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THE INFLUENCE OF VARIOUS REDOX CONDITIONS ON STABILIZATION OF ARSENIC IN CONTAMINATED SOIL

DIPLOMA THESIS

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Declaration

I hereby declare that this Diploma Thesis, titled “The influence of various redox conditions on stabilization of Arsenic in contaminated soils” was independently written, under the direction of Zuzana Michálková, PhD. I have listed all literature and publications from which I have acquired information.

In Prague, 18th of April 2018

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Vincent Nesley Addo Kavianu.

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Abstract

In this study, amorphous manganese oxide (AMO) and biochar + amorphous manganese oxide (AMOchar) immobilizing potential of Arsenic (As) concentration in solution under redox conditions was studied. Also, the stability of these sorbents were studied. A modified sol-gel procedure (excluding the heating step) was used for the preparation of the AMO and pyrolysed grape stalks at approximate temperature (600 °C) was used to prepare the biochar. After which the pure AMO and biochar were mixed in the ratio of 2:1(w/w) to form the AMOchar. Incubation batch experiment was conducted under two soil moisture contents – 70% water holding capacity (oxic) and full saturation with water with the maximum time interval of of 10 weeks. After the set periods, the soil solution was collected for analysis.

The content of metals/metalloids and DOC (dissolved organic carbon) was determined using ICP-OES and a TOC/DOC analyzer, respectively. The pH and Eh of the soil solutions were all measured immediately after collection.

Results showed that AMO was capable of removing 92% of As contents of the control, whereas AMOchar removed 59% of As content of the control, all under oxic condition.

However, the immobilising efficiency of the two amendments were comparatively low under oversaturated conditions, thus the two amendments were ineffective as such. Mn leaching into solution was used to assess the stability of the two amendments. Comparing results, AMO leached more Mn than AMOchar in all incubation periods and time. Implying that AMOchar was more stable than AMO.

Keywords;

Arsenic (As), Remediation, Biochar, AMOchar (amorphous manganes oxide/Biochar), stabilization.

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1. INTRODUCTION

Globally, most soils are contaminated with organic and inorganic toxins mostly due to waste emissions from industrial activities, waste (i.e., biosolids and manures) application, mining activities, wastewater irrigation, and poor techniques of chemicals and pesticides utilization in farmlands (Bolan et al., 2004; Mench et al., 2010). Metal(loids) mostly commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) (GWRTC,1997). Soil contamination by metals (e.g. Cd, Cu, Mn, Ni, Pb, Zn) and metalloids (e.g., As, Sb) is a current global phenomenon threatening food security and groundwater quality (USEPA, 1996). The concentration of trace elements in the Earth’s crust is constant and their production in one area causes depletion in others. Pollutants in soils are not only harmful to ecosystems and agricultural production but also a serious threat to human wellbeing.

Metal(loids) have been used by human beings for several years. Despite negative health effects of metal(loids), there is still long exposure, and even continues to rise in less developed countries (Jarup, 2003). Even though, the economy in China has been developing on fast rate in recent times, it has also brought some environmental draw backs. For instance, 20 % of the total agricultural land area in China which are arable land impacted by heavy metal contamination is close to 20 million hectares (Xi et al., 2011). In Europe, it has been established that 3.5 million soil sites are potentially contaminated, hence, soil contamination has been targeted as an important subject for action in the European Community strategy for soil protection and enrichment (Petruzzelli, 2012).

Arsenic (As), especially As(III), is toxic to both plants and animals and carcinogenic in humans (Ng, 2005).

In Smolotely village (Czech Republic), the soil is highly contaminated with As (Michálková et al., 2016a). This has occurred due to the presence of naturally As bearing minerals. Amorphous manganese oxide (AMO) is a potential amendment for chemical stabilization of metals and metalloids in soils because of its composition and adsorption behavior (Della Puppa et al., 2013, Ettler et al., 2014 and Michálková et al., 2016a). Biochar (BC) as chemical amendment is able to decrease the mobility of metal(loid)s in contaminated soil due its sorption capacity (Mohan et al., 2014, Mohan et al., 2015, Han et al. 2015, Trakal et al.,2016, and Yan et al.,2015).

This work focused on evaluating the potential of two chemical amendments, that is amorphous Mn oxide on one hand and combination of AMO+BC(AMOchar) on the other, to stabilize As in contaminated soil from Smolotely village and examine their stabilization influence under different redox conditions.

2. PROJECT AIM/OBJECTIVES

2.1. Aim

To assess the influence of redox conditions on stabilization of arsenic (As) in contaminated soil from Smolotely village (the Czech Republic) using AMO and AMOchar.

2.2. Objectives

1. To determine the influence of AMO and AMOchar on mobility of As in soil with special respect to redox status.
2. To examine any differences in stability (esp. Mn release) of AMO and AMOchar under the influence of redox.

