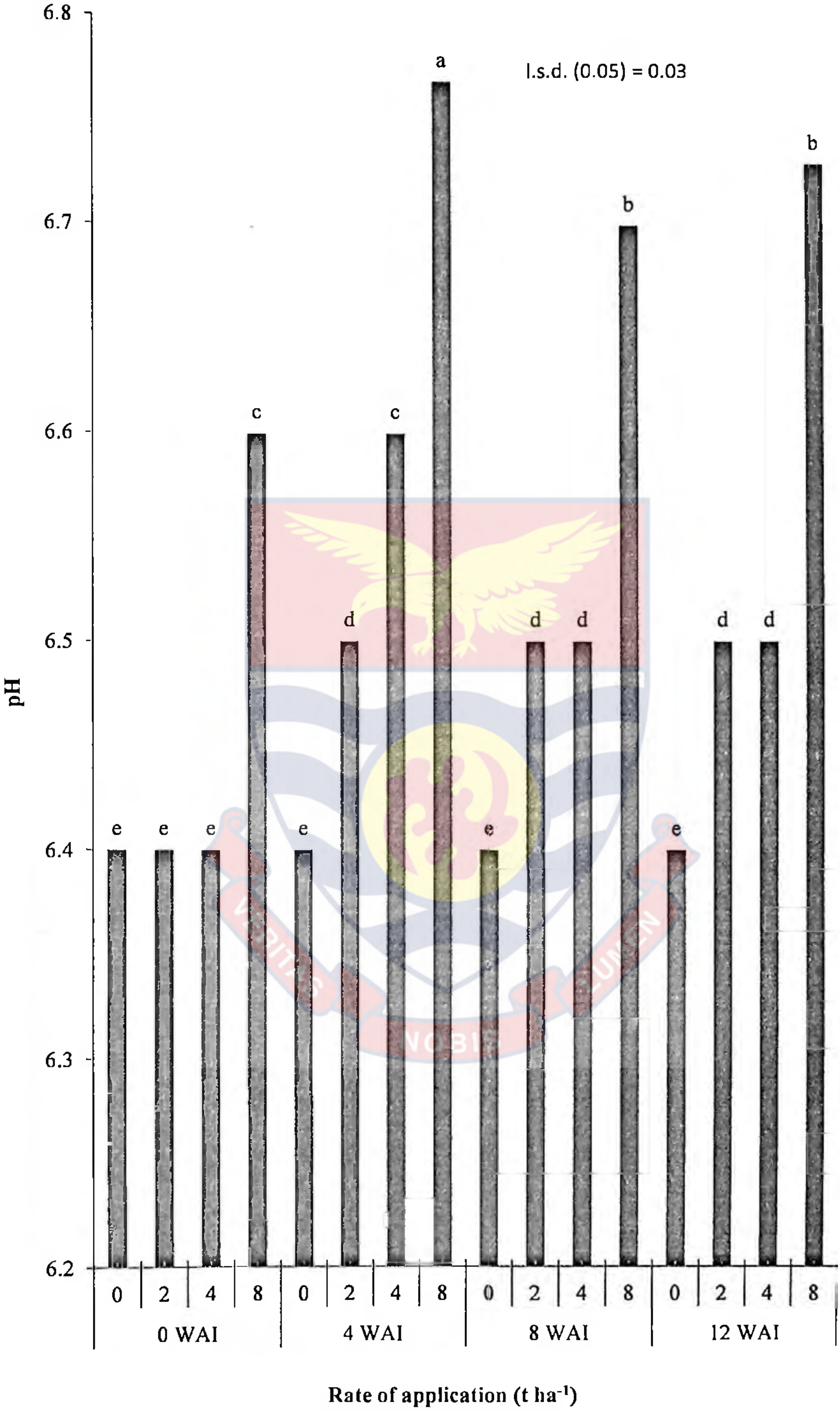


Figure 7. Effects of Biochar on the pH of Capped Tailings

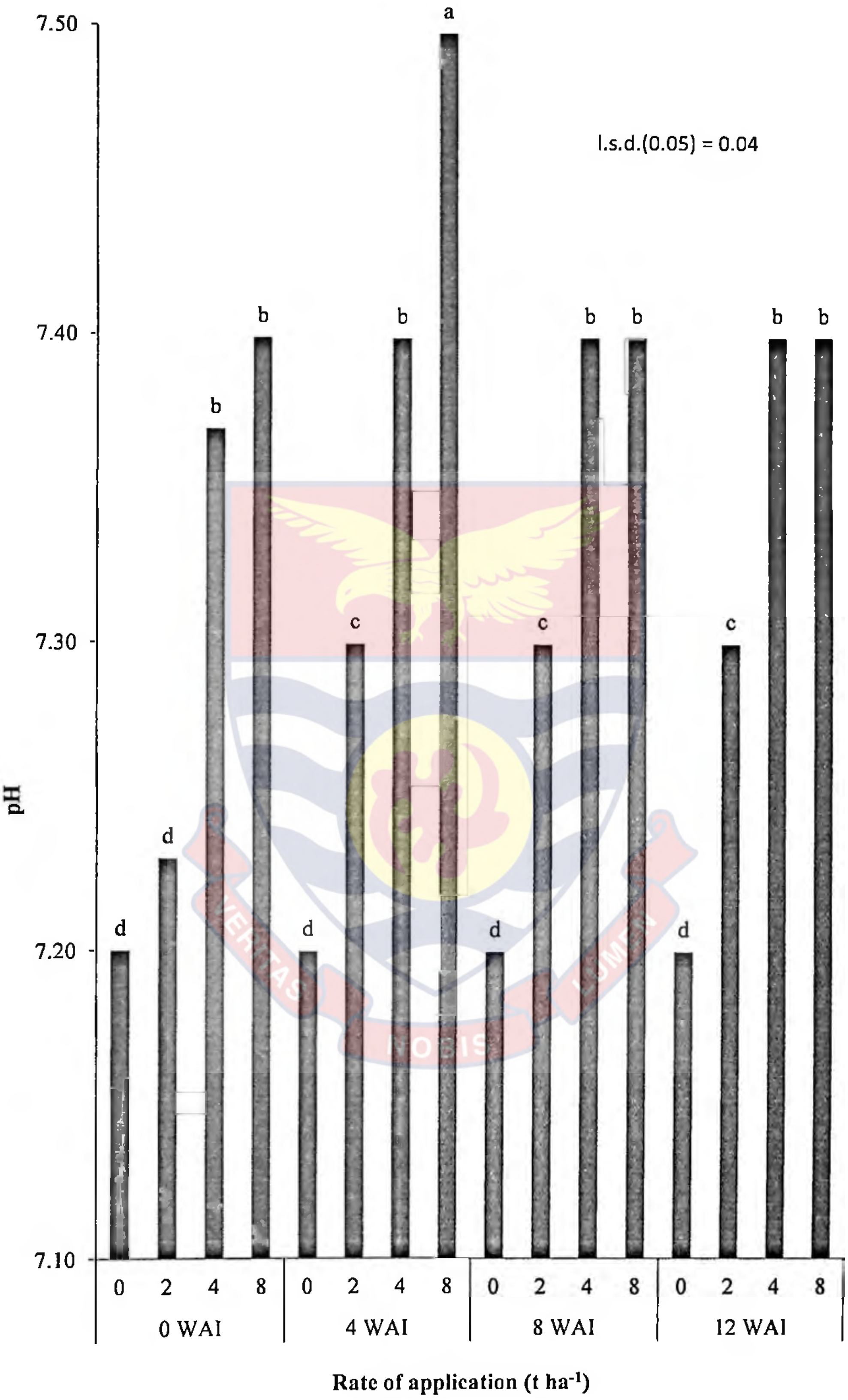


Figure 8. Effects of Biochar on the pH of Uncapped Tailings

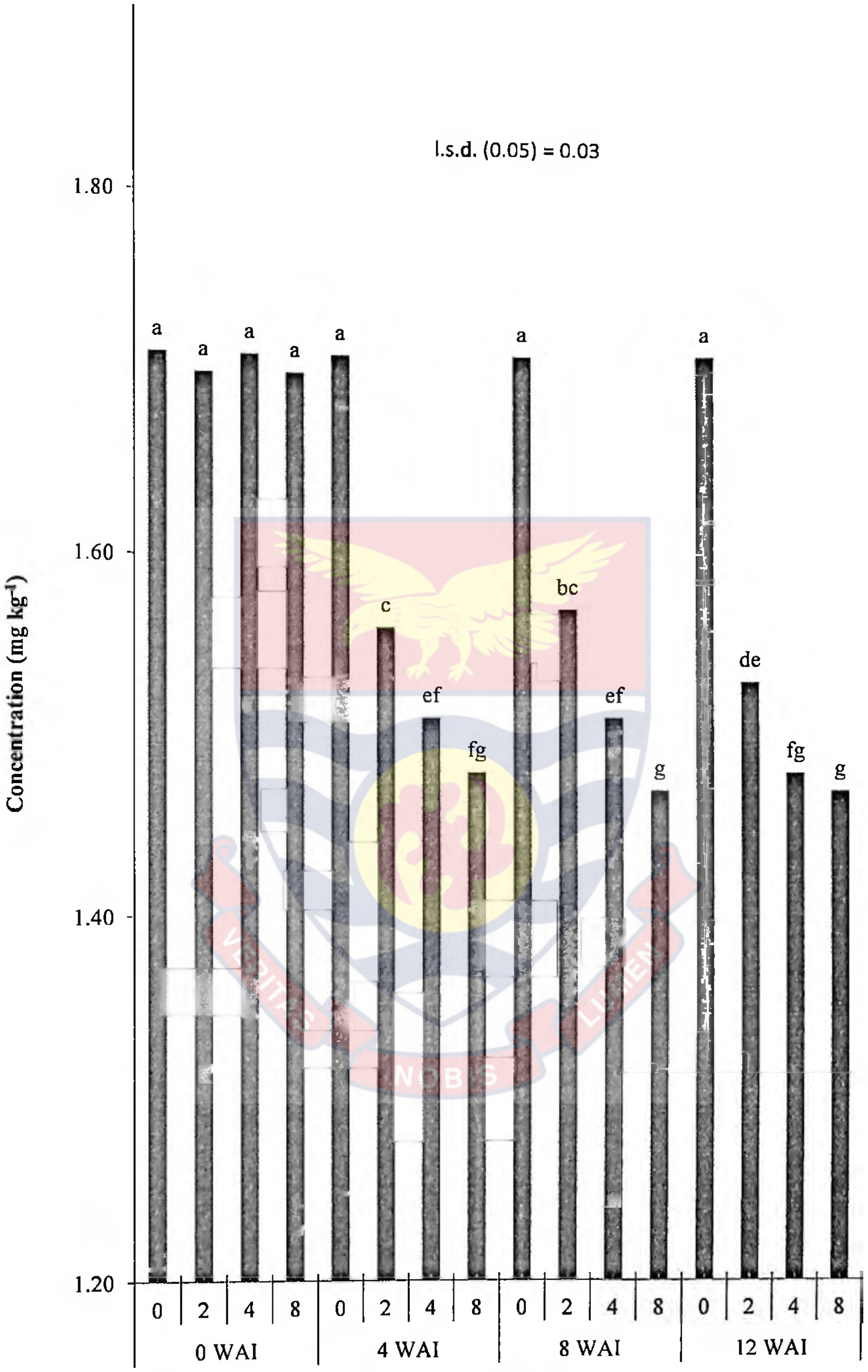
biochar yielded similar pH values in uncapped tailings ($P > 0.05$) (Figures 6, 7 and 8).

The pH value of 9.35 (± 0.07) of the biochar applied was greater than the pH of 5.3 (± 0.0), 6.45 (± 0.07) and 7.2 (± 0.0) for un-amended non-mined soil, capped and uncapped tailings, respectively. This could have contributed to the alkalisation of soil/ tailings through the neutralisation of H^+ ions by OH^- ions derived from the formation of carboxyl, carbonyl and phenolic groups in the biochar structure (Lau et al., 1986; Lehmann et al., 2005). The increased pH observed in biochar-amended soil/tailings has implications on heavy metal mediation. This is because the concentration of cationic metals such as Pb in soil solution decreases with increasing alkalinity (Oste et al., 2002; USEPA, 1992b).

Effects of Biochar on EDTA-extractable Pb of Non-mined soil, Capped and Uncapped Tailings

The different rates of application of biochar at 2, 4 and 8 t ha^{-1} each led to significantly lower concentrations of EDTA-Pb compared to the control (0 t ha^{-1}) in non-mined soil, capped and uncapped tailing ($P < 0.05$) (Figures 9, 10 and 11).

At the end of the incubation period at 12 WAI, 4 t ha^{-1} and 8 t ha^{-1} of biochar yielded insignificantly different concentrations of EDTA-Pb ($P > 0.05$) in non-mined soil (Figures 9). However, each of these rates of biochar application resulted in significantly lower concentration of EDTA-extractable Pb than that of the control at 12 WAI ($P < 0.05$)(Figure 9). The concentration of EDTA-extractable Pb was significantly lower than that of unamended soil/



Rate of application (t ha^{-1})