3. LITERATURE REVIEW

3.1 General properties of Arsenic (As)

Arsenic is in Group 15 of the periodic table and is classified as a metalloid, as it has both the properties of a metal and a non-metal. Arsenic is, however, mostly known to as a metal (ATSDR, 2007). Elemental arsenic is a silver-grey brittle, crystalline (hexagonal, rhombic), metallic-looking substance which exists in three allotropic forms (yellow, black, and grey). It is odorless and nearly tasteless. Arsenic is soluble in nitric acid, cold hydrochloric, and sulfuric acids. It is insoluble in water and nonoxidizing acids. Arsenic compounds are generally non-volatile except for gaseous arsines and arsenic trioxide.

Arsenic is the twentieth most abundant and ubiquitous element in the earth’s crust, 14th in the seawater, and 12th in the human body (Woolson, 1975, Mandal and Suzuki, 2002). Arsenic is still used in the field of medicine (ATSDR, 2007, Nriagu and Azcue, 1990), and in other disciplines such as electronics, industry agriculture, livestock, and metallurgy (Nriagu, 1990). It is currently established that even at low levels of arsenic intake leads to carcinogenesis.

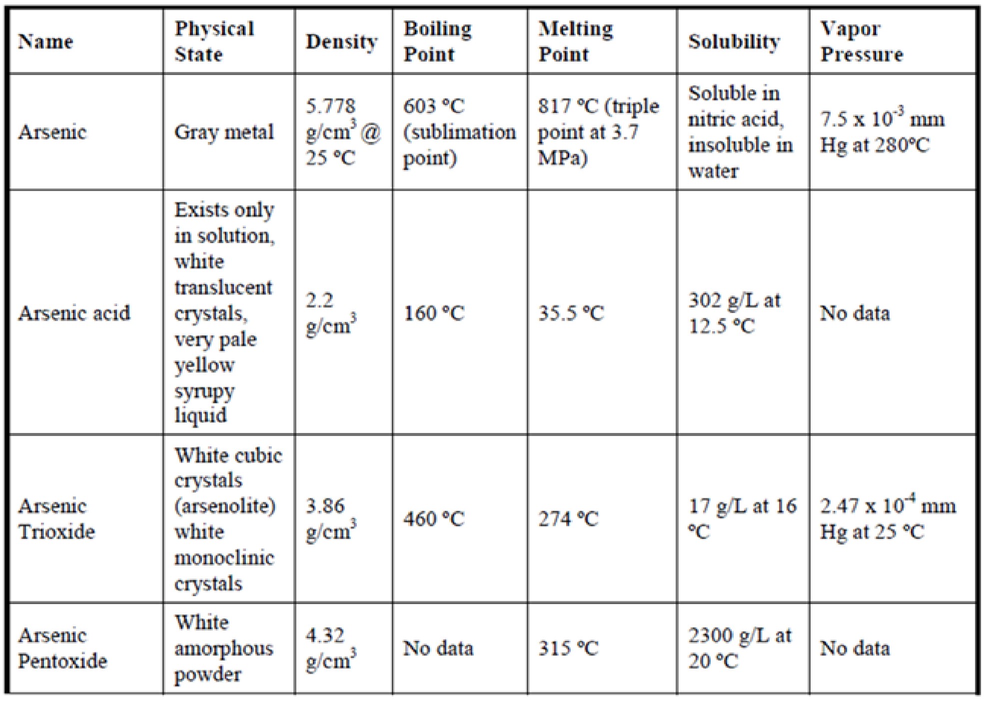
3.1.1 Chemical properties of Arsenic

Arsenic has different oxidation states. Elemental arsenic (As (0)) or metallic arsenic has two forms: the alpha-forms and beta-forms. The alpha-form exist a crystalline, brittle, and steel gray in color. But, beta-form exist as amorphous and dark grey in color. Hence, arsenic can react with other elements as inorganic and organic arsenic. Oxygen, chlorine, and sulfur react with arsenic to form inorganic, whiles in the organic form, arsenic react with carbon and hydrogen only (ATSDR, 2007).

Arsenic exists in four oxidation states arsenate As (V), arsenite As (III), elemental arsenic As (0), and arsine As (–III), varying in their toxicity, mobility, and bioavailability (Sharma and Sohn, 2009).

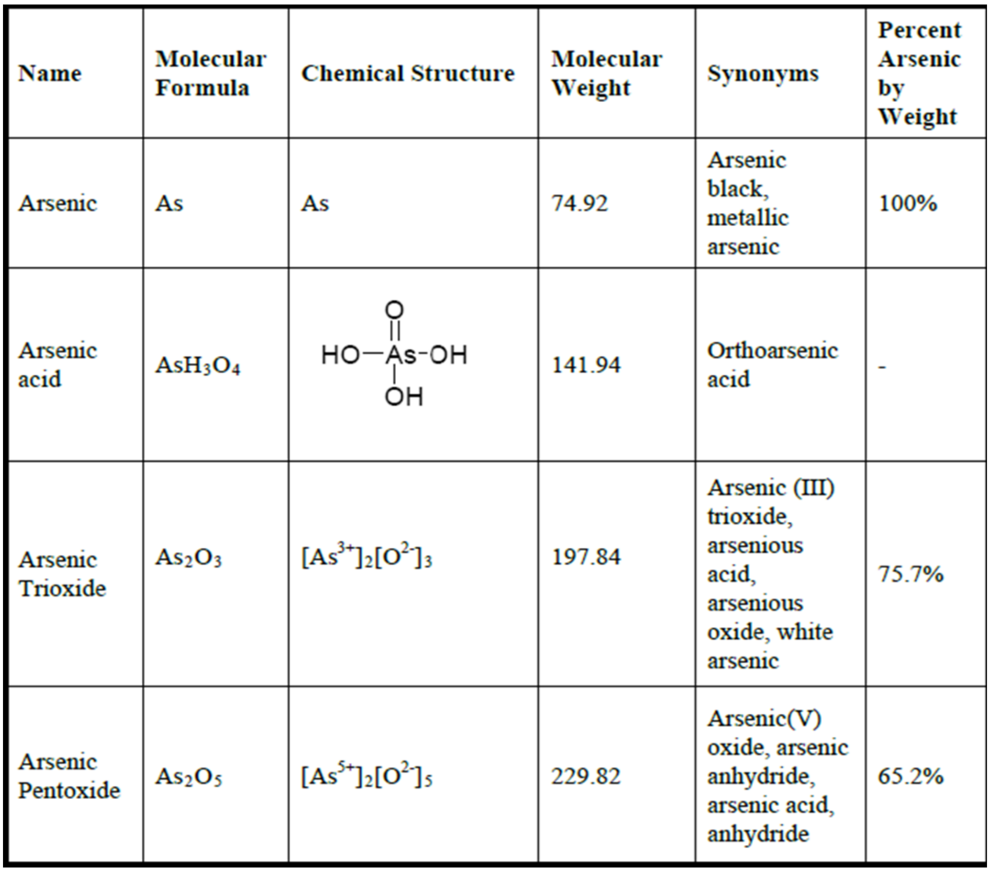
The main physical and chemical properties of arsenic and select inorganic arsenic species are summarized in Tables 1 and 2.

Table 1: Physical and Chemical properties of Arsenic and Inorganic Compounds (ATSDR, 2007)



Name	**Physical State**	**Density**	**Boiling Point**	**Melting Point**	**Solubility**	**Vapor Pressure**
Arsenic	Gray metal	5.778 g/cm^3 @ 25 °C	603 °C (sublimation point)	817 °C (triple point at 3.7 MPa)	Soluble in nitric acid, insoluble in water	7.5 x 10^{-3} mm Hg at 280°C
Arsenic acid	Exists only in solution, white translucent crystals, very pale yellow syrupy liquid	2.2 g/cm^3	160 °C	35.5 °C	302 g/L at 12.5 °C	No data
Arsenic Trioxide	White cubic crystals (arsenolite) white monoclinic crystals	3.86 g/cm^3	460 °C	274 °C	17 g/L at 16 °C	2.47 x 10^{-4} mm Hg at 25 °C
Arsenic Pentoxide	White amorphous powder	4.32 g/cm^3	No data	315 °C	2300 g/L at 20 °C	No data

Table 2: Physical and Chemical Properties of Arsenic and Inorganic Arsenic Compounds (ATSDR, 2007)



Name	**Molecular Formula**	**Chemical Structure**	**Molecular Weight**	**Synonyms**	**Percent Arsenic by Weight**
Arsenic	As	As	74.92	Arsenic black, metallic arsenic	100%
Arsenic acid	AsH_3O_4	O HO—As-OH OH	141.94	Orthoarsenic acid	-
Arsenic Trioxide	As_2O_3	$[As^{3+}]_2[O^{2-}]_3$	197.84	Arsenic (III) trioxide, arsenious acid, arsenious oxide, white arsenic	75.7%
Arsenic Pentoxide	As_2O_5	$[As^{5+}]_2[O^{2-}]_5$	229.82	Arsenic(V) oxide, arsenic anhydride, arsenic acid, anhydride	65.2%

3.2 Sources of As

Soils contains various metals and metalloids including arsenic (As) (Calderón et al., 2001; Caussy et al., 2003, Díaz-Barriga et al., 1993). The content of arsenic is around 1.5–3 mg kg^{-1} in terrestrial abundance. Sources of arsenic in the environment can be divided to geogenic (natural) and anthropogenic.

3.2.1 Geogenic sources

Arsenic is spread throughout earth crusts, soil, sediments, water, air and living organisms long before man's activities. The earth's crust, constitutes nearly 3.4 parts per million (ppm) arsenic widely distributed (ATSDR, 2007). Only a small percentage of arsenic exists in its elemental form in the environment. From the United States Geological Survey (USGS, 2006), the most frequent widespread natural source of arsenic is pyrite, which is made up of iron, sulfur, and arsenic. Arsenic is produced into the environment by the weathering of rocks, volcanic eruptions, forest fires, and volatilization of methylarsines from the soil (ATSDR, 2007).