Figure 9. Effects of Biochar on EDTA-extractable Lead in Non-mined Soil

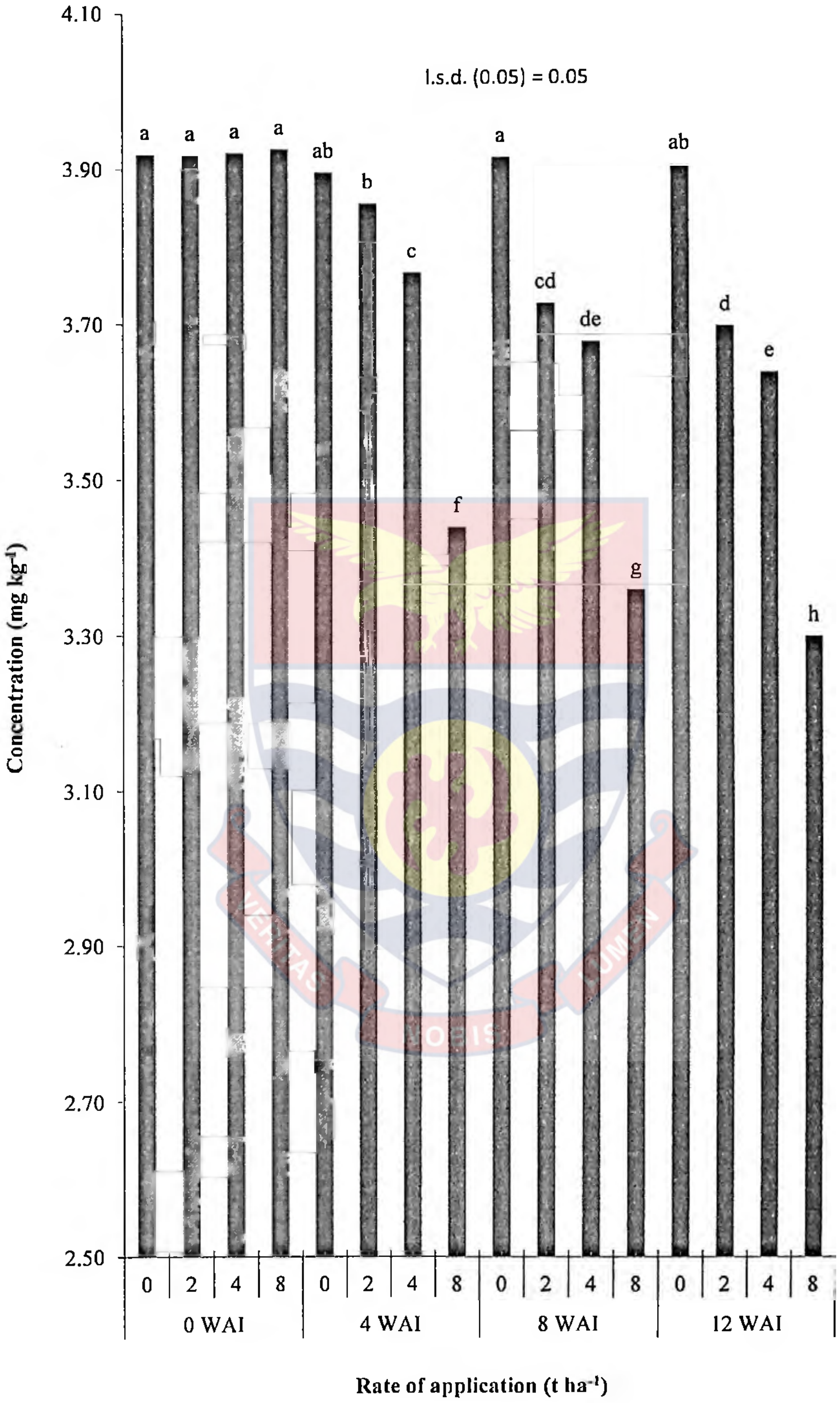


Figure 10. Effects of Biochar on EDTA-extractable Lead in Capped Tailings

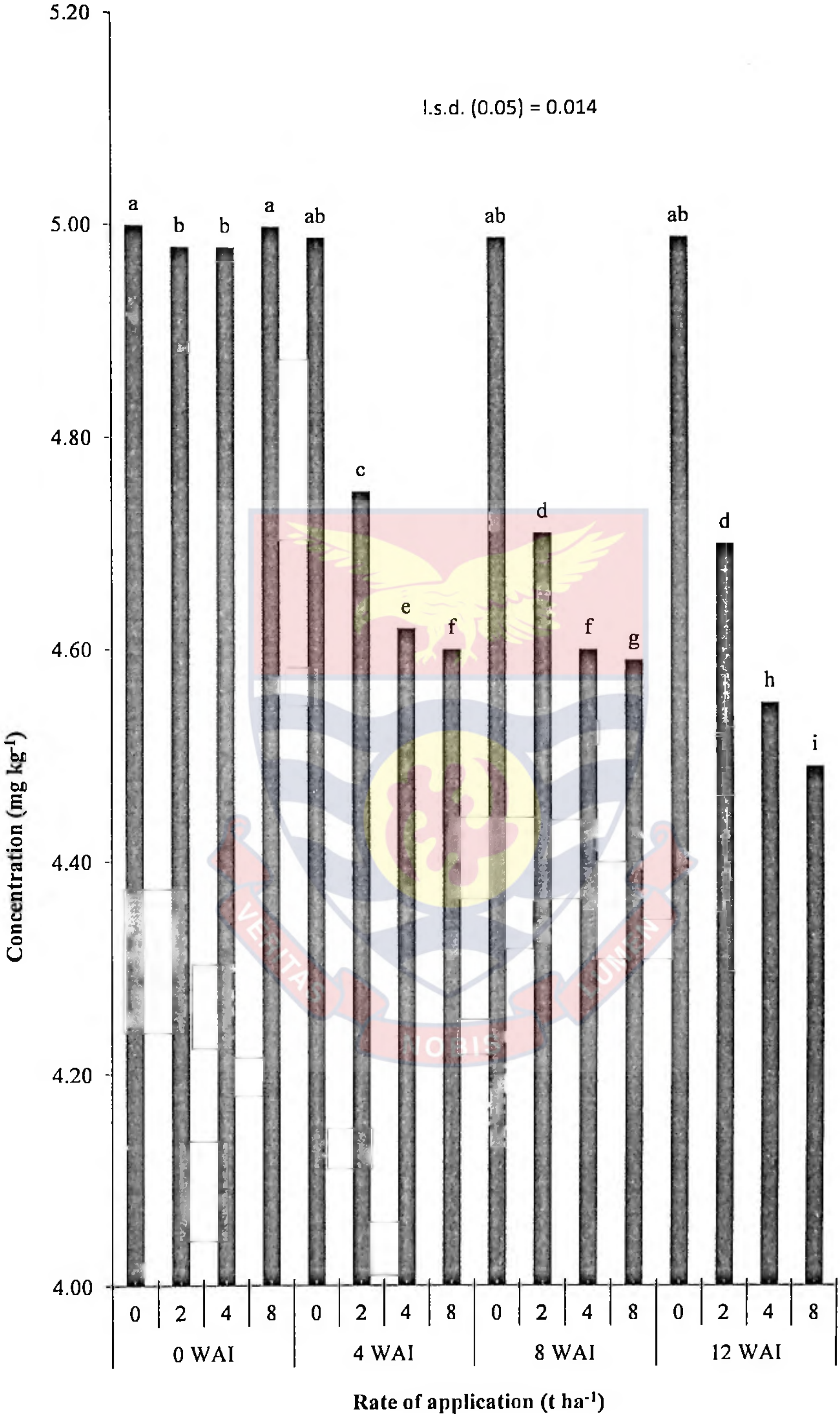


Figure 11. Effects of Biochar on EDTA-extractable Lead in Uncapped Tailings

tailings ($P < 0.05$) (Figures 9 – 11) possibly due to the increase in the pH of biochar-amended soil/tailings (Figures 6 – 8) and subsequent retention and immobilisation of Pb. Similarly, Harter (1983) noted that the adsorption of cationic metals increases with increasing pH. Secondly, the significantly lower concentrations of EDTA-extractable Pb in amended soil/tailings could also be attributed to the high specific surface area, charge density and negative surface charge possessed by biochar that result in a very high sorption and retention capacity of exchangeable cations (Liang et al., 2006).

Effects of Biochar on Water Soluble Pb of Non-mined Soil, Capped and Uncapped Tailings

The results of the effects of biochar on water soluble Pb in non-mined soil, capped and uncapped tailings are presented in Figures 12, 13 and 14. In the non-mined soil, there was no significant difference in the level of water soluble lead between the 4 and 8 t ha^{-1} rates of application of biochar at 4 and 8 WAI (Figure 12). However, the application of either 4 t ha^{-1} or 8 t ha^{-1} of biochar in non-mined soil resulted in significantly lower concentrations of water soluble lead at 12 WAI ($P > 0.05$) compared to the control (Figure 12). The significantly lower concentrations of water soluble lead (Figures 12, 13 and 14) could be related to the corresponding significantly lower concentrations of EDTA-extractable Pb (Figures 9 – 11) in biochar-amended soil/tailings. The decreased concentration of Pb extracted with EDTA implies that there was an increase in the residual fraction of Pb as a result of increased immobilisation of lead. The increased pH of biochar amended soil/tailings compared to un-amended samples (Figures 6 – 8) might have also contributed

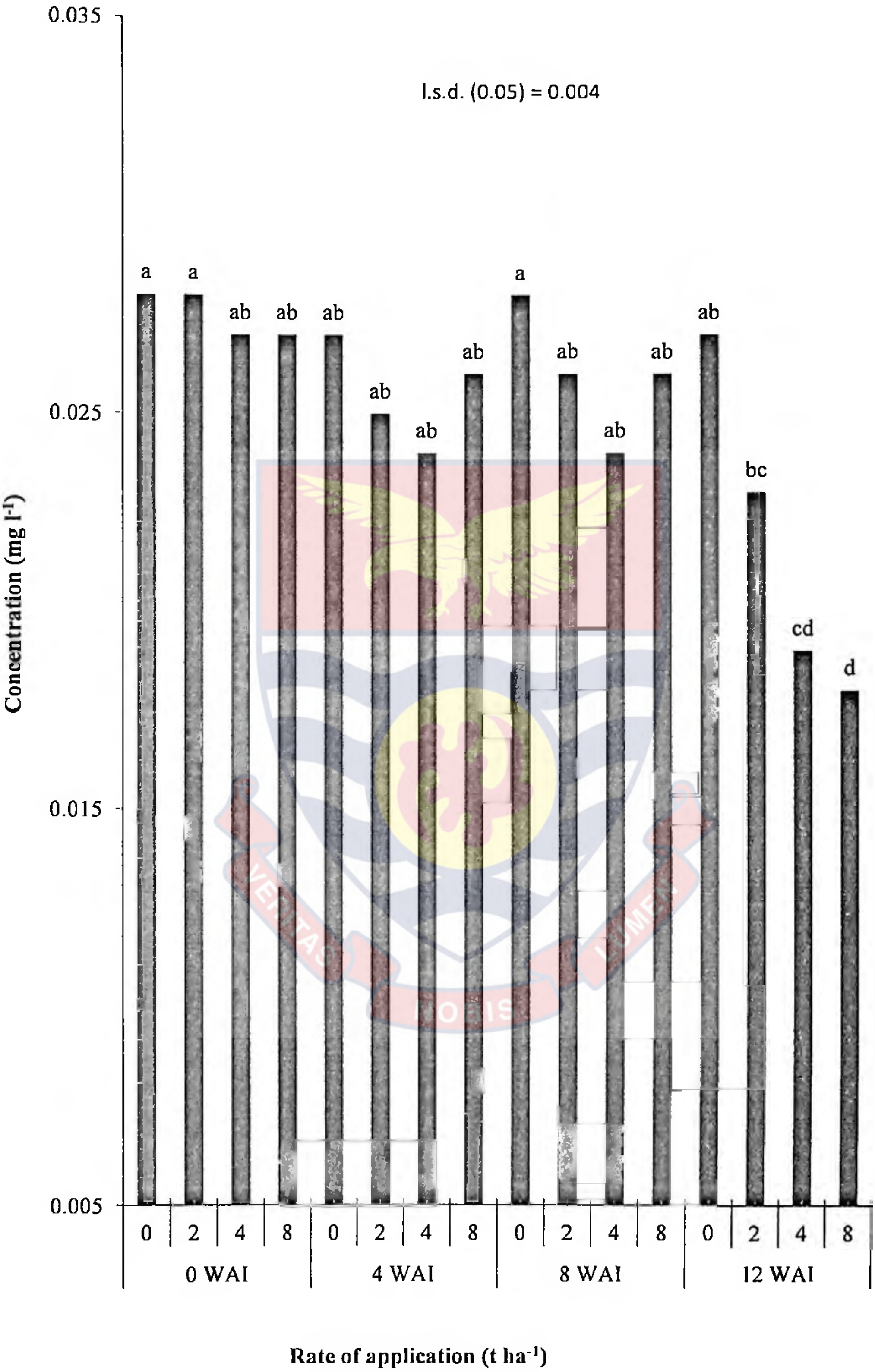


Figure 12. Effects of Biochar on Water Soluble Lead in Non-mined Soil

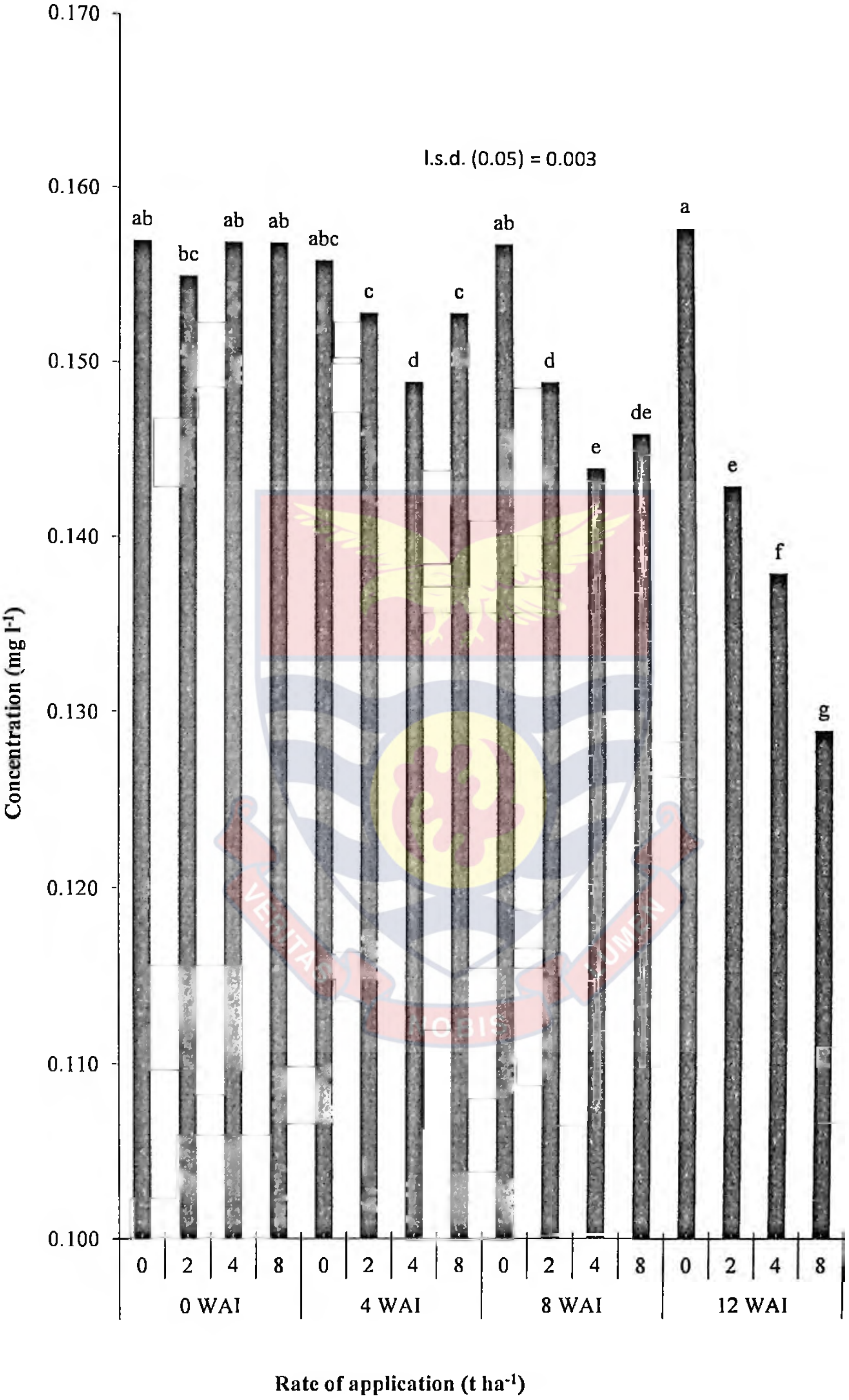


Figure 14. Effects of Biochar on Water Soluble Lead in Uncapped Tailings

to the significantly lower levels of water soluble lead (Figures 12 – 14) compared to un-amended samples. This assertion is confirmed by Oste et al. (2002) and USEPA (1992b) who report that the concentration cationic metals such as Pb in soil solution decreases with increasing alkalinity. The oxidation of black carbon does not only increase its mineralisation but also creates negative charges that subsequently lead to greater CEC and nutrient retention in the soil (Glaser et al., 2002). This could also explain the significantly lower concentrations of water soluble lead in biochar amended non-mined soil, capped and uncapped tailings.

Effects of Biochar on EDTA-extractable and Water Soluble Arsenic of Non-mined Soil, Capped and Uncapped Tailings

The application of different rates of biochar to non-mined soil, capped and uncapped tailings had no effect on EDTA-extractable arsenic as indicated by the F-probability (P-values) of the analysis of variance (ANOVA) that were > 0.05 (Table 23). The rate of application of biochar (rate) and incubation period (WAI) each had no effect on EDTA-extractable arsenic. There was also no interaction effect (WAI × rate).

Table 23: Probability values of ANOVA of Effects of Biochar on EDTA-Extractable and Water Soluble Arsenic

Soil/tailing	Source of Variation	EDTA-As	Water soluble As
		F – Probability value	
Non-mined soil	WAI	0.124	0.548
	Rate	0.263	0.239
	WAI ×Rate	0.821	0.726
Capped Tailings	WAI	0.587	0.915
	Rate	0.602	0.064
	WAI ×Rate	0.987	0.526
Uncapped Tailings	WAI	0.97	0.258
	Rate	0.3	0.612
	WAI ×Rate	0.645	0.928

Note. WAI represents weeks after incubation

Bioavailability of Arsenic and Lead in Soil/Tailings Mediated with Biochar

The results on the influence of biochar on the concentration of lead and arsenic in lettuce grown on non-mined soil, capped tailing and uncapped tailings are presented in Figure 15 and Table 24, respectively.

Effects of Biochar on the Concentration of Lead in Lettuce Grown on Non-mined Soil, Capped Tailing and Uncapped Tailings

A steady decrease in the concentration of Lead in lettuce was observed with successive increases in the rate of application of biochar in non-mined soil, capped tailing and uncapped tailings (Figure 15). The reduction in the

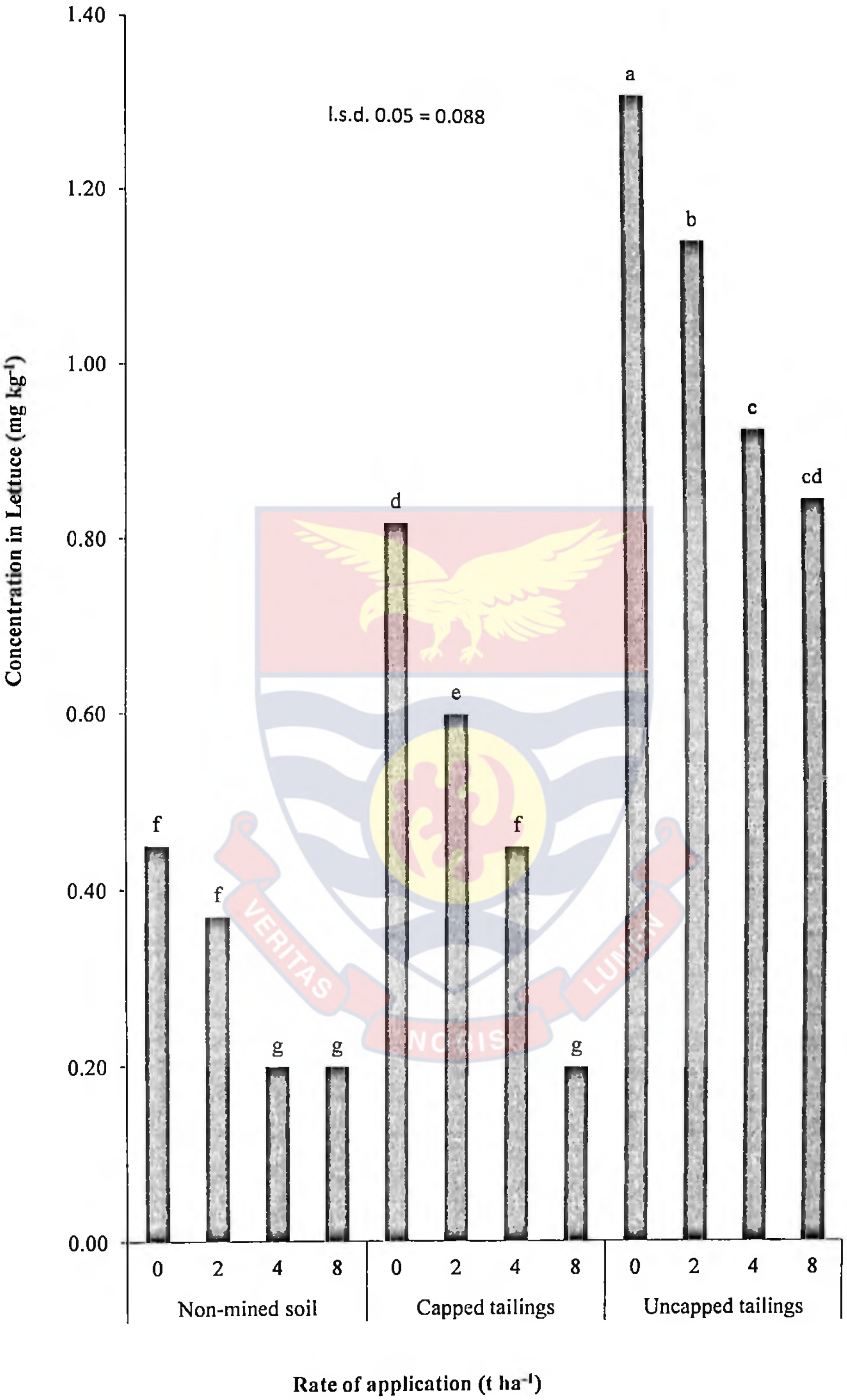


Figure 15. Bioavailability of Lead in *Lactuca sativa* L. after Mediation with Biochar

concentration of water soluble lead of biochar-amended soil/tailings with successive increases in the rate of application (Figures 12 – 14) might have contributed to the corresponding lower concentrations of Pb in lettuce.