3.2.2 Anthropogenic sources

Most arsenic released into the environment is from anthropogenic sources. According to Liao et al. (2005) about 52,000-1,120,000 ton of arsenic is released into the environment yearly through anthropogenic sources. Again, mining activities have polluted soil and water in other countries such as England, China, Thailand, Ghana, Zimbabwe, Mexico, Canada, U.S.A., and Brazil (Asante et al., 2007; Bissen and Frimmel, 2003; Borba et al., 2003; Li and Thornton, 1993). Moreover, in the world, arsenic production

from smelting activities has been approximated to 6200 ton annually but, smelting of copper alone constitute nearly 80% of world arsenic discharge yearly (Bissen and Frimmel, 2003). The average arsenic concentration for United States (US) coal is approximately 24 ppm (USGS, 2006). Furthermore, arsenic is released into the environment during pesticide/fertilizers applications (agriculture), coal combustion, wood combustion, and waste incineration processes (USEPA, 2004). The main anthropogenic sources of (risky elements) metal(loids) are summarized in

Table *3*.

.

Table 3: The main anthropogenic sources of metal(loids) (adapted from Alloway, 2013)

Metal(loids)	**Contamination source**
Arsenic (As)	Fossil fuel combustion, pyrometallurgical industry, wood processing, tailing, smelting, pesticides, landfills (discarded heaps), poultry manure
Cadmium (Cd)	Battery industry, fertilizers (phosphates), refuse disposal, sewage sludge, heaps of metal scrap, mining, smelting, plastic industry, microelectronics manufacture
Chromium (Cr)	Pyrometallurgical industry, wood processing, plastic manufacture, landfills, heaps of metal scrap, refineries
Copper (Cu)	Smelting, mining, pyrometallurgical industry, microelectronic manufacture, pesticide, farm animal manure, wood processing, refuse dump, heaps of metal scrap
Lead (Pb)	Battery industry, fossil fuel combustion, smelting, mining, steel and iron work, refineries, paint manufacture, refuse dump, heaps of metal scrap, sewage sludge, military operation (firing of arsenals)
Mercury (Hg)	Paper manufacture, fungicides and insecticides, plastic manufacture, smelting, mining, refuse dump, electrolysis treatment

3.3 Arsenic-affected areas in the world

Mostly, arsenic is located in the alluviums of the Indian states of West Bengal, Assam, Bihar, Jharkhand, Uttar Pradesh, and Bangladesh (Arpan and Biswajit, 2016). These are the key arsenic producers in the world China, Russia, France, Mexico, Germany, Peru, Namibia, Sweden, and USA, and estimated for 90% of the global discharge (Mandal and Suzuki, 2002). Also, arsenic toxicity relatively affects other nations such as Nepal, China, Mongolia, Myanmar, Thailand, Taiwan, Vietnam, Cambodia, Sri Lanka, Pakistan, Afghanistan, Japan, Hungary, Ghana, Mexico, Bolivia, and Argentina (Arpan and Biswajit, 2016). Arsenic toxicity above threshold value in water and soil has been investigated in the following countries: Iran, Australia, New Zealand, European, Iceland, Brazil, Canada, and U.S.A (Barringer and Reilly, 2013; Garelick and Jones, 2008; Mukherjee et al., 2006).

According to Peterson (1981), arsenic concentrations are higher in soils than in rocks. However, uncontaminated soils contain 1–40 mg kg^{-1} of arsenic, with least concentrations in sandy soils and the rest derived from granites, but Kabata-Pendias and Pendias (1984) reviewed that larger concentrations are found in alluvial and organic soils. Moreover, the principal factors influencing the concentration of elements in soils are the parent rock and human activities (Sarkar et al., 2007). Factors such as climate, the organic and inorganic components of the soils and redox potential status also affect the level of arsenic in soils.

Ministry of Water Resources and River Development and Ganga Rejuvenation (2014) disclosed that, more than 150 million people have been affected by arsenic contaminated drinking water. According to World Health Organization (2010), nearly 9100 deaths and 125,000 disability-adjusted life years (DALYs) has been identified because of intake of arsenic contaminated water in Bangladesh. A map of global probability of getting arsenic in reducing and oxidative states in groundwater is given in Fig.1 and approximate number of people affected by groundwater arsenic contamination in various countries has been tabulated in Table 4.

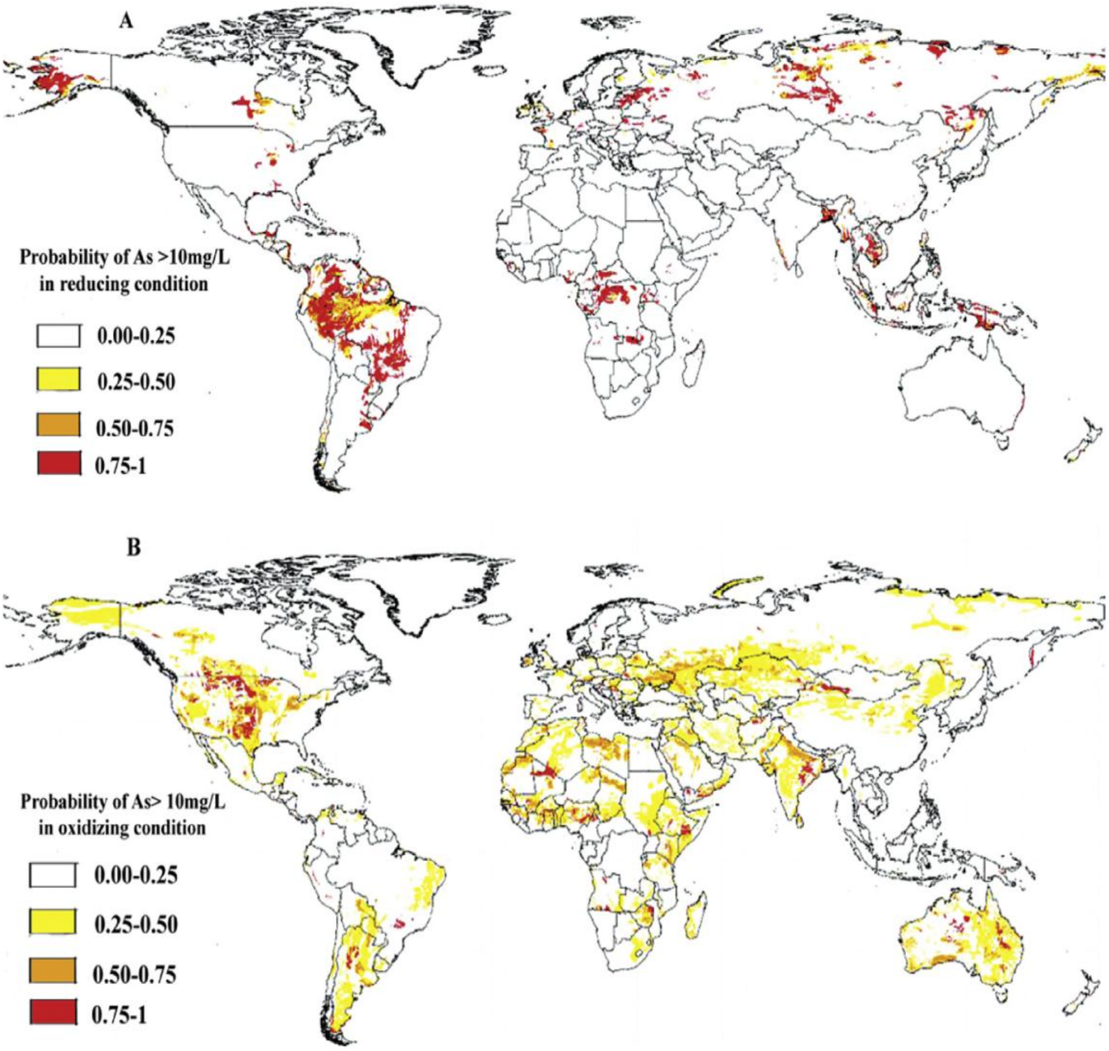


Fig. 1. A map showing (modeled) global probability of getting geogenic contamination in groundwater in A) reducing conditions and B) in oxidizing conditions (Amini et al., 2008, Sarkar and Paul, 2016).

Table 4. Groundwater arsenic concentrations and approximate number of affected people in some countries (Mukherjee et al., 2006; Kouras et al., 2007).

Country	Groundwater as concentration in μg/L (1 μg/l=0.001 mg/L)	Approximate size of pop. at risk
India	<10=3200	70,400,000
Bangladesh	<1=2500	32,000,000
China (Mainland China)	50=2000	>2,300,000
Vietnam	1=3050	>100,000
Thailand	1= >5000	15,000
Taiwan	10=1820	200,000
Inner Mongolia	<1=2400	600,000
Argentina	<1=9900	2,000,000
Chile	100=1000	400,000
Mexico	8=620	400,000
Hungary, Romania	<2=176	400,000
Greece	1=1840	150,000
Spain	<1=100	>50,000
U.K.	<1=80	minimal
U.S.A., Canada	<1=>10,000	minimal
Ghana	<1= 175	<100,000

3.4 Toxicity of Arsenic

The toxicity of As(III) has been found to be prevailing among the species of arsenic and even, inorganic forms of arsenic are potentially more poisonous than its organic state (Mass et al., 2001). More importantly, arsenic is toxic to both plants and animals and inorganic arsenicals are effectively more carcinogenic in humans (Ng, 2005). The range of arsenic toxicity depends on arsenic speciation.