The pH of the biochar applied (9.4 ± 0.1) was greater than those of un-amended soil/tailings. This could have contributed to the alkalisation of non-mined soil, capped and uncapped tailings (Figures 6 – 8). The increased pH observed in biochar-amended soil/tailings possibly led to a reduction in the concentration of lead in soil solution as observed by Oste et al. (2002) and USEPA (1992b). This subsequently resulted in a significantly lower level of Pb in lettuce grown on amended soil/tailings compared to un-amended samples (Figure 15).

The content of lead in lettuce grown on biochar-amended non-mined soil (0.2 – 0.37 mg kg^{-1}), capped (0.2 – 0.6 mg kg^{-1}) and uncapped (0.85–1.15 mg kg^{-1}) tailings were lower than the permissible limits of 2.0 – 2.5 mg kg^{-1} (Samara et al., 1992) and 2.0 mg kg^{-1} (MFA, 1983) in food items. Lettuce cultivated on non-mined soil, capped and uncapped tailings would therefore have no adverse effects on the health of humans after consumption with respect to Pb toxicity. However, with the more stringent maximum limit of 0.3 mg Pb kg^{-1} dry matter set by FAO/WHO (1999) only capped tailings and non-mined soil mediated with 8 t ha^{-1} and 4 t ha^{-1} biochar, respectively would be safe for human consumption. Lettuce with Pb content of 0.85 mg kg^{-1} harvested from 8 t ha^{-1}biochar-amended uncapped tailings would not be suitable for human consumption under FAO/WHO (1999) standards.

Effects of Biochar on the Concentration of Arsenic in Lettuce Grown on Non-mined Soil, Capped Tailing and Uncapped Tailings

The application of different rates of biochar had no effect on the concentration of arsenic in lettuce grown on non-mined soil, capped and uncapped tailings as indicated by the F-probability (P-values) of the analysis of variance (ANOVA) that were greater than 0.05 (Table 24 and Appendix B).

Table 24: Probability values of ANOVA of effects of Biochar on the Content of Arsenic in Lettuce

Source of Variation	Concentration of Arsenic
	F – Probability value
Soil/tailings	< 0.001
Rate	0.204
Soil/tailings × Rate	0.918

Note. WAI represents weeks after incubation

The rate of application (rate) had no effect on the concentration of arsenic in lettuce grown on soil/tailings. There was also no interaction effect (soil/tailings × rate). The significant differences ($P < 0.01$) in the content of arsenic in lettuce among the different soil/tailings could therefore be attributed to anthopogenic causes rather than the effects of biochar application (Table 24). Biochar is therefore not effective in reducing the concentrations of arsenic in the soil matrix and in soil solution.

Conclusions

Generally, the application of 8 t ha^{-1} biochar to soil/tailings resulted in the highest alkalisation and lowest concentrations of water soluble and EDTA-extractable (available) Pb of non-mined soil, capped and uncapped tailings. The application of 8 t ha^{-1} biochar resulted in the most significant increase alkalinity of non-mined soil and uncapped tailings in contrast to un-amended samples. However, the alkalinity of capped tailings was insignificantly different with the application of either 4 t ha^{-1}or 8 t ha^{-1}, although the alkalinity at each rate of application was significantly greater than that of un-amended samples. The increased alkalinity possibly contributed immensely to the reduced concentration of EDTA-extractable and water soluble Lead and the immobilisation of lead in soil/tailings. However, the application of biochar resulted in insignificant changes in EDTA-extractable and water soluble arsenic in non-mined soil, capped and uncapped tailings.

The retention of adsorbed Pb, as evidenced by the reduced concentration of EDTA-extractable and water soluble Pb in soil/tailings, resulted in significantly lower content of lead in lettuce grown on biochar-amended soil/tailings compared to un-amended samples. There were no significant differences observed in the concentration of arsenic in lettuce grown on amended soil/tailings compared to un-amended samples. Biochar was therefore ineffective in the mediation of arsenic-polluted soil/tailings. It is however, effective in reducing the concentration of Pb in non-mined soil, capped and uncapped tailings.

CHAPTER SEVEN

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The research sought to establish the efficiency of the detoxification of effluent and assess the toxicity of heavy metals with respect to the EDTA-extractable and water soluble fractions in the AngloGold mining environment (soil, water and tailings). After the establishment of the toxic metals that are either above acceptable limits or are potentially hazardous due to their levels, different amendments (zeolite, beringite, poultry manure and biochar) were applied to the soil/cappings of the study area. The effectiveness of these amendments in the amelioration of the effects of these heavy metals was then assessed. Subsequently, the bioavailability of the heavy metals in mediated soil/tailings was determined since the ultimate objective of any decontamination process is to utilize the restored soil/tailings for agriculture or other purposes.

Summary

The study revealed that:

- The processing of gold ore resulted in effluent with elevated concentrations of free cyanide, As and Pb compared to water bodies downstream. The concentrations of free cyanide, Cd, As and Pb in treated effluent discharged into the environment were above the maximum permissible limits set by Ghana Environmental Protection Agency (GEPA)

(2006) and WHO (2008). The magnitude of toxicity of these metals, in decreasing order, was As > Cd > Pb. The concentrations of Cu, Fe and Zn were, however, within the GEPA and WHO maximum permissible limits.

- The concentrations of Zn, Cu and free cyanide in capped and uncapped tailings were within the maximum permissible limits for soils. However, the concentrations of EDTA-extractable As in capped and uncapped tailings were significantly greater than that of non-mined soil and also greater than the maximum permissible limits for agricultural land.

- The efficiencies of the free cyanide remediation technologies (% decrease of the concentration of free cyanide) of the waste water were in the following decreasing order: bacterial degradation (98.6 %) > photo-oxidation (96.8 %) > hydrogen peroxide (H_2O_2) (95.9 %) > CIS (66.3 %). The treated effluent discharged into the environment after bacterial degradation also had the least concentration of Cu. The carbon-in-solution remediation measure resulted in the highest percentage decreases of 64.5, 47.1 and 31.3 % in the concentrations Zn, Cd and Fe in treated effluent, respectively. The concentrations of Pb after bacterial degradation and photo-oxidation were the same and the most efficient in reducing the concentrations of Pb in treated effluent by 40.1 and 41.2 %, respectively.

- The application of beringite to soil/tailings resulted in the least concentrations of EDTA-extractable and water soluble arsenic. The concentrations of EDTA-extractable and water soluble arsenic decreased respectively by 20 - 29 % and 61 - 85 % in non-mined soil, 14 - 31 % and 33 - 55 % in capped tailings and 7 - 9 % and 49 - 72 % in uncapped tailings after 12 weeks of incubation. The effectiveness of amendments in mediating As, in decreasing order of magnitude was, beringite > zeolite > poultry manure. Zeolite was the most effective amendment in immobilizing Pb in soil/tailings. The application of zeolite led to decreases in the concentrations of water soluble Pb by 14 - 32 %, 21 – 44 % and 32 - 51 % in non-mined soil, capped and uncapped tailings, respectively at 12 WAI. The concentration of EDTA-extractable Pb decreased by 14 - 33 %, 11 – 19 % and 41 - 48 % in zeolite-amended non-mined soil, capped and uncapped tailings respectively at 12 WAI. The effectiveness of amendments in mediating Pb, in decreasing order of magnitude was, zeolite > beringite > poultry manure. The concentration of EDTA-extractable and water soluble Pb increased with increasing rate of application of poultry manure in non-mined, capped and uncapped tailings. The application of poultry manure thus resulted in the mobilisation of lead.

- The application of biochar resulted in insignificant changes in the concentrations of EDTA-extractable and water soluble As in soil/tailings. However, the concentrations of EDTA-extractable Pb decreased significantly by 13 - 14 %, 7 - 16 % and 9 - 11 % in non-mined soil, capped and uncapped tailings, respectively 12 weeks after the application of biochar. The concentrations of Pb in soil solution also decreased by 30 - 33 % in non-mined soil, 33 - 37 % in capped tailings and 13 - 18 % and in uncapped tailings in biochar-amended soil/tailings.

- The least content of As in lettuce plants was obtained at the 60 kg ha^{-1} rate of application of beringite to soil/tailings. The application of beringite to soil/tailings resulted in lettuce As contents of 0.27, 0.37 and 2.10 mg kg^{-1} that represented percentage decreases of 67, 82 and 12 % in non-mined soil, capped and uncapped tailings, respectively. The concentration of As in lettuce harvested from 60 kg ha^{-1}beringite-amended non-mined soil (0.27 mg kg^{-1}), capped tailings (0.37 mg kg^{-1}) and un-amended non-mined soil (0.83 mg kg^{-1}) were within the UK maximum permissible limit of 1.0 mg kg^{-1} in food and therefore safe and for human consumption.

- The concentration of Pb in lettuce cropped on biochar-amended non-mined soil (0.2 mg kg^{-1}) and capped tailings (0.2 mg kg^{-1}) were within the FAO/WHO (1999) maximum limit of Pb (0.3 mg kg^{-1}) in vegetables. In non-mined soil and capped tailings, the application of zeolite resulted in Pb concentrations of lettuce that were respectively lower (0.2 mg kg^{-1}) and higher (0.33 mg kg^{-1}) than the FAO/WHO set limit. The application of biochar and zeolite yielded lettuce with concentrations of 0.85 mg kg^{-1} and 0.67 mg Pb kg^{-1}, respectively in uncapped tailings.

Conclusions

- The Hydrogen peroxide treatment was the most efficient detoxification method for gold ore effluent in reducing the concentration of As.
- The concentrations of Fe, Zn and Cu in treated effluent were below the WHO drinking water quality guidelines and do not pose a threat to the environment and human health.
- The concentrations of Pb and Cd released into the environment were in compliance with the IFC/WB guidelines for effluent discharges but higher than the GEPA and WHO standards.
- The carbon-in-solution detoxification method was most efficient in reducing the concentrations of Fe, Zn and Cu.

- The levels of Pb, Cu and Zn in non-mined soil, capped and uncapped tailings of the AngloGold Ashanti mining area were within the maximum permissible limits of GEPA and WHO standards. Thus they could be considered safe to humans and other organisms.
- The levels of EDTA-extractable Pb in capped and uncapped tailings were significantly greater than that of non-mined soil and the seepage of Pb from treated effluent that has concentrations higher than the GEPA and WHO standards, into the surrounding water bodies and soil could exacerbate its levels.
- The capping of tailings with lateritic soil could be an effective method of reducing the levels of free cyanide in contaminated soil and tailings.
- Beringite seemed to be the most effective amendment for reducing EDTA-extractable arsenic in the non-mined soil and capped tailings; however, arsenic toxicity was high in lettuce cropped on 60 kg ha^{-1} beringite-amended uncapped tailings (2.1 mg kg^{-1}) and would be injurious to human health if consumed.
- The application of zeolite may not be effective in the immobilisation of arsenic; however, it proved most effective for reducing the concentration of Pb in the polluted environment.
- Biochar was ineffective in the mediation of arsenic-polluted soil/tailings; however it proved most effective for reducing the concentration of Pb in non-mined soil and the tailings.
- With respect to the percentage decrease in the concentrations of Pb, zeolite application was more efficient than biochar in the remediation of Pb.

- The application of bioachar to soil/tailings was ineffective in the mediation of As-polluted capped and uncapped tailings and resulted in insignificant differences in the concentration of As in lettuce plants.
- Lettuce cropped on biochar- and zeolite-amended uncapped tailings samples would have toxic effects of Pb on humans according to the FAO/WHO standards.
- The hypotheses (H_0) postulated for this research was that, the mediation of polluted tailings and the detoxification of wastewater at the AngloGold Ashanti does not result in reduced toxicity and mobility of heavy metals that are within maximum permissible limits at the study area. From the foregone summary of the results, the detoxification of the effluents resulted in free cyanide and lead contents that were above the recommended standards set by the Ghana Environmental Protection Agency [GEPA], (2006) and WHO (2008). The capping of tailings with laterite produced arsenic concentration that was above the Canadian limit for contaminated and agricultural sites. The postulated hypothesis is therefore accepted.

Recommendations

- The high concentrations of free cyanide in detoxified effluent of AngloGold Ashanti, Obuasi mine could be decreased by attaining an effluent pH of 9 – 10 and maintaining a copper catalyst concentration of 50 mg L^{-1}.
- Zeolite and beringite are amendments that have the potential in effectively reducing the concentrations of Pb and As, respectively to

the maximumum acceptable limit and could be recommended for the mediation of tailings resulting from gold ore processing after long term studies have been conducted.

- Vegetables cultivated on capped and uncapped tailings have levels of arsenic and lead that are above maximum acceptable limits and are not safe for human consumption.

REFERENCES

Abbas, M., Parveen, Z., Iqbal, M., Riazuddin, M., Iqbal, S., Ahmed, M., & Bhutto, R. (2010). Monitoring of toxic metals (cadmium, lead, arsenic and mecury) in vegetables of Sindh, Pakistan. *Kathmandu University Journal of Science, Engineering and Technology, 6*(2), 60-65.

Abbott, D. E., Essingston, M. E., Mullen, M. D., & Ammons, J. T. (2001). Fly ash and lime-stabilized biosolid mixtures in mine spoil reclamation: Simulated weathering. *Journal of Environmental Quality, 30*, 608-616.

Adeniji, A. (2004). *Bioremediation of arsenic, chromium, lead and mecury.* Washington, D C: National Network of Environmental Management Studies. Retrieved July 4, 2008, from http://www.clu-in.org.

Adriano, D. C. (2001). *Trace elements in terrestrial environments: Biogeochemistry, bioavailability and risks of metals* (2nd ed.). New York, NY: Springer.

Adriano, D. C., Wenzel, W. W., Vangronsveld, J., & Bolan, N. (2004). Role of assisted natural remediation in environment cleanup. *Geoderma, 122*, 121-142.

Adu, S. V. (1992). *Soils of Kumasi, Ashanti Region, Ghana.* Kumasi: Soil Research Institute.

Agency for Toxic Substances and Disease Registry. (1990). *Toxicological profile of copper.* Atlanta, GA: ATSDR.

Agency for Toxic Substances and Disease Registry. (1994). *Toxicological profile of zinc.* Atlanta, GA: ATSDR.

Agency for Toxic Substances and Disease Registry. (1999 a). *Toxicological profile of lead.* Atlanta, GA: ATSDR.

Agency for Toxic Substances and Disease Registry. (1999 b). *Toxicological profile of arsenic.* Atlanta, GA: ATSDR.

Agricultural Development and Advisory Services. (1986). *The analysis of agricultural materials: Manual of methods.* London: ADAS.

Akcil, A. (2003). Destruction of cyanide in gold mill effluents: biological versus chemical treatments. *Biotechnology Advances, 21*(6), 501-511.

Alloway, B. J. (1995). *Heavy metals in soils* (2nd ed.). London: Blackie & Sons Ltd.

Alloway, B. J., & Ayres, D. C. (1997). *Chemical principles of environmental pollution.* London: Blackie Academic and Professional.

Almås, A., Singh, B. R., & Salbu, B. (1999). Mobility of cadmium-109 and zinc-65 in soil influenced by equilibrium time, temperature and organic matter. *Journal of Environmental Quality, 28*, 1742-1750.

American Public Health Association, American Water Works Association, Water Environment Association. (1998). *Standard Methods for Water and Wastewater Examination* (20th ed.). Washington, DC: APHA, AWWA, WEA.

Anderson, J. M., & Ingram, J. S. (1993). *Tropical soil biology and fertility. A handbook of methods.* Wallingford: CAB International.

Anderson, M. C., & Malotky, D. T. (1979). The adsorption of protolyzable anions on hydrous oxides at the isoelectric pH. *J. Colloid Interface Sci., 72*, 413-427.

Anderson, M. C., Ferguson, J. F., & Gavis, J. (1976). Arsenate adsorption on amorphous aluminium hydroxide. *J. Colloid Interface Sci., 54*, 391-399.

AngloGold Ashanti. (2006). *Environmental Laborotory Methods and Operating Manual 2.* Obuasi: AngloGold Ashanti.

AngloGold Ashanti. (2007a). *www.mining-technology.com/projects/obuasi/.* Retrieved September 27, 2007, from www.mining-technology.com/ terms.html.

AngloGold Ashanti. (2007b). *Country report, Ghana. Obuasi.* Obuasi: AngloGold Ashanti.

AngloGold Ashanti. (2008a). *AngloGold Ashanti (AGA) Meteorological Data - 2008*. Obuasi, Ashanti, Ghana: AGA Meteorological Station.

AngloGold Ashanti. (2008b). *The june environmental quality and compliance monitoring report.* Accra: African Environmental Research and Consulting Company.

Aoyama, M. (1996). Fractionation of water-soluble organic substances formed during plant residue decmposition and high performance size exclusion chromatography of the fractions. *Soil Sc. Plant Nutr., 42*, 31-40.

Aubynn, A. K. (1997). *Economic restructuring dynamics and environmental problems in Africa: Empirical examples from the forestry and mining sectors of Ghana. UNU/IAS Working Paper No. 34.* UNU/IAS.

Awudi, G. B. (2002). Role of foriegn direct investment (FDI) in the mining sector of Ghana and the economy. *Foriegn Direct Investment (FDI) and the Environment Conference.* Paris: OECD.

Barber, S. A. (1984). *Soil nutrient bioavailability: A mechanistic approach.* New York: John Wiley & Sons.

Barry, G. A., Chudek, P. J., Best, E. K., & Moody, P. W. (1995). Estimating sludge application rates to land based on heavy metal and phosphorus sorption characteristics of soil. *Water research, 29*, 2031-2034.

Baydina, N. L. (1996). Inactivation of heavy metals by Humus and Zeolites in industrially contaminated soils. *Eurasian Soil Sci.,* 28, 96-105.

Beesley, L., Moreno-Jimenez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B., & Sizmur, T. (2011). A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environmental Pollution, 159*(12), 3269-3282.

Berglund, S., Davis, R. D., & L'Hermite, P. (1984). *Utilization of sewage sludge on land: rates of application and long-term effects of metals.* Dordrecht : D. Reidel Publishing.