The World Health Organization (WHO) has set a guideline of 10 μg L^{-1} as the drinking water standard. However, Ng et al. (2003) reported nearly 60–100 million people worldwide may be at risk of exposure to excessive levels of arsenic. Undoubtedly, current reviews on arsenic toxicity (Goessler and Kuehnett, 2002, Meharg and Hartley-Whitaker, 2002, Ng, 2005) have stated inorganic arsenic species are more toxic than organic forms to living organisms, and even humans and other animals. Arsenite (As(III)) is certainly more poisonous than arsenate (As(V)) (Mass et al., 2001). Petrick et al. (1993, 2000), suggested MMA(III) (monomethylarsonic acid) and DMA(III) (dimethylarsinic acid) are even more dangerous and genotoxic than their parent compounds.

3.5 Metal(loid)s speciation, bioavailability and bioaccessibility

Owing to divergent views associated to the concept "bioavailability and bioaccessibility" which are potential terminologies for metal(loids) mobility in plants and animals' system. However, other researchers made the effort to address meaning. Notably among them is, Adriano (2001), stated that, bioavailability is the ability of living organism to obtain chemicals from food or from the abiotic environment intended for the chemical metabolism of an organism. But, Vangronsveld and Cunningham (1998) also defined bioavailability as the fraction of the total chemical that can combine with a biological target. Again, Semple et al. (2004) reviewed a contrast between bioavailable and bioaccessibility substance: in that, the concept bioavailable defines a compound which is "readily available to cross an organism's cellular membrane from the medium to the organism at a particular time" Whiles, bioaccessibility represent substance that is "available to cross an organism's cellular membrane from the environment, if the organism has access to the chemical." Even though, there is no acceptable distinct meaning globally, the National Research Council (NRC), (2003) have resolved it under field of soil and sediment contamination. The National Research Council (NRC), (2003), defined bioavailable "the interaction with individual plants and animals through physical, chemical, and biological corresponding to amount of chemicals associated with soils and sediments". Semple et al. (2004) suggested a contrast between bioavailability and bioaccessibility compounds: in that, bioavailable "is a substance freely available to cross an organism's cellular membrane from the medium to the organism at a given time." Whiles, bioaccessibility on the other hand, is a compound "available to cross an organism's cellular membrane from the environment, if the organism has access to the chemical."

Certainly, the type of organism and the nature of chemical (physical-chemical characteristics, concentration etc.), even environmental factors (in soil e.g., pH, cation exchange capacity, type and the concentration of organic matter, redox potential, amount of Fe, Mn oxides, clay minerals and others) affect bioavailability/bioaccessibility of specific substance. Moreover, various system changing the speciation and redistribution of metal(loids) in soil are schematically outlined in Fig. 2 (Adriano, 2001).

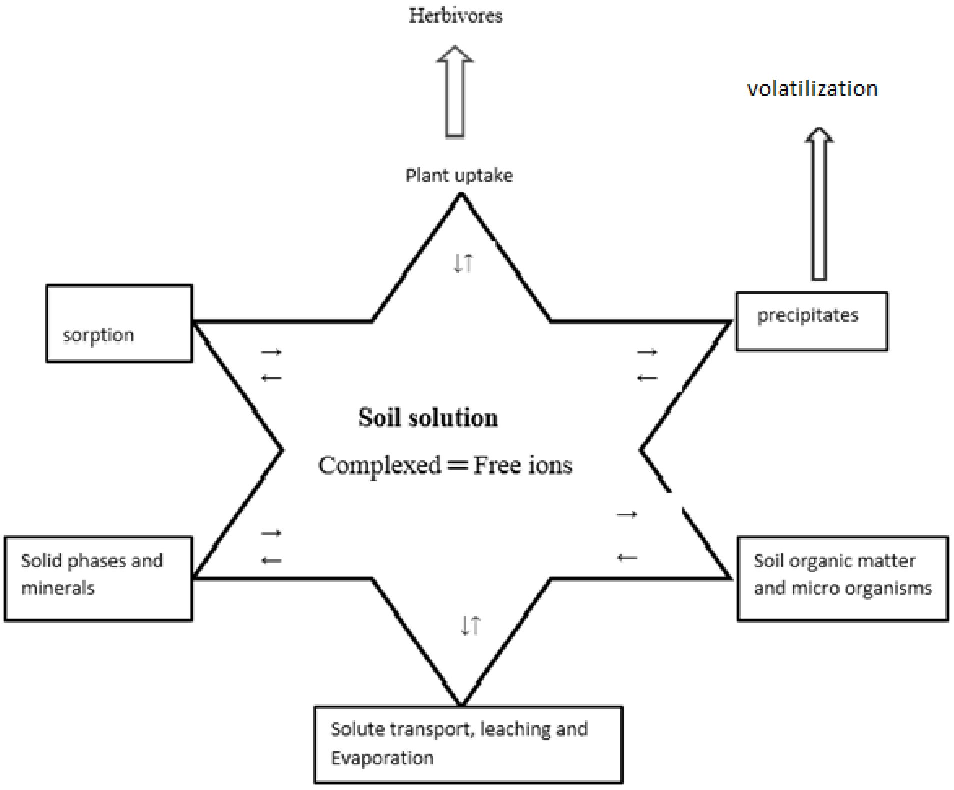


Fig. 2: Diagram of main processes affecting metal(loids) behavior and distribution in soil conditions (Adopted from Adriano, 2001).

Off course, bioavailability/bioaccessibility of metal(loid) links to speciation, which defines actual chemical form of an element differing in oxidation state, stoichiometry, coordination, complexation, association with other phases in a system (Templeton et al., 2000). According to Reeder et al., (2006) these chemical properties and free movement of specific species play the key role for element to be poisonous. Additionally, it is sometimes difficult or even impossible to evaluate a direct chemical species in environmental matrices. Henceforth, the chemical species of a given element can be sorted into fractions based on their chemical (e.g., bonding, reactivity) or physical (e.g., size, solubility) behavior. Fractionation analyses of an element (filtration, size-exclusion chromatography, bonding, reactivity) describe a general and important instrument in environmental system (Templeton et al., 2000). Also, fractionation of targeted elements into distinct fractions, i) oxidizable (bound to organic matter) ii) reducible (bound to Al, Fe and Mn oxides) iii) exchangeable (freely available) and iv) residual fraction (not available) play a key role in evaluating mobility of risk metal(loids) in soil contaminants (Akcay et al., 2003)

3.6 Behavior of arsenic in the environment

Arsenic mostly exists as inorganic species, however, it can react with organic materials in soils. Large fraction of arsenates As(V) are bound to clay, iron and manganese oxides/hydroxides and organic matters under oxidizing conditions (Arpan and Biswajit, 2016). Then, under reducing conditions, arsenites As(III), are the common arsenic compounds. Microorganisms enhances inorganic arsenic compounds to synthesis monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAsO) (Mandal et al., 2002, Fergusson, 1990). But under anaerobic conditions these can be reduced to gaseous state and easily oxidized methylarsines. The behavior of arsenic present in soils depends on the type and amounts of sorbing components in the soil, the pH, and redox potential.

Again, the adsorbed arsenate fraction in soils is controlled by soil pH and redox potential (Eh) (Arpan and Biswajit, 2016). Fordyce et al. (1995) stated that arsenates of Fe and Al ($AlAsO_4$, $FeAsO_4$) are the major phases in acid soils and are less soluble than calcium arsenate (Ca_3AsO_4). However, oxidizing factors can convert H_3AsO_3 into H_3AsO_4. Theoretical oxidation– reduction potential of the system is 0.557 V at 20 °C. Hence, soil depends on the redox potentials of all the reducing and oxidizing systems occurring in the soils: these correlations are very complex and the redox value for soils is not inversely proportional to the As (V) to As (III) ratio (Mandal et al., 2002). There is approximately 200 mineral forms of arsenic. The major mineral forms can be grouped as the arsenates (~60%), the sulfides and the sulfo-salts (~20%) of arsenic. Nriagu (1994) suggested that silicates and native arsenic are the least. The arsenate minerals contain oxyanions of As such as As_4^{3-}**,** $AsO_3(OH)^{2-}$. The following are examples of arsenic sulfide minerals; orpiment (arsenic trisulfide As_2S_3), realgar (tetraarsenic tetrasulfide As_4S_4), α- and β-dimorphite (tetraarsenic trisulfide As_4S_3), tetraarsenic pentasulfide (As_4S_5) but, arsenopyrite ($FeAsS_2$), cobaltite (CoAsS), are the only two compounds of the mixed sulfides of arsenic (M(II)AsS) (Arpan and Biswajit, 2016).

In the environment, +III and +V of arsenic oxidation state, are the most common in soil and water environments. As mentioned above, As(V) is the main species in an oxidative conditions whiles, As(III) is the dominant species in the reducing conditions. But, sulfides containing arsenic are rapidly weathered compared to other sulfides which are slightly resistant. However, this is confirmed by Sarkar et al. (2007), that all forms of arsenic are biodegradable by microbes; but sulfides of arsenic, Mn/Fe/Al oxides and hydroxides of arsenic are stable and resist the microbial activities. In support Murdoch and Clair (1986), Welch and Stollenwer (2007) reported that under the influence of oxidation conditions, arsenic sulfides are able to release arsenic to contaminate the main parts of the environment like soil, water, and air.

However, in comparison to other oxyanion-forming elements, arsenic is the most problematic to the environment due to its relative mobility over a large range of redox conditions (Mandal et al., 2002). Other oxyanion-forming elements like Se, Cr mobilizes and immobilize in different oxidative and reducing environment, but the arsenic compounds do not immobilize in any of these conditions (Sharma and Sohn, 2009). Welch et al. (1988) and Bell (1998) reviewed that, As(III) and As(V) are soluble in water over a wide range of pH and Eh (redox potential). Thus, at average or high redox potentials arsenic is immobilized in pentavalent (arsenate) oxyanions forms, such as H_3AsO_4, $H_2AsO_4^{-}$, $HAsO_4^{-2}$ and AsO_4^{-3}, and under extreme reducing (acidic and slightly basic) conditions and least redox potential, the trivalent arsenite species (H_3AsO_3) is predominate, whereas, As^0 and As^{3-} are not common in aquatic systems (Mandal et al., 2002).