Bhattachartya, P., Jacks, G., Ahmed, K. M., Routh, J., & Khan, A. A. (2002). Arsenic in groundwater of the Bengal delta plain acquifers in Bangladesh. *Bulletin of Environmental Contamination and Toxicology, 69*, 538-545.

Bigdeli, M., & Seilsepour, M. (2008). Investigation of metals accumulation in some vegetables irrigated with waste water in Shahre Rey-Iran and toxicological implications. *American-Eurasian J. Agric. & Environ. Sci., 4*(1), 86-92.

Bigdeli, M., & Seilsepour, M. (2008). Investigation of metals accumulation in some vegetables irrigated with waste water in Shahre Rey-Iran and toxicological implications. *American-Eurasian J. Agric. & Environ. Sci.,, 4*(1), 86-92.

Birke, M., & Rauch, U. (2000). Urban geochemistry: Investigations in the Berlin metropolitan area. *Environmental Geochemistry and Health, 22*, 233-248.

Blaylock, M. J., Salt, D. E., Dushenkov, S., Zakharova, O. & Gussman, C. (1997). Enhanced accumulation of Pb in Indian mustard by soil applied chelating agents. *Environ. Sci. Technol., 31,* 860-865.

Boehm, H. P. (1994). Some aspects of soil chemistry of carbon blacks and other blacks. *Carbon, 32*, 759-770.

Boisson, J., Ruttens, A., Mench, M. & Vangronsveld, J. (1999). Immobilization of trace metals and arsenic by different soil additives: Evaluation by means of chemical extractions. *Communication in Soil Science and Plant Analysis, 30*, 365-387.

Bolan, N. S., & Duraisamy, V. P. (2003). Role of organic and inorganic soil ammendments on immobilization and phytoavailability of heavy metals. *Australian Journal of Soil Research, 41*, 533-555.

Bowel, R. J. (1993). Mineralogy and geochemistry of tropical rain forest soils: Ashanti, Ghana. *Chemical Geology, 106*, 345-358.

Bradl, H. B. (2004). Adsorption of heavy metals ions on soils and soils constituents. *Journal of Colloidal and Interface Science, 277,* 1-18.

Bremner, I., & Beattie, J. H. (1995). Copper and Zinc metabolism in health and disease: Speciation and interactions. *Proc. Nutr. Soc., 54*, 489-499.

Bruemmer, G. W., Gerth, J. & Herms, U. (1986). Heavy metals species, mobility and availability in soils. *Z. Pflanzenernaehr. Bodenk, 149*, 382-398.

Campbell, P. G. (1995). Interactions between trace metals and aquatic organisms: A critique of the free-ion activity model. In A. Tessier, & R. Turner (Eds.), *Metal speciation and bioavailability in aquatic systems: IUPAC series on analytical and physical chemistry of environmental systems* (pp. 45-102). Chichester: John Wiley & Sons.

Campbell, P. G., & Tessier, A. (1996). Ecotoxicology of metals in the aquatic environment: Geochemical aspects. In M. C. Newman (Ed.), *Ecotoxicology: A hierarchical treatment* (pp. 11-58). Boca Raton, FL: Lewis Publishers.

Canadaian Council of Ministers of the Environment. (1991). *Interim environmental quality criteria for contaminated sites. Report CCME EPC-CS34.* Winipeg, Manitoba.

Cao, X. D., Ma, L. Q., & Shiralipour, A. (2003). Effects of compost and phosphate amendments on arsenic mobility in soils and arsenic uptake by the hyperacumulator, *Pteris vittata* L. *Environmental Pollution, 126*, 157-167.

Castaldi, P., Santona, L., & Melis, P. (2005). Heavy metal immobilization by chemical amendments in a polluted soil and influence on white lupin growth. *Chemosphere, 60*, 365-371.

Cavallaro, N., & McBride, M. B. (1978). Copper and cadmium adsorption characteristics of selected acid and calcareous soils. *Soil Science Society of America Journal, 42*, 550-556.

Chakravarty, S., Dureja, V., Bhattacharyya, G., Maity, S. & Bhattacharjee, S. (2002). Removal of arsenic from groundwater using low-cost ferruginous manganese ore. *Water Research, 36*, 625-632.

Chatterjee, A., Das, D., & Chakraborti, D. (1993). A study of groundwater contamination by arsenic in the residential area of Behala, Calcutta, due to industrial pollution. *Environmental Pollution, 80*, 57-65.

Chefetz, B., Hatcher, P. G., Hadar, Y., & Chen, Y. (1996). Chemical and biological characterization of organic matter during composting of municipal solid waste. *Journal of Environmental Quality, 25*, 776-785.

Chen, M., & Ma, L. Q. (2001). Comparison of three aqua regia digestion methods for twenty Florida soils. *Soil Science Society of America Journal, 65*, 491-499.

Chen, M., & Chen, C. (1999). Bioaccumulation of sediment-bound heavy metals in Grey Mullet, *Liza macrolepis*. *Marine Pollution Bulletin, 39*, 239-244.

Chen, Z. N., Lee, G. J., & Lui, J. C. (2000). The effects of chemical remediation of cadmium and lead in contaminated soils. *Chemosphere, 41*, 235-242.

Chen, Z. S., Tsai, C. C., & Tsui, C. C. (1999). Proposal regulation of soil pollutants in Taiwan soils. In Z. S. Chen (Ed.), *Proceedings of 6th workshop on soil pollution and prevention: Soil remediation techniques on soils contaminated by organic pollutants (In Chinese, with English abstract and tables)*., (pp. 169-207). Taipei, Taiwan: Linking Publ. Co.

Cheng, C., Lehmann, J., Thies, J. E., Burton, S. D., & Engelhard, M. H. (2006). Oxidation of black carbon by biotic and abiotic processes. *Organic Geochemistry, 37*, 1477-1788.

Chinese Department of Preventive Medicine. (1994). *Threshold for food hygiene*. Beijing: CDPM.

Chlopecka, A., & Adriano, D. C. (1997). Influence of zeolite, apatite and fe-oxide on Cd and Pb uptake by crops. *Sci. Total Environ., 207*, 195-206.

Choprapawon, C., & Rodcline, A. (1997). Chronic arsenic poisoning in Ronpibool Nakon Sri Thammarat, The Southern Province of Thailand. In C. O. Abernathy, R. L. Calderon, & W. R. Chappell (Ed.), *Arsenic: Exposure and health effect* (pp. 69-78). Bangkok: Chapman and Hall.

Coutsoukis, P. (2004). *www.ghanagold2.htm*. Retrieved 2007, from http://www.photius.com/countries/ghana/economy/ ghana_ economy_ gold.html.

Czupyrna, G., & Levy, A. I. (1989). *In-situ Immobilization of heavy-metal-contaminated soils. Pollution Technol. Rev. No. 173*. Park Ridge, NJ: Noyes Data Corp.

Damian, F., & Damian, D. (2007). Detoxification of heavy metal contaminated soils. *American Journal of Environmental Sciences, 3*(4), 193-198.

Daniels, M. (1968). Radiolysis and photolysis of the aqueous nitrate system. In R. F. Gould (Ed.), *Advances in Chemistry Series, Radiation Chemistry* (pp. 153-163).

De Anil, K. (2000). *Environmental Chemistry* (4th ed.). New Delhi: New Age International Publishers Ltd.

De Sousa, C. (2003). Turning brownfields into green space in the city of Toronto. *Landscape and Urban Planning, 62*, 181-198.

Dermatas, D., Moon, D. H., Menounou, N., Meng, X., & Hires, R. (2004). An evaluation of arsenic release from monolithic solids using a modified semi-dynamic leaching test. *Journal of Hazardous Materials, 116*, 25-38.

Dhargava, B. S., & Raghupathi, H. B. (1993). Analysis of plant materials for Micro- and Macro-cronutrients. In H. L. Tandoh (Ed.), *Methods of analysis of soil, plant, water and fertilizers* (First ed., pp. 49-82). New Delhi: Fertilizer Development and Consultation Organization (FDCO).

Dictor, M. C., Battaglia-Brunet-Bayyaglia, F., Morin, D., Bories, A., & Clarens, M. (1997). Biological treatment of gold ore cyanidation wastewater in fixed bed reactors. *Environmental Pollution, 97*(3), 287-294.

Din-Normen. (1984). *Determination of leachability by water (S4) Din-Normen. Din 38414. German standard methods for the examination of water, wastewater and sludge.* Sludge and Sediments (Group S). Retrieved 2007, from http://www.ecn.nl/docs/society/horizontal/E_DIN_38414-17_%28E%29-EOX.pdf

Dudley, L. M., McLean, J. E., Furst, T. H., & Jurinak, J. J. (1991). Sorption of Cd and Cu from an acid mine waste extract by two calcareous soils: column studies. *Soil Science, 151*, 121-135.

Duker, A., Carranza, E. J., & Hale, M. (2005). Arsenic geochemistry and health. *Environment International, 31*, 631-641.

Ebbs, S. (2004). Biological degradation of cyanide compounds. *Current Opinion In Biotechnology, 15*, 231-236.

Edwards, R., Rebedea, I., Lepp, N. W., & Lovell, A. J. (1999). An Investigation into the mechanisms by which synthetic Zeolites reduce labile metal concentrations in soils. *Environmental Geochemistry and Health, 21*, 157-173.

Environment Agency. (2004). The state of soils in England and Wales. *Landscape and Urban Planning, 62*, 32.

European Commission. (2006a). *Thematic strategy for soil protection, communication from the commission to the council, the european parliament, the economic and social committee and the committee of the regions.* Brussels: European Commission.

European Commission. (2006b). *Impact assessment of the thematic strategy on soil protection. Communication from the commission to the council, the European Parliament, the Economic and Social Committee and the Committee of the Regions.* Brussels: European Commission.

European Topic Centre Soil (ETCS). (1998). *Topic report - Contaminated sites.* Copenhagen: European Environment Agency.

Evanko, C. R. & Dzombak, D. A. (1997). *Remediation of heavy-metals-contaminated soil and groundwater.* Retrieved July 19, 2009, from http://www.gwrtac.org

Farrell, M., & Jones, D. L. (2000). Use of composts in the remediation of heavy metal contaminated soil. *Journal of Hazardous Materials, 175*, 575-582.

Figueira, M. M., Volesky, B., Azarian, K., & Ciminelli, S. T. (2000). Biosorption column performance with a metal mixture. *Environmental Science and Technology, 34*, 4320-4326.

Food and Agriculture Organization. (2006). *Arsenic contamination of irrigation water, soil and crops in Bangladesh: Risk implications for sustainable agriculture and food safety in Asia*, Rap Publication 2006/20. (A. Heikens, Ed.) Bangkok, Thailand: Regional Office for Asia and the Pacific. Retrieved from http://www.fao.org/docrep/009/ ag105e/AG105E00.htm.

Food and Agriculture Organization/International Union of Soil Sciences. (2006). *World reference base for soil resources. A framework for international classification, correration and communication. World soil resources reports, 103*. Rome: FAO.

Food and Agriculture Organization/World Health Organization. (1999). *Expert committee on food additive, summary and conclusions, 53rd Meeting*. Rome: FAO.

Food and Agriculture Organization/World Health Organization. (2001). *Food additives and contaminants. Joint FAO/WHO food standards program 2001. ALINORM 01/12A:1-289*. Rome: FAO/WHO.

Food Standards Agency. (2007). *Food standards*. Retrieved June 3, 2012, from Food Standards Agency website: http://www.food.gov.uk/ multimedia/pdf /fsismetals

Fotovat, A., Naidu, R., & Suer, M. E. (1997). Water: soil ratio influences aqueous phase chemistry of indigenous copper and zinc in soils. *Aust. J. Soil Res., 35*, 687-710.

Fox, M. A., & Dulay, M. T. (1993). Heterogeneous photocatalysis. *Chem. Rev., 93*, 341-357.

Garau, G., Castaldi, P., Santona, L., Deiana, P., & Melis, P. (2007). Influence of red mud, zeolite and lime on heavy metal immobilization, culturable heterotrophic populations and enzyme activities in a contaminated soil. *Geoderma, 142*, 47-57.

Garbisu, C., & Alkorta, I. (2001). Phytoextraction: A cost-effective plant-based technology for the removal of metals from the environment. *Bioresource Technology, 77*, 229-236.

Garcia, C., Hernandez, T., & Costa, F. (1991). Study of water extract of sewage sludge composts. *Soil Sc. Plant Nutri., 37*, 399-408.

Geiszinger, A., Goessler, W., Kuehnelt, D., Francesconi, K., & Kosmus, W. (1998). Determination of arsenic compounds in earthworms. *Environmental Science and Technology, 32*, 2238-2243.

Genstat. (2008). *Genstat discovery* (3rd ed.). *Genstat Procedure Library Release PL15.2.* London: VSN International Ltd.

Ghana Environmental Protection Agency. (2006). *Guidelines for effluent discharges into natural water bodies. maximum permissible levels.* Accra: Ghana Environmental Protection Agency.

Glaser, B., Guggenberger, G., Zech, W., & Ruivo, M. L. (2003). Soil organic matter stability in Amazonian Dark Earths. In J. Lehmann (Ed.), *Amazonian Dark Earths: Origin, properties, management* (pp. 141-158). Dordrecht, The Netherlands: Kluwer Academic Publishers.

Glaser, B., Lehmann, J., & Zech, W. (2002). Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - A review. *Biology and Fertility of Soils, 35*, 219-230.

Glisic, P. M., Glisic, I. S., & Milosevic, N. T. (2009). the effect of natural zeolites and organic fertilizers on the characteristics of degraded soils and yield of crops grown in Western Serbia. *Land Degradation & Development, 20*, 33-40.

Google Maps (2013). Obuasi - Google Maps. Retrieved from http://maps. google.com/obuasi?q=obuasi

Goldstein, M. (1976). Economics of treating cyanide wastes. *Poll. Eng., 8*, 36-38.

Gonzalez, R. C., & Gonzalez-Chavez, M. C. (2006). Metal accumulation in wild plants surrounding mine wastes. *Environmental Pollution, 144*, 84-92.

Gregorich, E. G., Turchenek, L. W., Carter, M. R., & Angers, D. A. (2001). *Soil and environmental science dictionary.* Boca Raton, FL: CRC Press.

Grubben, G. J. (2004). *Lactuca Sativa* L. In G. H. Grubben (Ed.), *Plant resources of tropical Africa 2. Vegetables.* (pp. 348-353). Wageningen: PROTA Foundation/Backhuys Publishers/CTA.

Gustafson, O. & Gschwend, P. M. (1997). Soot as a strong partition medium for polycyclic aromatic hydrocarbons. In R. P. Eganhouse (Ed.), *Molecular markers in environmental geochemistry* (pp. 365 - 381). washington, D C, USA: American Chemical Society.

Harter, R. D. (1983). Effect of soil pH on adsorption of lead, copper, zinc and nickel. *Soil Sci. Soc. Am. J., 47*, 47-51.

Hayes, A. W. (2007). *Principles and methods of toxicology.* Philadelphia: CRC Press.

Hickey, M. G., & Kittrick, J. A. (1984). Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals. *Journal of Environmental Quality, 13*, 372-376.

Hindmarsh, J. T. (2002). Caveats in hair analysis in chronic arsenic poisoning. *Clinical Biochemistry, 35*, 1-11.

Ho, S. P., Wang, Y. Y., & Wan, C. C. (1990). Electronic decomposition of cyanide effluent with an electrochemical reactor packed with stainless steel fibre. *Water Res., 24*(11), 1317-1321.

Hoecker, W., & Muir, D. (1987). Degradation of cyanide. In *Research and development in extractive metallurgy* (pp. 29-36). Adelaide: The SAIMM Adelaide Branch, RDEM.

Hooda, P. S., & Alloway, B. J. (1996). The effect of liming on heavy metal in wheat, carrots and spinach grown on previously sludge-applied Soils. *J. Agric. Sci., 127*, 289-294.

Hrudey, S. E., Chen, W., & Rousseaux, C. G. (1995). *Bioavailability in environmental risk assessment.* Boca Raton, FL: Lewis Publ.

Huang, J. W., Chen, J., Berti, W. R., & Cunningham, S. D. (1997). Phytoremediation of lead contaminated soil: Role of synthetic chelates in lead phytoextraction. *Environmental Science and Technology, 31*(3), 800-805.

Huang, X., Sillanpaa, M., Duo, B., & Gjessing, E. T. (2008). Water quality in the Tibetian plateau: metal contents of four selected rivers. *Environmental Pollution, 156*, 270-277.

Hudson-Edwards, K. A., Houghton, S. L., & Osborn, A. (2004). Extraction and analysis of arsenic in soils and sediments . *Trends in Analytical Chemistry, 23*(10-11), 745-752.

Ingvorsen, K., Hojer-Pederson, B., & Godtfredsen, S. E. (1991). Novel cyanide-hydrolysing enzyme from *Alcalingenes xylosoxidans* subs. denitrificans. *Applied Environmental Microbiology, 57*, 1783-1789.

International Agency for Research on Cancer. (1987). *Arsenic and arsenic compounds (Group 1). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans* (Vols. 1-47). Rome: WHO.

International Council on Mining and Metals. (2006). *Ghana. Executive summary. The challenge of mineral wealth: Using resource endownments to foster sustainable development.* Washington, DC: International Council on Mining and Metals.

International Cyanide Management Institute. (2006). Cyanide. *http://www. cyanidecode.org/about_faq.php.* Retrieved October 2007

International Finance Corporation & World Bank Group. (2007). Performance indicators and monitoring. Environment. Emissions and effluent guidelines. *Environmental, health and safety guidelines for mining.* Washington, DC: IFC, WB Group.

International Programme on Chemical Safety. (1995). *Inorganic lead.environmental health criteria 165.* Geneva: WHO/IPCS.

International Soil Reference and Information Centre / Food and Agriculture Organization. (2004). *Guiding principles for the quantitative assessment of soil degradation with focus on salinization, nutrient decline and soil pollution.* Rome: ISRIC/FAO.

Jones, L. H., Jarvis, S. C., & Cowling, D. W. (1973). Lead uptake from soils by perennial ryegrass and its relation to the supply of an essential element (sulphur). *Plant and Soil, 38*, 605-619.

Joubert, A. V., Lucas, L., Garrido, F., Joulian, C., & Jauzein, M. (2007). Effect of temperature, gas phase composition, pH and microbial activity on As, Zn, Pb and Cd mobility in selected soils in the Ebro and Meuse Basins in the context of global change. *Environmental Pollution, 148*, 749-758.

Kabata-Pendias, A. (2001). *Trace elements in soils and plants* (3rd ed.). Boca Raton, FL.: CRC Press.

Kertulis-Tartar, G. M., Ma, L. Q., Tu, C., & Chirenje, T. (2006). Phytoremediation of an arsenic-contaminated site using *Pteris Vittata* L.: A Two-year study. *International Journal of Phytoremediation, 8*, 311-322.

Khalkaliani, D. N., Mesdaghinia, A. R., Mahvi, A. H., Nouri, J., & Vaezi, F. (2006). An experimental study of heavy metal extraction, using various concentrations of EDTA in a sandy loam soil. *Pakistan Journal of Biological Sciences, 9*(5), 837-842.

Khan, S., Cao, Q., Zheng, Y. M., Huang, Y. Z., & Zhu, Y. G. (2008). Health risks of heavy metals in contaminated soils and food cops irrigated with wastewater in Beijing, China. *Environmental Pollution, 152*, 686-692.

Khodadadi, A., Abdolahi, M., & Teimoury, P. (2005). Detoxification of cyanide in gold processing wastewater by hydrgen peroxide. *Iran. J. Environ. Health Sci. Eng., 2*(3), 177-182.

Kiekens, L. (1983). Behaviour of heavy metals in soils. In S. Berglund, R. D. Davis, & P. L'hermite (Eds.), *Utilization of sewage sludge on land: Rates of application and long-term effects of metals.* Dordrecht: Reidel Publishing.

Kolb, S. E., Fermanich, K. J., & Dornbush, M. E. (2009). Effect of charcoal quantity on microbial biomass and activity in temperate soils. *Soil Science Society of America Journal, 73*(4), 1173-1181.

Kotuby-Amacher, J., & Gambrell, R. P. (1988). *Factors affecting trace metal mobility in subsurface soils. Report No. EPA/600/2-88/036.* Washington, DC.: USEPA.

Kuo, S., Heilman, P. E., & Baker, A. S. (1983). Distribution and forms of copper, zinc, cadmium, iron and manganese in soils near a copper smelter. *Soil Science, 135*, 101-109.

LaGrega, M. D., Buckingham, P. L., Evans, J. C., & Management, E. R. (2001). *Hazardous waste management* (2nd ed.). Boston, MA: Mc-Graw Hill Inc.

Lau, A. C., Furlong, D. N., Healy, T. W., & Gieser, F. (1986). The electrokinetic properties of black carbon and graphitized carbon black aqueous colloids. *Colloids and Surfaces, 18*, 93-104.

Lee, J. S., Lee, S. W., Chon, H. T., & Kim, K. W. (2008). Evaluation of human exposure to arsenic due to rice ingestion in the vicinity of abandoned Myungbong Au-Ag mine site, Korea. *Journal of Geochemical Exploration, 96*, 231-235.

Lehmann, J. (2007). Bio-energy in the black. *Front. Ecol. Environ., 5*, 381-387.

Lehmann, J., & Rondon, M. (2006). Bio-char soil management in highly weathered soils in the humid tropics. In N. Uphoff (Ed.), *Biological approaches to sustainable soil systems* (pp. 517-530). Boca Raton, FL: CRS Press.

Lehmann, J., da Silva Jr., J. P., Steiner, C., Nehis, T., Zech, W., & Glaser, B. (2003). Nutrient availability and leaching in an archaeological Anthrosol of Central Amazon Basin: Fertilizer, manure and charcoal amendment. *Plant & Soil, 249*, 343-375.

Lehmann, J., Laing, B. Q., Solomon, D., Lerotic, M., Luizao, F., Kinyangi, J., . . . Jacobsen, C. (2005). Near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy for mapping nano-scale distribution of organic carbon forms in soil: Application to black carbon particles. *Global Biogeochem. Cycles, 19*, 1013.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., . . . Neves, E. G. (2006). Black carbon increases cation exchange capacity in soils. *Soil Science Society of America Journal, 70*, 1719-1730.

Lien, R. H., & Altringer, P. B. (1993). Case Study: Bacterial cyanide detoxification during closure of the Green Springs gold heap leach operation. In A. E. Torma, M. L. Apel, & C. L. Brierley (Eds.), *Biohydrometallurgical Technologies* (pp. 219-227). Warrendale, PA: The Minerals, Metals and Materials Society.

Linsay, W. L. (1979). *Chemical equilibria in soils*. New York: John Wiley & Sons Inc.

Lombi, E., & Gerzabek, M. H. (1998). Determination of mobile heavy metal fraction in soil: result of a plot experiment with sewage sludge. *Communications in Soil Science and Plant Analysis, 29*, 2545-2556.

Lombi, E., Zhao, F., Zhang, G., Sun, B., Fitz, W., Zhang, H., & McGrath, S. P. (2002). In-situ fixation of metals in soils using bauxite residue: Chemical assesement. *Environmental Pollution, 118*, 435-443.

Lui, C., Luo, C., Gao, Y., Li, F., Lin, L., Wu, C., & Li, X. (2010). Arsenic contamination and potential health risk implications at an abandoned tungsten mine, southern China. *Environmental Pollution, 158*, 820-826.

Ma, L. Q., & Rao, G. N. (1997). Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils. *Journal of Environmental Quality, 26*, 788-794.

Ma, L., Komar, K. M., Tu, C., Zhung, W., Chai, Y., & Kennelly, E. D. (2001). A fern that hyperaccumulates arsenic. *Nature, 409*, 579.

Malaysian Food Act. (1983). *Food Act 1983 (Act 281) and Regulations.* Malaysia: Commissioner of Law Review Revision.

Malhotra, S., Pandit, M., Kapoor, J. C., & Tyagi, D. K. (2004). Photo-oxidation of cyanide in aqueous solution by the UV/H_2O_2 process. *Journal of Chemical Technology and Biotechnology, 80*(1), 13-19.

Mandal, B. K., & Suzuki, K. T. (2002). Arsenic round the world: A review. *Talanta, 58*, 201-235.

Maplandia. (2005). *Obuasi Municipal - Coordinates.* Retrieved August 5, 2009, from Google Maps World Gazetter: http://www.maplandia.com/ghana/ashanti/ashanti/obuasi/obuasi

Marlowe, M., Cossairt, A., Moon, C., Errera, J., MacNeel, A., Peak, R., . . . Schroeder, C. (1985). Main and Interaction effects of metallic toxins on classroom behaviour. *J. Abnorm. Child Psychol.*, *13*(2), 185-198.

McBride, M. B. (1989). Reactions controlling heavy metal solubility in soils. In B. A. Stewart (Ed.), *Advances in Soil Science* (pp. 1-56). New York: Springer-Verlag.

McBride, M. B. (1994). *Environmental soil chemistry.* New York: Oxford University Press.

McBride, M. B., Richards, B. K., Steenhuis, T., Russo, J. J., & Sauve, S. (1997). Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. *Soil Science, 162*, 487-500.

McCarthy, J. F., & Zachara, J. M. (1989). Subsurface transport of contaminants: Role of mobile colloidal particles. *Environ. Sci. Technol., 23*, 496-504.

McGarth, S. P., & Loveland, P. J. (1992). *The soil geochemical atlas of England and Wales.* London, United Kingdom.

McGill, S. L., & Comba, P. G. (1990). *A Review of existing cyanide destruction practices.* Nevada Mining Association, Nevada Department of Wildlife, Wildlfe/Mining Workshop Held on March 29, 1990. Reno, Nevada.

McKinnon, E. (2002). The environmental effects of mining waste disposal at Lihir gold mine, Papua New Guinea. *Journal of Rural and Remote Environmental Health, 2*(1), 40-50.

Meeussen, J. L., Keizer, M. G., & Van Riemsdijk, W. H. (1992). Dissolution Behaviour of iron cyanide (prussian blue) in contaminated soils. *Environ. Sci. Technol., 26*, 1832-1838.

Meharg, A. A., & Hartley-Whitaker, J. (2002). Arsenic uptake and metabolism in arsenic resistant and non-resistant plant species. *New Phytologist, 154*, 29-43.

Mench, M., Vangronsveld, J., Beckx, C., & Ruttens, A. (2006). Progress In assisted natural remediation of an arsenic contaminated agricultural soil. *Environmental Pollution, 144*, 51-56.

Mineyev, V. G., Kochetavkin, A. V, & Van Bo, N. (1990). Use of natural zeolites to prevent heavy metal pollution of soils and plants. *Sov. Soil Sci., 22*, 72-79.

Mitch, M. L. (2002). Phytoextraction of toxic metals, a review of biological mechanisms. *Journal of Environmental Quality, 31*, 109-1.

Mizuta, K., Matsumoto, T., Hatate, y., Nishihara, K., & Nakanishi, T. (2004). Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal. *Bioresource Technology, 95*, 255-257.

Mohammed, M. M. (2002). Heat capacities, phase transitions and structural properties of cation-exchanged H-mordenite zeolites. *Thermochim. Acta, 387*, 121-130.

Montperrus, M., Bohari, Y., Bueno, M., Astrue, A. & Astrue, M. (2002). Comparison of extraction procedures for arsenic speciation in environmental solid reference materials by high–performance liquid chromatography-hydride generation atomic fluorescence spectroscopy. *Appl. Organomet. Chem., 16*, 347-354.

Morel, F. M. (1983). *Principles of aquatic chemistry.* New York: John Wiley & Sons.

Mosaferi, M., Yunesian, M., Mesdaghinia, A. R., Nasseri, S., Mahvi, A. H., & Nadim, H. 3. (2005). Correlation between Arsenic concentration in drinking water and human hair. *Iranian J. Env. Health Sci. Eng., 2*(1), 13-21.

Myneni, S. C., Traina, S. J., Logan, T. J., & Waychunas, G. A. (1997). Oxyanion behavior in alkaline environments: Sorption and desorption of arsenate in ettringite. *Environment, Science and Technology, 31*, 1762-1768.

Nadia, G., & Zaghloul, A. M. (2007). Minimizing the human health hazard of lettuce cultivated in some heavy metals affected soils. *Australian Journal of Basic and Applied Sciences, 1*(2), 79-86.

Naidu, R., Oliver, D., & McConnell, S. (2003). Heavy metal phytotoxicity in soils. In A. Langley, M. Gilbey, & B. Kennedy (Ed.), *Proceedings of the fifth national workshop on the assessment of site contamination.* Adelaide, SA: National Environment Protection Council Service Corporation.

Narwal, R. P., & Singh, B. R. (1998). Effect of organic materials on partitioning, exractability and plant uptake of metals in an alum shale soil. *Water, Air and Soil Pllution, 103*, 405-421.

National Coalition on Mining. (2009). *Press statement: "Envirionmental Protection Agency subverts community concerns".* Retrieved November 11, 2009, from Third World Network-Africa.

National Toxicology Program. (2008). *11th Report on Carcinogens.* Retrieved November 22, 2008, from http://ntp.niehs.nih.gov/index.cfm?objectid=32BA9724-F1F6-975E-7FCE50709CB4C932

Navarro, M. C., Perez-Sirvent, C., Martinez-Sanchez, M. J., Vidal, J., & Marimon, J. (2006). Lead, cadmium and arsenic bioavailability in the abondoned mine site of Caezo Rajao (Murcia, SE Spain). *Chemosphere*, 63, 484-489.

Needleman, H. L., & Gatsonis, C. A. (1990). Low-level lead exposure and the IQ of children: A meta-analysis of modern studies. *J. Am. Med. Assoc., 263*(5), 673-678.

Nissen, L. R., Lepp, N. W., & Edwards, R. (2000). Synthetic zeolites as amendments for sewagesludge-based compost. *Chemosphere, 41*, 265-269.

Nogawa, K., Kobayashi, E., Okubo, Y., & Suwazono, Y. (2004). Environmental cadmium exposure, adverse effects and preventative measures in Japan. *Biometals, 17*(5), 581–587.

Olajire, A. A., Ayodele, E. T., Oyedirdan, G. O., & Oluyemi, E. A. (2003). Levels and speciation of heavy metals in soils of industrial Southern Nigeria. *Environmental Monitoring and Assessment, 85*, 135-155.

Opong, E. A. (2008). *Biological cyanide detoxification - Laboratory, pilot and main plants updates.* Obuasi: AngloGold Ashanti.

Organization for Economic Cooperation and Development. (2002). OECD global forum on international investment. In C. N. Boocock (Ed.), *Environmental impacts of foreign direct investment in the mining sector in Sub-Saharan Africa.* Paris: OECD.

Oste, L. A., Lexmond, T. M., & Van Riemsdijk, W. H. (2002). Metal immobilization in soils using synthetic zeolites. *Journal of Environmental Quality, 31*, 813-821.

Owusu-Koranteng, H. (2005). *Presentation on the social impact of gold mining in Ghana - Unequal distribution of burdens and benefits and its implications on human rights at the 11th EADI General Conference.* Retrieved November 2009, 11, from www.wacamghana. com.

Panstar-Kallio, M., & Manninen, P. K. (1997). Speciation of mobile arsenic in soil samples as a function of pH. *Science of the Total Environment, 204*, 193-200.

Panuccio, M. R., Sorgona, A., Rizzo, M. & Cacco, G. (2009). Cadmium adsorption on vermiculite, zeolite and pumice: Batch experimental studies. *Journal of Environmental Management, 90*(1), 364-374.

Papassipi, N., Tambouris, S., & Kontopoulos, A. (1997). Removal of heavy metal calcareous contaminated soils by EDTA leaching. *Water, Air and Soil Pollution, 109*, 1-15.

Patil, Y. B., & Paknikar, P. K. (2000). Removal of metal cyanides from waste waters. *Process Biochem., 35*, 1139-1151.

Pendersen, E. J., & Marinas, B. J. (1995). *Cyanogen chloride formation in drinking water from the reaction between Chloramines and Formaldehyde.* Proceedings of the American Water Works Association Annual Conference, Water Research. Anaheim, CA. Held from 18-22 June 2003 (pp. 359-369). Denver, CO: American Water Works Association.

Perić, J., Trgo, M., & Vukojevic-Medvidovic, N. (2004). Removal of zinc, copper and lead by natural zeolite - A comparison of adsorption isotherms. *Water Res., 38*(7), 1893-1899.

Pierangeli, M. A., Guilherme, L. R., Oliveira, L. R., Curi, N., & Silvia, M. L. (2003). Efeito da força iônica da solução de equilíbrio na adsorção de cádmio em Latossolos brasileiros. *Pesquisa Agropecuária Brasileira, 38*, 737-745.

Pocknee, S., & Summer, M. E. (1997). Carbon and nitrogen contents of organic matter determine its liming potential. *Soil Science Society of America Journal, 61*, 86-92.

Pocock, S. J., Smith, M., & Baghurst, P. (1994). Environmental Lead and Children's Intelligence: A Systematic review of the epidemiological evidence. *Br. Med. J., 309*, 1189-1197.

Podlesakova, E., Nemecek, J., & Vacha, R. (2001). Trace elements in soil. bioavailability, flux and transfer. In I. K. Iskandar, & M. B. Kirkham (Eds.), *Mobility and bioavailabilty of trace elements in soils.* Boca Raton, FL: CRC Press.

Poggio, L., Vrscaj, B., Schulin, R., Hepperle, E., & Marsan, F. A. (2008, August 12). *Metal pollution and human bioaccessibility of topsoils in Grugliasco (Italy). Environmental Pollution.* Retrieved June 13, 2009, from www.elsevier.com/locate/envpol:www.elsevier.com/locate/envpo

Puls, R. W., Powell, D. A., Clark, D., & Eldred, C. J. (1991). Effect of pH, solid/solution ratio, ionic strength and organic acids on Pb and Cd sorption on kaolinite. *Water, Air and Soil Pollution, 57-58*, 423-430.

Radovic, L. R., Moreno-Castilla, C., & Rivera-Utrilla, J. (2001). Carbon materials as adsorbents in aqueous solutions. In L. R. Radovic (Ed.), *Chemistry and physics of carbon* (pp. 227-405). New York: Marcel Dekker.

Rakovan, J., & Reeder, R. J. (1994). Differential incorporation of trace elements and dissymmetrization in apatite: The role of surface structure during growth. *American Mineralogist, 79*, 892-903.

Raphael, E. C., Eunice, O. E., & Frank, E. O. (2010). Trace metal distribution in some common tuber crops and leafy vegetables grown in the Niger Delta Region of Nigeria. *Pakistan Journal of Nutrition, 9*(10), 957-961.

Raskin, I., Smith, R. D., & Salt, D. E. (1997). Phytoremediation of metals: Using plants to remove pollutants from the evironment. *Curent Opin. Biotechnol.,* 8, 221-226.

Ritcey, G. M. (1989). *Tailings management problems and solutions in the mining industry. Process Metallurgy 6.* London: Elsevier Science.

Roman, R., Fortun, C., De Sa, M., & Almendros, G. (2003). Successful soil remediation and reforestation of a calcic regosol amended with composted urban waste. *Arid Land Research and Management, 17*, 297-311.

Romic, M., Romic, D., Dolanjski, D., & Stricevic, I. (2004). Heavy metals accumulation in topsoils from wine-growing regions. Part 1. Factors which control retention. *Agriculturae Conspectus Scientificus, 69*(1), 1-10.

Ross, S. M. (1994). Retention, transformation and mobility of toxic metals in soils. In S. M. Ross (Ed.), *Toxic metals in soil-plant systems* (pp. 63-152). Chichester: John Wiley And Sons Ltd.

Sabienë, N., Brazuaskiene, D. M., & Rimmer, D. (2004). Determination of heavy metal mobile forms by different extraction methods. *Ekologija, 1*, 36-41.

Salt, D. E., Blaylock, M., Kumar, P. B., Dushenkov, V., Ensley, B. D., Chet, L., & Raskin, L. (1995). Phytoremediation: A novel strategy for the removal of toxic metals from the environment using plants. *Biotechnology, 13*, 468-474.

Salt, D. E., Smith, R. D., & Raskin, I. (1998). Phytoremediation. *Annu. Rev. Plant Physiol. Plant Mol. Biol., 49*, 643-668.

Samara, C. P., Misaelides, P., Tsalev, D., Anousis, I., Koui, T., & Tzis, M. (1992). Trace elements distribution in vegetables grown in the industrial area of Thessaloniki, Greece-Frasenius. *Environmental Bulletin, 1*, 577-582.

Sastre, I., Vicente, M. A., & Lobo, M. C. (2001). Behavior of cadmium and nickel in a soil amended with sewage sludge. *Land Degradation and Development, 12*, 27-33.

Sauvé, S., Martinez, C. E., McBride, M., & Hendershot, W. (2000). Adsorption of free lead (Pb^{2+}) by pedogenic oxides, ferrihydrite and leaf compost. *Soil Science Society of America Journal, 64*, 595-599.

Sauvé, S., McBride, M. B., & Hendershort, W. (1998). Lead Phosphate Solubility in Water and Soil Suspensions. *Environ. Sci. Technol, 32*, 388-393.

Savin, A., Veselinovic, D., & Markovic, D. (2004). The correlation of the values of plant-available Pb and Cd in soil determined using different types of extragens. *J. Serb. Chem. Soc., 69*(12), 1145-1151.

Schwab, P., Zhu, D., & Banks, M. K. (2007). Heavy metal leaching from mine tailings as affected by organic amendments. *Bioresource Technology, 98*, 2935-2941.

Schwartz, J. (1994). Low-level lead exposure and children's IQ: A meta-analysis and search for a threshold. *Environ. Res., 65*, 42-55.

Sharma, O. P., Bangar, K. S., Rajesh-Jain, K. S., & Sharma, P. K. (2004). Heavy metals accumulation in soils irrigated by municipal and industrial effluent. *J. Environ. Sci. Eng., 46*, 65-73.

Shi, W., Shao, H., Li, H., Shao, M., & Du, S. (2009). Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite. *Journal of Hazardous Materials, 170*, 1-6.

Shrestha, G., Traina, S. J., & Swanston, C. W. (2010). Black carbon's properties and role in the environment: A comprehensive review. *Sustainability, 2*, 294-320.

Shuman, L. M. (1999). Organic waste amendments effect on zinc fractions of two soils. *J. Environ. Qual., 28*, 1442-1447.

Silveira, M. L., Alleoni, L. R., & Guilherme, L. R. (2003, October/December). Biosolids and heavy metals in soils. *Scientia Agricola, 60*(4), 793-806.

Singh, B. R., & Myhr, K. (1998). Cadmium uptake by barley as affected by Cd sources and pH levels. *Geoderma, 84*, 185-194.

Skjemstad, J. O., Clarke, P., Taylor, J. A., Oades, J. M., & McClure, S. G. (1996). The chemistry and nature of protected carbon in the soil. *Austr. J. Soil Res., 34*, 251-271.

Smedley, P. L. (1996). Arsenic in rural groundwater in Ghana. *Journal of African Earth Sciences, 22*(4), 549-470.

Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry, 217*, 517-568.

Smith, A., & Mudder, T. I. (1991). *The chemistry and treatment of cyanidation wastes.* London: Mining Journal Books Ltd.

Sposito, G. (1983). The chemical forms of trace metals in soils. In I. Thornton (Ed.), *Applied environmental Geochemistry* (pp. 123-170). London: Academic Press.

State Environmental Protection Administration. (2005). *The limits of pollutants in food. GB 2762-2005.* China: SEPA

Stewart, B. A., Robinson, C. A., & Parker, D. B. (2000). Examples and case studies of beneficial reuse of beef cattle by-products. In W. A. Dick (Ed.), *Land application of industrial and municipal by-products* (pp. 387-407). Madison: Soil Science Society of America Inc.

Stolz, J., Yang, P., & Ambruster, T. (2000). Cd-exchanged Heulandite: Symmetry lowering and site preference. *Micropore. Mesopore. Mater, 37*(1-2), 233-242.

Stratford, J., Dias, A. E., & Knowles, C. J. (1994). The utilization of thiocyanate as a nitrogen source by heterotrophic bacterium: The degradative pathway involves formation of ammonium and tetrathionate. *Microbiology, 140*, 2657-2662.

Stronach, S. A., Walker, N. L., Macphee, D. E., & Glaser, F. P. (1997). Reactions between cement and As(III) oxide: The system CaO-SiO_2-As_2O_3-H_2O at 25 °C. *Waste Management, 17*(1), 9-13.

Tan, T. C., Teo, W. K., & Chin, D. T. (1985). Electrochemical destruction of complex cyanide. *Chem. Eng. Comm., 38*, 125-133.

Temminghoff, E. J., Van der Zee, S. E., & De Haan, F. A. (1997). Copper mobility in a Cu-contaminated sandy soil as affected by pH and solid and dissolved organic matter. *Environ. Sci. Technol., 31*, 1109-1115.

Terry, M., & Jack, C. (2007). *Cyanide.* Retrieved October 13, 2007, from http://www.infomine.com/

Theis, T. L., & West, M. J. (1986). Effects of cyanide complexation on adsorption of trace metals at the surface of goethite. *Environmental Technology Letters, 7*, 309-316.

Tordoff, G. M., Baker, A. J., & Willis, A. J. (2000). Current approaches to the revegetation an reclamation of metalliferous mine wastes. *Chemosphere, 41*, 219-228.

Trgo, M., Peric, J., & Vukojevic-Medvdovic, N. (2006). Investigations of different kinetic models for zinc ions uptake by natural zeolite tuff. *Journal of Environmental Management, 79*, 298-304.

Trompowsky, P. M., Benites, V. M., Madari, B. E., Primenta, A. S., Hockaday, W. C., & Hatcher, P. G. (2005). Characterization of humic like substances obtained by chemical oxidation of eucalyptus charcoal. *Organic Geochemistry, 36*, 1480-1489.

Tu, C., & Ma, L. Q. (2002). Effects of arsenic concentrations and forms on arsenic uptake by the hyperaccumulator Ladder Brake. *J. Environ. Qual., 31*, 641-647.

Tu, C., Ma, L. Q., & Bondada, B. (2002). Arsenic accumulation in the Hyperaccumulator Chinese brake and its utilization potential for Phytoremediation. *J. Environ. Qual.*, 31, 1671-1675.

Turpeinen, R. R., Panstar-Kallio, M., Häggblom, M., & Kairesalo, T. (2002). Role of microbes in controlling the speciation of arsenic and production of arsines in contaminated soils. *Sci. Total Environ., 285*, 133-145.

United States Environmental Protection Agency. (1992 a). *Test methods for evaluating solid waste and clays by a Dithionite-citrate system buffered with sodium bicarbonate. Laboratory manual. Physical & chemical methods, SW 846* (3rd ed., Vol. IA). Washington DC.: Government Print Office.

United States Environmental Protection Agency . (1992 b). Behavior of metals in soils. (J. E. McLean, & B. E. Bledsoe, Eds.) *EPA Ground Water Issue, EPA/540/S-92/018*, 1-25.

United States Environmental Protection Agency. (1994 a). *Treatment of cyanide heap leaches and tailings.* Washington, DC: USEPA.

United States Environmental Protection Agency. (1994 b). *Background for NEPA reviewers: Non-coal mining operations.* Washington, D. C.: United States Environmental Protection Agency.

University of Melbourne. (2005). *Working with cyanide: The treatment of cyanide poisoning and disposal of cyanide residue.* Retrieved

September 15, 2007, from http://safety.chemistry.unimelb.edu.au/ cyanide.php.

Van Herwijnen, R., Hutchings, T. R., Al-Tabba, A., Moffat, A. J., Johns, M. L., & Ouki, S. K. (2007). Remediation of contaminated soil with mineral-amended composts. *Environmental Pollution, 150*, 347-354.

Vangronsveld, J., & Cunningham, S. D. (1998). *Metal contaminated soils. In-situ inactivation and phytorestoration.* Geogia, TX: R. G. Landes Co.

Vangronsveld, J., Ruttens, A., & Clijsters, H. (1999). The use of cyconic ashes of fluidized bed burning of coal mine refuse for long-term immobilization of metals in soils. In K. S. Sajwan, A. K. Alva, & R. F. Keefer (Eds.), *Biogoechemistry of trace elements in coal and coal combustion By-Products* (pp. 223-233). New York: Academic Publ.

Verberk, M. M., Willems, T. E., Verplanke, A. J., & De Wolffab, F. A. (1996). Environmental lead and renal effects on children. *Archives of Environmental Health, 51*(1), 83-87.

Vergunst, R. D., Iamarino, B. T., & Devuyst, E. A. (1991). Heap pad detoxification at snow caps mine using the INCO Process. *30th Annual Conference of Metallurgists Held from 18th to 21st August, 1991.* Ottawa: CIM.

Visoottiviseth, P., Francesconi, K., & Sridokchan, W. (2002). The potential of Thai plant species for the phytoremediation of arsenic-contaminated land. *Environmental Pollution, 118*, 453-461.

Vousta, D. A., Graminas, A., & Samara, C. (1996). Trace elements in vegetables grown in an industrial area in relation to soil and air particulate matter. *Environ. Pollut., 94*, 325-335.

Walker, D. J., Clemente, R., & Bernal, M. P. (2004). Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. *Chemosphere, 57*, 215-224.

Walker, D. J., Clemente, R., Roig, A., & Bernal, M. P. (2003). The effects of soil amendments on heavy metal bioavailabilty in two contaminated mediterranean soils. *Environmental Pollution, 122*, 303-312.

Wassa Association of Communities Affected by Mining. (2003). *Fact finding mission (FFM) on human rights abuses of Ashanti Goldfields Company (Obuasi Mine); The case of Sansu community.* (H. Owusu-Koranteng, Ed.) Retrieved November 11, 2009, from www.wacamghana.com: http://www.wacamghana.com/ app/webroot/ img/documents/4af45f8961a48.pdf

Wassa Association of Communities Affected by Mining. (2008). *Joint statement by WACAM and Concerned Farmers Association of Teberebie on the seepage of cyanide containment of AngloGold Ashanti, Iduapriem mine.* Retrieved November 12, 2009, from WASSA Association of Communities Affected by Mining: http://www.wacam.com

Wauchope, R. D. (1983). Uptake, translocation and phytotoxicity of arsenic in plants. In W. H. Lederer, & R. J. Fensterheim (Eds.), *Arsenic: Industrial, Biomedical, Environment Perspectives.* New York: Van Nostrand Reinhole.

Whelton, A. J., Jensen, J. L., Richards, T. E., & Valdivia, R. M. (2003). *The cyanic threat to portable water.* Denver, CO: AWWA.

Whitlock, J. L., & Mudder, T. I. (1985). The homestake wastewater treatment process: biological removal of toxic parameters from cyanidation wastewaters and bioassay effluent evaluation. *Fundamental and Applied Biohydrometallurgy. Proceedings of the Sixth International Symposium on Biohydrometallurgy*, (pp. 327-339) *Held at Vancouver, BC., Canada.* Amsterdam : Elsevier Science Publishers.

Wikimedia. (2009). *Cadmium. Chemical characteristics*. Retrieved October 19, 2009, from www.wikimediafoundation.org/: http://wikimediafoundation.org/

Woolson, E. A. (1977). Fate of arsenicals in different environmental substrate. *Environ. Health Perspect., 19*, 73-81.

World Gold Council. (2006). *Trust in gold - Production.* Retrieved August 21, 2009, from http://MHTML2files\Trust In Gold - Production.mht.

World Health Organisation. (2008). *Guidelines for drinking-water quality.* Retrieved April 6, 2008, from http://who.int/bookorders/anglais/dartprt1.jsp?sesslan=1&codlan=1&codcol=15...

Wu, S. C., Luo, Y. M., Cheung, K. C., & Wong, M. H. (2006). Influence of bacteria on Pb and Zn Speciation, mobility and availability in soil: A laboratory study. *Environmental Pollution, 144*, 756-773.

Young, C. A. & Jordan, T. S. (1995). Cyanide remediation: Current and past technologies. In L. E. Erickson, D. L. Tillison, S. C. Grant, & J. P. McDonald (Ed.), *Hazardous waste research. Proceedings of the 10th annual conference on hazardous waste research* (pp. 104-129). Manhattan, Kansas: Great Plains-Rocky Mountain Hazardous Substance Research Center (HSRC).

Zaghloul, A. M., & Abou-Seeda, M. (2005). *Evaluation of chemical remediation techniques of Pb-contaminted soils using Kinetic approach.* Mansoura: Mansoura University.

Zakrzewski, S. F. (1991). *Principles of environmental toxicology: ACS professional reference book.* Washington, D C: American Chemical Society.

Zeng, Q. R., Sauve, S., Allen, H. E., & Hendershot, W. H. (2005). Recycling EDTA solution to remediate metal-polluted soils. *Environmental Pollution, 133*, 225-231.

Zhao, D., Sengupta, A. K., & Stewart, L. (1998). Selective removal of Cr (IV) oxyanions with a new anion exchanger. *Industrial and Engineering Chemistry Research, 37*, 4383-4387.

Zurera-Cosano, G. R., Moreno-Rojas, R., Salmeron-Egea, J., & Pozo-Lora, R. (1984). Heavy metal uptake from greenhouse border soils for edible vegetables. *J. Sci. Food Agric., 49*(3), 307-314.

APPENDIX A

DATA USED FOR THE ANALYSIS OF VARIANCE

Appendix A1. Preliminary Data 1 on the properties of of effluent of AngloGold Ashanti, Obuasi Mine

Treatment	Sample	Temp, (°C)	pH of effluent	Free cyanide (mg L^{-1})
1. Tailings slurry (TS)	1	28.6	8.99	40.00
	2	28.5	9.03	40.00
	3	28.8	8.92	35.00
	Mean	28.63	8.98	38.33
2. Tailings dam effluent (TD)	1	31.0	7.58	35.00
	2	31.2	7.61	30.00
	3	31.0	7.59	30.00
	Mean	31.07	7.59	31.67
3. Holdings pond effluent (HP)	1	30.4	7.45	10.00
	2	30.8	7.42	12.00
	3	30.7	7.44	10.00
	Mean	30.63	7.44	10.67
4. Sulphide treatment plant effluent (STP)	1	30.3	7.71	5.00
	2	30.6	7.76	6.00
	3	30.1	7.72	6.00
	Mean	30.33	7.73	5.67
5. Pond 2 effluent (Feeds Pond 3)	1	30.2	7.33	5.00
	2	30.3	7.38	5.00
	3	30.7	7.35	6.00
	Mean	30.40	7.35	5.33
6. Photo-oxidation (Pox)	1	31.6	6.81	1.00
	2	31.7	6.83	1.00
	3	31.8	6.81	1.00
	Mean	31.70	6.82	1.00
7. Hydrogen peroxide treatment (Pond 3) (PD 3)	1	30.1	7.23	0.2
	2	30.4	7.21	0.2
	3	30.3	7.22	0.3
	Mean	30.27	7.22	0.23

Appendix A2. **Effects of application of different rates of biochar on EDTA-extractable Arsenic**

	Rep.	Rate (t ha^{-1})	As-Edta (0 WAI)	As-Edta (4 WAI)	As-Edta (8 WAI)	As-Edta (12 WAI)
Non-mined	1	0	20.05	19.89	19.87	19.97
Non-mined	1	2	19.87	19.21	19.33	19.06
Non-mined	1	4	19.83	19.81	19.09	20.18
Non-mined	1	8	20.12	19.51	19.01	19.54
Non-mined	2	0	19.87	19.76	19.98	19.83
Non-mined	2	2	20.06	19.19	19.32	19.98
Non-mined	2	4	19.83	19.05	19.98	20.01
Non-mined	2	8	19.77	19.49	19.97	20.45
Non-mined	3	0	19.78	20.03	19.66	19.87
Non-mined	3	2	19.78	19.22	19.35	20.86
Non-mined	3	4	19.80	19.65	19.06	19.18
Non-mined	3	8	19.73	19.53	19.01	18.11
Capped tailing	1	0	178.2	180.3	179.7	181.6
Capped tailing	1	2	179.3	181.6	180.3	181.8
Capped tailing	1	4	180.1	178.8	179.5	179.4
Capped tailing	1	8	178.7	180.1	179.7	180.1
Capped tailing	2	0	180.1	180.2	179.4	180.9
Capped tailing	2	2	179.3	180.6	178.9	180.5
Capped tailing	2	4	178.7	180.3	179.7	181.9
Capped tailing	2	8	180.1	180.9	180.7	181.9
Capped tailing	3	0	181.3	181.2	181.6	179
Capped tailing	3	2	181.7	180.5	181.2	178.1
Capped tailing	3	4	180.3	179.7	179.3	180.3
Capped tailing	3	8	181.2	181.2	180.8	179.5
Uncapped tailing	1	0	790.7	789.6	790.9	788.5
Uncapped tailing	1	2	790.3	791.6	790.5	790.6
Uncapped tailing	1	4	791.7	790.1	790.0	790.2
Uncapped tailing	1	8	790.9	793.2	791.4	791.8
Uncapped tailing	2	0	790.6	790.9	790.3	792.5
Uncapped tailing	2	2	792.1	790.9	790.8	793.8
Uncapped tailing	2	4	793.3	790.6	791.8	791.9
Uncapped tailing	2	8	790.7	791.1	792.3	790.8
Uncapped tailing	3	0	790.3	791.6	790.4	791.2
Uncapped tailing	3	2	790.6	790.5	791.9	790.1
Uncapped tailing	3	4	791.8	790.9	792.6	790.6
Uncapped tailing	3	8	790.7	790.7	790.7	791.7

Appendix A3. Effects of application of different rates of biochar on water soluble Arsenic

Soil/tailings	Rep.	Rate (t ha^{-1})	As-H_2O (0 WAI)	As-H_2O (4 WAI)	As-H_2O (8WAI)	As-H_2O (12WAI)
Non-mined	1	0	0.226	0.225	0.225	0.225
Non-mined	1	2	0.225	0.226	0.225	0.226
Non-mined	1	4	0.226	0.227	0.225	0.226
Non-mined	1	8	0.227	0.225	0.226	0.226
Non-mined	2	0	0.225	0.226	0.225	0.226
Non-mined	2	2	0.227	0.225	0.227	0.226
Non-mined	2	4	0.225	0.226	0.226	0.224
Non-mined	2	8	0.226	0.225	0.228	0.227
Non-mined	3	0	0.227	0.226	0.226	0.225
Non-mined	3	2	0.226	0.227	0.226	0.226
Non-mined	3	4	0.227	0.225	0.227	0.226
Non-mined	3	8	0.228	0.226	0.225	0.227
Capped tailing	1	0	0.448	0.448	0.449	0.448
Capped tailing	1	2	0.448	0.448	0.448	0.446
Capped tailing	1	4	0.447	0.448	0.447	0.447
Capped tailing	1	8	0.448	0.449	0.449	0.45
Capped tailing	2	0	0.447	0.447	0.448	0.448
Capped tailing	2	2	0.449	0.448	0.448	0.449
Capped tailing	2	4	0.449	0.451	0.45	0.449
Capped tailing	2	8	0.449	0.449	0.449	0.448
Capped tailing	3	0	0.448	0.448	0.447	0.448
Capped tailing	3	2	0.45	0.447	0.449	0.449
Capped tailing	3	4	0.448	0.45	0.45	0.45
Capped tailing	3	8	0.448	0.449	0.448	0.449
Uncapped tailing	1	0	3.113	3.112	3.115	3.116
Uncapped tailing	1	2	3.111	3.111	3.11	3.12
Uncapped tailing	1	4	3.112	3.063	3.082	3.112
Uncapped tailing	1	8	3.12	3.098	3.121	3.123
Uncapped tailing	2	0	3.111	3.111	3.12	3.116
Uncapped tailing	2	2	3.11	3.112	3.115	3.108
Uncapped tailing	2	4	3.107	3.132	3.124	2.923
Uncapped tailing	2	8	3.11	3.121	3.083	2.939
Uncapped tailing	3	0	3.108	3.108	3.112	3.1
Uncapped tailing	3	2	3.101	3.119	3.114	3.094
Uncapped tailing	3	4	3.109	3.116	3.114	3.121
Uncapped tailing	3	8	3.109	3.12	3.123	3.122

Appendix A4. **Effects of different rates of application of biochar on soil/ tailings pH**

Soil/Tailings	Rep.	Rate (t ha^{-1})	pH (0WAI)	pH (4WAI)	pH (8WAI)	pH (12WAI)
Non-mined	1	0	5.3	5.3	5.3	5.3
Non-mined	1	2	5.3	5.4	5.4	5.4
Non-mined	1	4	5.3	5.5	5.6	5.6
Non-mined	1	8	5.4	6	5.7	5.7
Non-mined	2	0	5.3	5.3	5.3	5.3
Non-mined	2	2	5.3	5.4	5.5	5.5
Non-mined	2	4	5.3	5.5	5.5	5.5
Non-mined	2	8	5.4	6	5.7	5.7
Non-mined	3	0	5.3	5.3	5.3	5.3
Non-mined	3	2	5.3	5.4	5.4	5.4
Non-mined	3	4	5.3	5.6	5.6	5.6
Non-mined	3	8	5.4	6.1	5.8	5.8
Capped tailings	1	0	6.4	6.4	6.4	6.4
Capped tailings	1	2	6.4	6.5	6.5	6.5
Capped tailings	1	4	6.4	6.6	6.5	6.5
Capped tailings	1	8	6.6	6.8	6.7	6.8
Capped tailings	2	0	6.4	6.4	6.4	6.4
Capped tailings	2	2	6.4	6.5	6.5	6.5
Capped tailings	2	4	6.4	6.6	6.5	6.5
Capped tailings	2	8	6.6	6.7	6.7	6.7
Capped tailings	3	0	6.4	6.4	6.4	6.4
Capped tailings	3	2	6.4	6.5	6.5	6.5
Capped tailings	3	4	6.4	6.6	6.5	6.5
Capped tailings	3	8	6.6	6.8	6.7	6.7
Uncapped tailings	1	0	7.2	7.2	7.2	7.2
Uncapped tailings	1	2	7.3	7.3	7.3	7.3
Uncapped tailings	1	4	7.4	7.4	7.4	7.4
Uncapped tailings	1	8	7.4	7.5	7.4	7.4
Uncapped tailings	2	0	7.2	7.2	7.2	7.2
Uncapped tailings	2	2	7.2	7.3	7.3	7.3
Uncapped tailings	2	4	7.4	7.4	7.4	7.4
Uncapped tailings	2	8	7.4	7.5	7.4	7.4
Uncapped tailings	3	0	7.2	7.2	7.2	7.2
Uncapped tailings	3	2	7.2	7.3	7.3	7.3
Uncapped tailings	3	4	7.3	7.4	7.4	7.4
Uncapped tailings	3	8	7.4	7.5	7.4	7.4

Appendix A5. Effects of application of different rates of biochar on EDTA- extractable Lead

Soil/tailings	Rep.	Rate (t ha^{-1})	Pb-Edta (0 WAI)	Pb-Edta (4 WAI)	Pb-Edta (8 WAI)	Pb-Edta (12 WAI)
Non-mined	1	0	1.714	1.699	1.71	1.713
Non-mined	1	2	1.698	1.549	1.556	1.532
Non-mined	1	4	1.701	1.511	1.501	1.471
Non-mined	1	8	1.687	1.501	1.441	1.461
Non-mined	2	0	1.698	1.711	1.699	1.703
Non-mined	2	2	1.688	1.563	1.546	1.527
Non-mined	2	4	1.704	1.513	1.497	1.481
Non-mined	2	8	1.713	1.449	1.489	1.469
Non-mined	3	0	1.721	1.712	1.709	1.706
Non-mined	3	2	1.699	1.555	1.617	1.532
Non-mined	3	4	1.717	1.512	1.545	1.475
Non-mined	3	8	1.697	1.503	1.478	1.469
Capped tailing	1	0	3.894	3.897	3.912	3.872
Capped tailing	1	2	3.916	3.862	3.732	3.702
Capped tailing	1	4	3.875	3.768	3.684	3.642
Capped tailing	1	8	3.887	3.445	3.372	3.299
Capped tailing	2	0	3.956	3.9	3.949	3.951
Capped tailing	2	2	3.921	3.853	3.715	3.699
Capped tailing	2	4	3.897	3.771	3.669	3.638
Capped tailing	2	8	4.003	3.446	3.349	3.296
Capped tailing	3	0	3.911	3.9	3.897	3.913
Capped tailing	3	2	3.931	3.864	3.728	3.7
Capped tailing	3	4	4.001	3.772	3.697	3.64
Capped tailing	3	8	3.899	3.448	3.362	3.306
Uncapped tailing	1	0	5	4.988	4.993	4.996
Uncapped tailing	1	2	4.973	4.752	4.706	4.702
Uncapped tailing	1	4	4.997	4.623	4.607	4.545
Uncapped tailing	1	8	4.99	4.603	4.588	4.486
Uncapped tailing	2	0	4.985	4.963	4.976	4.98
Uncapped tailing	2	2	4.988	4.749	4.712	4.7
Uncapped tailing	2	4	4.967	4.619	4.601	4.55
Uncapped tailing	2	8	5	4.6	4.591	4.492
Uncapped tailing	3	0	5.001	5.009	5	4.996
Uncapped tailing	3	2	4.99	4.75	4.709	4.699
Uncapped tailing	3	4	4.986	4.62	4.603	4.561
Uncapped tailing	3	8	5.001	4.598	4.592	4.489

Appendix A6. Effects of application of different rates of biochar on water soluble Lead

Soil/tailings	Rep.	Rate (t ha^{-1})	Pb-H_2O (0 WAI)	Pb-H_2O (4 WAI)	Pb-H_2O (8 WAI)	Pb-H_2O (12 WAI)
Non-mined	1	0	0.026	0.025	0.027	0.026
Non-mined	1	2	0.029	0.024	0.025	0.022
Non-mined	1	4	0.027	0.024	0.025	0.018
Non-mined	1	8	0.028	0.029	0.029	0.017
Non-mined	2	0	0.031	0.031	0.03	0.029
Non-mined	2	2	0.028	0.021	0.024	0.023
Non-mined	2	4	0.027	0.025	0.024	0.019
Non-mined	2	8	0.028	0.026	0.026	0.018
Non-mined	3	0	0.027	0.026	0.026	0.027
Non-mined	3	2	0.027	0.031	0.029	0.023
Non-mined	3	4	0.028	0.023	0.023	0.019
Non-mined	3	8	0.024	0.022	0.023	0.018
Capped tailings	1	0	0.045	0.046	0.049	0.047
Capped tailings	1	2	0.044	0.037	0.035	0.033
Capped tailings	1	4	0.043	0.036	0.031	0.03
Capped tailings	1	8	0.046	0.034	0.03	0.029
Capped tailings	2	0	0.046	0.045	0.046	0.045
Capped tailings	2	2	0.045	0.037	0.035	0.032
Capped tailings	2	4	0.046	0.035	0.031	0.031
Capped tailings	2	8	0.046	0.034	0.03	0.029
Capped tailings	3	0	0.047	0.045	0.046	0.046
Capped tailings	3	2	0.044	0.036	0.035	0.033
Capped tailings	3	4	0.047	0.033	0.032	0.031
Capped tailings	3	8	0.049	0.032	0.031	0.03
Uncapped tailings	1	0	0.158	0.156	0.158	0.157
Uncapped tailings	1	2	0.156	0.153	0.151	0.145
Uncapped tailings	1	4	0.155	0.149	0.143	0.14
Uncapped tailings	1	8	0.157	0.154	0.144	0.131
Uncapped tailings	2	0	0.157	0.156	0.157	0.161
Uncapped tailings	2	2	0.155	0.154	0.147	0.143
Uncapped tailings	2	4	0.158	0.148	0.143	0.138
Uncapped tailings	2	8	0.157	0.154	0.145	0.129
Uncapped tailings	3	0	0.156	0.155	0.155	0.157
Uncapped tailings	3	2	0.155	0.152	0.15	0.141
Uncapped tailings	3	4	0.158	0.149	0.146	0.137
Uncapped tailings	3	8	0.157	0.151	0.148	0.128

Appendix A7. Bioavailability of Arsenic and Lead in mediated soil/tailings

Soil/Tailings	Rep.	Rate	As	Pb	As	Pb
			------(mg l^{-1})--------		-------(mg kg^{-1})-------	
Non-mined	1	0	0.017	0.009	0.85	0.45
Non-mined	1	2	0.011	0.006	0.55	0.3
Non-mined	1	4	0.009	0.004	0.45	0.2
Non-mined	1	8	0.005	0.004	0.25	0.2
Non-mined	2	0	0.016	0.008	0.8	0.4
Non-mined	2	2	0.009	0.007	0.45	0.35
Non-mined	2	4	0.007	0.006	0.35	0.3
Non-mined	2	8	0.004	0.004	0.2	0.2
Non-mined	3	0	0.015	0.010	0.75	0.5
Non-mined	3	2	0.008	0.009	0.4	0.45
Non-mined	3	4	0.006	0.006	0.3	0.3
Non-mined	3	8	0.004	0.004	0.2	0.2
Capped tailing	1	0	0.038	0.017	1.9	0.85
Capped tailing	1	2	0.023	0.011	1.15	0.55
Capped tailing	1	4	0.011	0.010	0.55	0.5
Capped tailing	1	8	0.010	0.006	0.5	0.3
Capped tailing	2	0	0.039	0.017	1.95	0.85
Capped tailing	2	2	0.027	0.014	1.35	0.7
Capped tailing	2	4	0.013	0.009	0.65	0.45
Capped tailing	2	8	0.011	0.004	0.55	0.2
Capped tailing	3	0	0.036	0.015	1.8	0.75
Capped tailing	3	2	0.024	0.013	1.2	0.65
Capped tailing	3	4	0.015	0.010	0.75	0.5
Capped tailing	3	8	0.011	0.004	0.55	0.2
Uncapped tailing	1	0	0.075	0.026	3.75	1.3
Uncapped tailing	1	2	0.054	0.022	2.7	1.1
Uncapped tailing	1	4	0.050	0.019	2.5	0.95
Uncapped tailing	1	8	0.048	0.018	2.4	0.9
Uncapped tailing	2	0	0.070	0.025	3.5	1.25
Uncapped tailing	2	2	0.061	0.023	3.05	1.15
Uncapped tailing	2	4	0.053	0.017	2.65	0.85
Uncapped tailing	2	8	0.050	0.017	2.5	0.85
Uncapped tailing	3	0	0.072	0.028	3.6	1.4
Uncapped tailing	3	2	0.059	0.024	2.95	1.2
Uncapped tailing	3	4	0.056	0.020	2.8	1
Uncapped tailing	3	8	0.052	0.016	2.6	0.8

Appendix A8. Biomass of Lettuce in biochar-amended soil/tailings

Soil/Tailing	Replication	Rate of application of Biochar (t ha^{-1})	Fresh wt. (g)	Dry wt. (g)
Non-mined	1	0	34.31	7.55
Non-mined	1	2	39.78	8.75
Non-mined	1	4	40.63	8.94
Non-mined	1	8	51.22	11.27
Non-mined	2	0	30.67	6.75
Non-mined	2	2	32.76	7.21
Non-mined	2	4	39.12	8.61
Non-mined	2	8	46.75	10.29
Non-mined	3	0	31.86	7.01
Non-mined	3	2	36.73	8.08
Non-mined	3	4	43.89	9.66
Non-mined	3	8	48.34	10.63
Capped tailings	1	0	24.13	5.31
Capped tailings	1	2	24.01	5.28
Capped tailings	1	4	28.23	6.21
Capped tailings	1	8	32.74	7.20
Capped tailings	2	0	26.58	5.85
Capped tailings	2	2	29.22	6.43
Capped tailings	2	4	30.63	6.74
Capped tailings	2	8	30.37	6.68
Capped tailings	3	0	22.67	4.99
Capped tailings	3	2	23.10	5.08
Capped tailings	3	4	26.75	5.89
Capped tailings	3	8	30.10	6.62
Uncapped tailings	1	0	8.89	3.73
Uncapped tailings	1	2	9.25	3.89
Uncapped tailings	1	4	10.17	4.27
Uncapped tailings	1	8	12.62	5.30
Uncapped tailings	2	0	7.74	3.25
Uncapped tailings	2	2	8.48	3.56
Uncapped tailings	2	4	8.87	3.73
Uncapped tailings	2	8	10.86	4.56
Uncapped tailings	3	0	8.01	3.36
Uncapped tailings	3	2	8.31	3.49
Uncapped tailings	3	4	9.30	3.91
Uncapped tailings	3	8	9.94	4.17

APPENDIX B

TABLES OF ANALYSIS OF VARIANCE

Appendix B1. Analysis of variance (ANOVA) of the pH of non-mined soil 0 week after incubation (WAI)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.0007407	0.0003704	0.50	0.615
Rate	2	0.0029630	0.0014815	2.00	0.164
Amendment*rate	4	0.0014815	0.0003704	0.50	0.736
Residual	18	0.033333	0.0007407		
Total	26	0.0185185			

Appendix B2. ANOVA of the pH of non-mined soil 4 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.296296	0.148148	28.57	< 0.001
Rate	2	1.449630	0.724815	139.79	< 0.001
Amendment*rate	4	0.274815	0.068704	13.25	< 0.001
Residual	18	0.070370	0.005185		
Total	26	2.114074			

Appendix B3. **Analysis of variance (ANOVA) of the pH of non-mined soil 12 weeks after incubation (WAI)**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.367407	0.183704	49.60	< 0.001
Rate	2	2.420741	1.210370	326.80	< 0.001
Amendment*rate	4	0.285926	0.071481	19.30	< 0.001
Residual	18	0.066667	0.003704		
Total	26	3.140741			

Appendix B4. **ANOVA of the pH of capped tailings 0 WAI**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.011852	0.005926	3.20	0.065
Rate	2	0.000741	0.000370	0.20	0.821
Amendment*rate	4	0.021481	0.005370	2.90	0.051
Residual	18	0.033333	0.001852		
Total	26	0.067407			

Appendix B5. **ANOVA of the pH of capped tailings 4 WAI**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.045185	0.022593	11.17	0.001
Rate	2	0.405185	0.202593	91.17	< 0.001
Amendment*rate	4	0.043704	0.010926	4.92	0.007
Residual	18	0.040000	0.002222		
Total	26	0.534074			

Appendix B6. Analysis of variance (ANOVA) of the pH of capped tailings 8 weeks after incubation (WAI)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.658519	0.329259	127.00	< 0.001
Rate	2	0.082963	0.041481	16.00	< 0.001
Amendment*rate	4	0.428148	0.107037	41.29	< 0.001
Residual	18	0.046667	0.002593		
Total	26	1.216296			

Appendix B7. ANOVA of the pH of capped tailings 12 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	1.125185	0.562593	217.00	< 0.001
Rate	2	0.249630	0.124815	48.14	< 0.001
Amendment*rate	4	0.921481	0.230370	88.86	< 0.001
Residual	18	0.046667	0.002593		
Total	26	2.342963			

Appendix B8. ANOVA of the pH of uncapped tailings 0 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.009630	0.004815	1.86	0.185
Rate	2	0.000741	0.000370	0.14	0.868
Amendment*rate	4	0.008148	0.002037	0.79	0.549
Residual	18	0.046667	0.002593		
Total	26	0.065185			

Appendix B9. **Analysis of variance (ANOVA) of the pH of uncapped tailings 4 weeks after incubation (WAI)**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.031852	0.015926	6.14	0.009
Rate	2	0.298519	0.149259	57.57	< 0.001
Amendment*rate	4	0.028148	0.007073	2.71	0.063
Residual	18	0.046667	0.002593		
Total	26	0.405185			

Appendix B10. **ANOVA of the pH of uncapped tailings 8 WAI**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.716296	0.358148	241.75	< 0.001
Rate	2	0.058519	0.029259	19.75	< 0.001
Amendment*rate	4	0.603704	0.150926	101.87	< 0.001
Residual	18	0.266667	0.001481		
Total	26	1.405185			

Appendix B11. **ANOVA of the pH of uncapped tailings 12 WAI**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	2.195556	1.097778	423.43	< 0.001
Rate	2	0.020000	0.010000	3.86	0.040
Amendment*rate	4	1.364444	0.341111	131.57	< 0.001
Residual	18	0.040000	0.002593		
Total	26	3.626667			

Appendix B12. **Analysis of variance (ANOVA) of EDTA-extractable Arsenic (As) in non-mined soil 0 week after incubation (WAI)**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.007319	0.003659	1.53	0.243
Rate	2	0.003207	0.001604	0.67	0.523
Amendment*rate	4	0.012904	0.003226	1.35	0.289
Residual	18	0.042950	0.002386		
Total	26	0.066380			

Appendix B13. ANOVA of EDTA-extractable As in non-mined soil 4 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	223.9456	111.9728	185.46	< 0.001
Rate	2	6.2902	3.1451	5.21	0.016
Amendment*rate	4	121.7365	30.4341	50.41	< 0.001
Residual	18	10.8677	0.6038		
Total	26	362.8400			

Appendix B14. ANOVA of EDTA-extractable As in non-mined soil 8 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	512.17627	256.08814	5475.87	< 0.001
Rate	2	34.01405	17.00703	363.66	< 0.001
Amendment*rate	4	296.14675	74.03669	1583.11	< 0.001
Residual	18	0.84180	0.04677		
Total	26	843.17887			

Appendix B15. **Analysis of variance (ANOVA) of EDTA-extractable Arsenic (As) in non-mined soil 12 weeks after incubation (WAI)**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	598.85627	299.428	7834.63	< 0.001
Rate	2	33.55959	16.7798	439.05	< 0.001
Amendment*rate	4	350.16959	87.5424	2290.58	< 0.001
Residual	18	0.67148	0.03822		
Total	26	983.27339			

Appendix B16. **ANOVA of EDTA-extractable As in capped tailings 0 WAI**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.3756	0.1878	0.41	0.669
Rate	2	1.4289	0.7144	1.56	0.237
Amendment*rate	4	3.2156	0.8039	1.76	0.181
Residual	18	8.2267	0.4570		
Total	26	13.2467			

Appendix B17. ANOVA of EDTA-extractable As in capped tailings 4 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	12147.245	6073.623	3714.33	< 0.001
Rate	2	199.401	99.700	60.97	< 0.001
Amendment*rate	4	7651.888	1912.972	1169.88	< 0.001
Residual	18	29.433	1.635		
Total	26	20027.967			

Appendix B18. **Analysis of variance (ANOVA) of EDTA-extractable Arsenic (As) in capped tailings 8 weeks after incubation (WAI)**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	20945.399	10472.699	5742.54	< 0.001
Rate	2	510.305	255.153	139.91	< 0.001
Amendment*rate	4	12839.224	3209.806	1760.05	< 0.001
Residual	18	32.827	1.824		
Total	26	34327.754			

Appendix B19. ANOVA of EDTA-extractable As in capped tailings 12 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	24482.516	12241.258	1893.52	< 0.001
Rate	2	439.665	219.833	34.00	< 0.001
Amendment*rate	4	14913.426	3728.356	576.72	< 0.001
Residual	18	116.367	6.465		
Total	26	39951.974			

Appendix B20. ANOVA of EDTA-extractable As in uncapped tailings 0 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.1474	0.0737	0.12	0.885
Rate	2	0.6941	0.3470	0.58	0.570
Amendment*rate	4	1.7948	0.4487	0.75	0.570
Residual	18	10.7600	0.5978		
Total	26	13.3963			

Appendix B21. **Analysis of variance (ANOVA) of EDTA-extractable Arsenic in uncapped tailings 4 weeks after incubation (WAI)**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	32692.714	16346.357	8566.61	< 0.001
Rate	2	253.032	126.516	66.30	< 0.001
Amendment*rate	4	18597.970	4649.493	2436.65	< 0.001
Residual	18	34.347	1.908		
Total	26	51578.063			

Appendix B22. ANOVA of EDTA-extractable As in uncapped tailings 8WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	47738.667	23869.334	7371.29	< 0.001
Rate	2	980.534	490.267	151.40	< 0.001
Amendment*rate	4	26999.586	6749.896	2084.49	< 0.001
Residual	18	58.287	3.238		
Total	26	75777.074			

Appendix B23.ANOVA of EDTA-extractable As in uncapped tailings 12 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	58095.672	29047.84	12775.56	< 0.001
Rate	2	1053.970	526.985	231.77	< 0.001
Amendment*rate	4	32697.328	8174.332	3595.16	< 0.001
Residual	18	40.927	2.274		
Total	26	91887.896			

Appendix B24. **Analysis of variance (ANOVA) of water soluble Arsenic (As) in non-mined soil 0 week after incubation (WAI)**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	5.185E-07	2.593E-07	0.33	0.721
Rate	2	1.407E-06	7.037E-07	0.90	0.422
Amendment*rate	4	4.593E-06	1.148E-06	1.48	0.251
Residual	18	1.304E-05	7.778E-07		
Total	26	2.052E-05			

Appendix B25. ANOVA of water soluble Arsenic in non-mined soil 4 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.1804476	0.090224	5201.55	< 0.001
Rate	2	0.0008234	0.000412	2.29	0.130
Amendment*rate	4	0.1061575	0.026539	147.53	< 0.001
Residual	18	0.0032380	0.000180		
Total	26	0.2906665			

Appendix B26. ANOVA of water soluble Arsenic in non-mined soil 8 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.2151302	0.1075651	2709.67	< 0.001
Rate	2	0.0008737	0.0004368	11.00	< 0.001
Amendment*rate	4	0.1242000	0.0310500	782.18	< 0.001
Residual	18	0.0007145	0.0000397		
Total	26	0.3409183			

Appendix B27. Analysis of variance (ANOVA) of water soluble Arsenic in non-mined soil 12 weeks after incubation (WAI)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.2330259	0.1165129	2702.62	< 0.001
Rate	2	0.0017805	0.0008903	20.65	< 0.001
Amendment*rate	4	0.1387108	0.0346777	804.38	< 0.001
Residual	18	0.0007760	0.0000431		
Total	26	0.3742932			

Appendix B28. ANOVA of water soluble Arsenic in capped tailings 0 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	2.074E-06	1.037E-06	1.87	0.183
Rate	2	2.074E-06	1.037E-06	1.87	0.183
Amendment*rate	4	5.259E-06	1.315E-06	2.73	0.091
Residual	18	1.000E-06	5.556E-07		
Total	26	1.941E-05			

Appendix B29. ANOVA of water soluble Arsenic in capped tailings 4 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.1895429	0.0947714	2246.56	< 0.001
Rate	2	0.0057287	0.0028643	67.90	< 0.001
Amendment*rate	4	0.1116098	0.0279024	661.43	< 0.001
Residual	18	0.0007593	0.0000422		
Total	26	0.3076407			

Appendix B30. Analysis of variance (ANOVA) of water soluble Arsenic in capped tailings 8 weeks after incubation (WAI)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.3126269	0.3126269	7391.35	< 0.001
Rate	2	0.0018729	0.0018729	44.28	< 0.001
Amendment*rate	4	0.1951016	0.1951016	2306.37	< 0.001
Residual	18	0.0003807	0.0002115		
Total	26	0.5099820			

Appendix B31. ANOVA of water soluble Arsenic in capped tailings 12 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.4116376	0.2058188	12572.64	< 0.001
Rate	2	0.0062403	0.0031202	190.60	< 0.001
Amendment*rate	4	0.2732082	0.0683020	4172.30	< 0.001
Residual	18	0.0002947	0.00001637		
Total	26	0.6913807			

Appendix B32. ANOVA of water soluble Arsenic in uncapped tailings 0 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.0001069	0.0000534	0.98	0.395
Rate	2	0.0000402	0.0000201	0.37	0.697
Amendment*rate	4	0.0001236	0.0000309	0.57	0.691
Residual	18	0.0008304	0.0000547		
Total	26	0.0012547			

Appendix B33. Analysis of variance (ANOVA) of water soluble Arsenic in uncapped tailings 4 weeks after incubation (WAI)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	4.808847	2.404423	745.97	< 0.001
Rate	2	0.214090	0.107045	33.21	< 0.001
Amendment*rate	4	2.885510	0.721378	223.81	< 0.001
Residual	18	0.045814	0.003223		
Total	26	7.966465			

Appendix B34. ANOVA of water soluble Arsenic in uncapped tailings 8 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	11.476036	5.738018	1917.03	< 0.001
Rate	2	0.560392	0.280196	93.61	< 0.001
Amendment*rate	4	6.837580	1.709395	571.10	< 0.001
Residual	18	0.053877	0.002993		
Total	26	18.927885			

Appendix B35. ANOVA of water soluble Arsenic in uncapped tailings 12 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	14.822723	7.411362	3202.07	< 0.001
Rate	2	0.787685	0.393843	170.16	< 0.001
Amendment*rate	4	8.582300	2.145575	926.99	< 0.001
Residual	18	0.041662	0.002315		
Total	26	24.234371			

Appendix B36. **Analysis of variance (ANOVA) of EDTA-extractable Lead in non-mined soil 0 week after incubation (WAI)**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.000067	0.000033	0.82	0.457
Rate	2	0.000000	0.000000	0.00	1.000
Amendment*rate	4	0.000067	0.000017	0.41	0.800
Residual	18	0.000733	0.000041		
Total	26	0.000867			

Appendix B37. ANOVA of EDTA-extractable Lead in non-mined soil 4 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	1.078496	0.539248	3309.02	< 0.001
Rate	2	0.000541	0.000270	1.66	0.218
Amendment*rate	4	0.869348	0.217337	1333.66	< 0.001
Residual	18	0.002837	0.000177		
Total	26	1.951319			

Appendix B38. ANOVA of EDTA-extractable Lead in non-mined soil 8 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	2.210007	1.105003	5967.02	< 0.001
Rate	2	0.007563	0.003782	20.42	< 0.001
Amendment*rate	4	1.695815	0.423954	2289.35	< 0.001
Residual	18	0.003333	0.000185		
Total	26	3.916719			

Appendix B39. **Analysis of variance (ANOVA) of EDTA-extractable Lead in non-mined soil 12 weeks after incubation (WAI)**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	2.837222	1.418611	7093.06	< 0.001
Rate	2	0.014689	0.007344	36.72	< 0.001
Amendment*rate	4	2.125356	0.531339	2656.69	< 0.001
Residual	18	0.003600	0.000200		
Total	26	4.980867			

Appendix B40. ANOVA of EDTA-extractable Lead in capped tailings 0 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.001207	0.000604	4.29	0.030
Rate	2	0.000474	0.000237	1.68	0.214
Amendment*rate	4	0.000482	0.000120	0.86	0.509
Residual	18	0.002533	0.000141		
Total	26	0.004696			

Appendix B41. ANOVA of EDTA-extractable Lead in capped tailings 4 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	2.026822	1.013411	4413.24	< 0.001
Rate	2	0.000600	0.000300	1.31	0.295
Amendment*rate	4	1.387111	0.346778	1510.16	< 0.001
Residual	18	0.004133	0.000230		
Total	26	3.418667			

Appendix B42. **Analysis of variance (ANOVA) of EDTA-extractable Lead (Pb) in capped tailings 8 weeks after incubation (WAI)**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	4.299430	2.149715	8535.63	< 0.001
Rate	2	0.028985	0.014493	57.54	< 0.001
Amendment*rate	4	2.905082	0.726270	2883.72	< 0.001
Residual	18	0.004533	0.000252		
Total	26	7.238030			

Appendix B43. ANOVA of EDTA-extractable Pb in capped tailings 12 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	5.313874	2.6569	11208.95	< 0.001
Rate	2	0.106554	0.05327	224.73	< 0.001
Amendment*rate	4	3.633015	0.90825	3831.70	< 0.001
Residual	18	0.004267	0.00024		
Total	26	9.057696			

Appendix B44. ANOVA of EDTA-extractable Pb in uncapped tailings 0 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.000563	0.000282	1.52	0.245
Rate	2	0.000141	0.000070	0.38	0.689
Amendment*rate	4	0.000237	0.000059	0.32	0.861
Residual	18	0.003333	0.000185		
Total	26	0.004274			

Appendix B45. Analysis of variance (ANOVA) of EDTA-extractable Lead (Pb) in uncapped tailings 4 weeks after incubation (WAI)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	1.663252	0.831626	3680.97	< 0.001
Rate	2	0.007207	0.003604	15.95	< 0.001
Amendment*rate	4	1.045748	0.261437	1157.18	< 0.001
Residual	18	0.004067	0.000226		
Total	26	2.720274			

Appendix B46. ANOVA of EDTA-extractable Pb in uncapped tailings 8 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	2.776096	1.388048	7348.49	< 0.001
Rate	2	0.011296	0.005648	29.90	< 0.001
Amendment*rate	4	1.778193	0.4445481	2353.49	< 0.001
Residual	18	0.003400	0.000189		
Total	26	4.568985			

Appendix B47. ANOVA of EDTA-extractable Pb in uncapped tailings 12 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	3.292807	1.646404	4779.88	< 0.001
Rate	2	0.012896	0.006448	18.72	< 0.001
Amendment*rate	4	2.158526	0.539632	1566.67	< 0.001
Residual	18	0.006200	0.000344		
Total	26	5.470430			

Appendix B48. Analysis of variance (ANOVA) of water soluble Lead in non-mined soil 0 week after incubation (WAI)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	9.630E-07	4.815E-07	0.72	0.499
Rate	2	5.185E-07	2.593E-07	0.39	0.683
Amendment*rate	4	3.259E-06	8.148E-07	1.22	0.336
Residual	18	1.200E-05	6.667E-07		
Total	26	1.674E-05			

Appendix B49. ANOVA of water soluble Lead in non-mined soil 4 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	3.749E-04	1.874E-04	202.44	< 0.001
Rate	2	3.267E-05	1.633E-05	17.64	< 0.001
Amendment*rate	4	3.518E-04	8.794E-05	94.98	< 0.001
Residual	18	1.667E-05	9.259E-07		
Total	26	7.760E-04			

Appendix B50. ANOVA of water soluble Lead in non-mined soil 8 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	6.001E-04	3.000E-04	426.37	< 0.001
Rate	2	4.830E-05	2.415E-05	34.32	< 0.001
Amendment*rate	4	4.197E-04	1.049E-04	149.11	< 0.001
Residual	18	1.267E-05	7.037E-07		
Total	26	1.081E-03			

Appendix B51. Analysis of variance (ANOVA) of water soluble Lead in non-mined soil 12 weeks after incubation (WAI)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	7.336E-04	3.668E-04	412.67	< 0.001
Rate	2	9.852E-06	4.926E-06	5.54	0.013
Amendment*rate	4	5.441E-04	1.360E-04	153.04	< 0.001
Residual	18	1.600E-05	8.889E-07		
Total	26	1.304E-03			

Appendix B52. ANOVA of water soluble Lead in capped tailings 0 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	6.667E-07	3.333E-07	0.75	0.487
Rate	2	4.667E-06	2.333E-06	5.25	0.016
Amendment*rate	4	1.333E-06	3.333E-07	0.75	0.571
Residual	18	8.000E-06	4.444E-07		
Total	26	1.467E-05			

Appendix B 53. ANOVA of water soluble Lead in capped tailings 4 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	2.274E-03	1.137E-03	713.88	< 0.001
Rate	2	9.919E-05	4.959E-05	31.14	< 0.001
Amendment*rate	4	1.194E-03	2.984E-04	187.38	< 0.001
Residual	18	2.867E-05	1.593E-06		
Total	26	3.595E-03			

Appendix B 54. Analysis of variance (ANOVA) of water soluble Lead in capped tailings 8 weeks after incubation (WAI)

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	2.897E-03	1.448E-03	1002.77	< 0.001
Rate	2	1.162E-04	5.811E-05	40.23	< 0.001
Amendment*rate	4	1.702E-03	4.254E-04	294.50	< 0.001
Residual	18	2.600E-05	1.444E-06		
Total	26	4.741E-03			

Appendix B 55. ANOVA of water soluble Lead in capped tailings 12 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	3.521E-03	1.760E-03	1131.64	< 0.001
Rate	2	8.867E-05	4.433E-05	28.50	< 0.001
Amendment*rate	4	1.853E-03	4.633E-04	297.86	< 0.001
Residual	18	2.800E-05	1.556E-06		
Total	26	5.491E-03			

Appendix B 56. ANOVA of water soluble Lead in uncapped tailings 0 WAI

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	9.630E-07	4.815E-07	0.87	0.437
Rate	2	1.185E-06	5.926E-07	1.07	0.365
Amendment*rate	4	1.259E-06	3.148E-07	0.57	0.690
Residual	18	1.000E-06	5.556E-07		
Total	26	1.341E-05			

Appendix B 57. **Analysis of variance (ANOVA) of water soluble Lead in uncapped tailings 4 weeks after incubation (WAI)**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	6.048E-03	3.024E-03	1512.00	< 0.001
Rate	2	1.946E-03	9.730E-04	486.50	< 0.001
Amendment*rate	4	3.484E-03	8.710E-04	435.50	< 0.001
Residual	18	3.600E-05	2.000E-06		
Total	26	1.151E-02			

Appendix B 58. **ANOVA of water soluble Lead in uncapped tailings 8 WAI**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	1.452E-02	7.258E-03	4355.00	< 0.001
Rate	2	3.603E-03	1.801E-03	1080.80	< 0.001
Amendment*rate	4	8.793E-03	2.198E-03	1319.00	< 0.001
Residual	18	3.000E-05	1.667E-06		
Total	26	2.694E-02			

Appendix B 59. **ANOVA of water soluble Lead in uncapped tailings 12 WAI**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	1.606E-02	8.032E-03	3143.09	< 0.001
Rate	2	4.275E-03	2.137E-03	836.35	< 0.001
Amendment*rate	4	1.043E-02	2.608E-03	1020.65	< 0.001
Residual	18	4.600E-05	2.556E-06		
Total	26	3.082E-02			

Appendix B 60. **ANOVA of the pH of non-mined soil 8 WAI**

Source of variation	d.f.	s.s.	m.s.	v.r.	F pr.
Amendment	2	0.351852	0.175926	47.50	< 0.001
Rate	2	1.745185	0.872593	235.60	< 0.001
Amendment*rate	4	0.292593	0.073148	19.75	< 0.001
Residual	18	0.066667	0.003704		
Total	26	2.456296			