3.7 Dependence of arsenic speciation on environmental parameters (*Effect of pH and Eh)*

3.7.1 Effect of pH

Forms of arsenic, As(III), As(V), MMA^{V}, and DMA^{V} undergo acid–base equilibria, this means, separate major and minor species will be ionized depending on the pH (Pierce and Moore, 1982). Fig. 3 below shows that concerning the As(III), at neutral pH, $As(OH)_3$ is the main species while $As(OH)_2O^{-}$ shows a small fraction (<1.0%) and even, the presences of $As(OH)_2O^{-}$ and AsO^{-}_3 is negligible (Goldberg and Johnston, 2001). In the case of As(V), at pH 7, thus same concentrations of $AsO_2(OH)^{2-}$ and $AsO_3\,(OH)^{2-}$ will be seen (Fig. 3) (Cox and Ghosh, 1994). At a neutral pH, both the MMA^{V} major species, $CH_3AsO_2(OH)^{-}$ and minor species, $CH_3AsO_3^{2-}$ will be present accordingly (Fig.3). But for DMA^{V}, both $(CH_3)_2AsO(OH)$ and $(CH_3)_2AsO_2^{-}$ co-exist at pH 7 (10%) (Fig. 3).

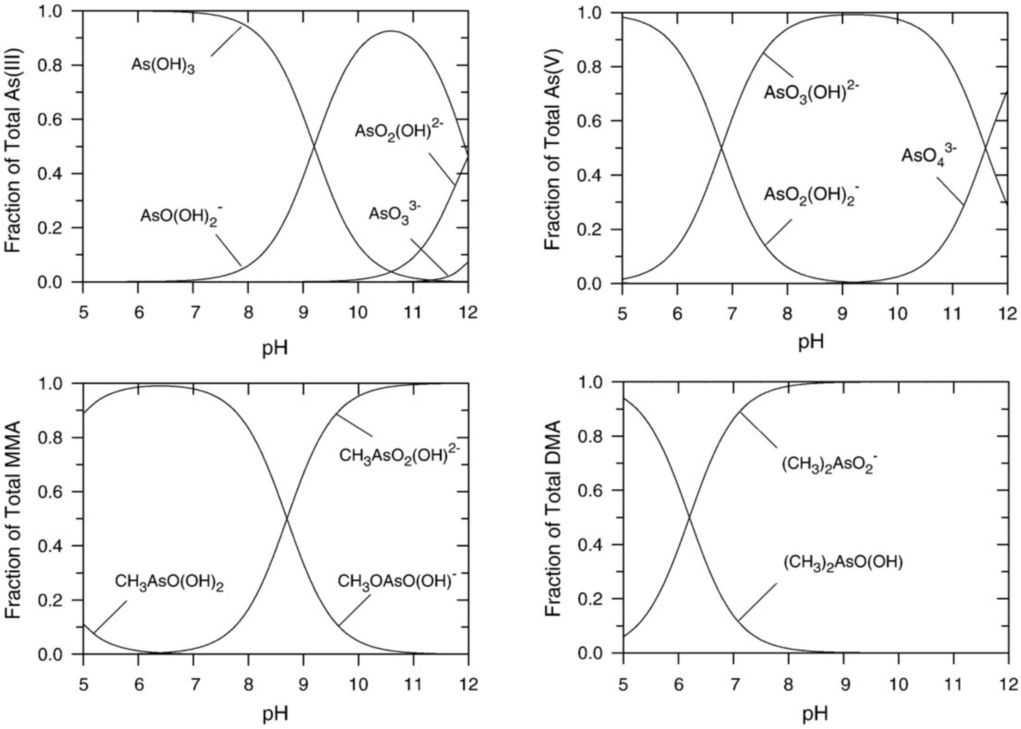


Fig. 3. Distribution of As(III), As(V), MMA, and DMA hydroxide species as a function of pH at 25 °C. (Adopted from Sharma, M. Sohn,2009)

Effect of Eh

Ferguson and Gavis (1972*)* reviewed that redox potential (Eh) and pH influence mechanism of arsenic speciation in the natural environment. Fig. 4 shows the Eh–pH diagram for inorganic As compounds in the natural environment. For oxidizing conditions (high Eh values), inorganic arsenic appears basically as H_3AsO_4 (As(V)) at pH <2, and whereas $H_2AsO_4^-$ and $HAsO_4^{2-}$ species occurs in the pH range from 2–11. At low Eh values, H_3AsO_3 is the main inorganic arsenic species (As(III)) for reducing conditions (Fig. 4). But for Eh values below −250 mV, arsenic compounds like As_2S_3 are produced in the presence of sulfur or hydrogen sulfide (Fig. 4) but even, these conditions are environmentally insignificant. Ferguson and Gavis (1972) reviewed that solubility of these compounds is low for both neutral and acidic environment. However, for very strong reducing environment, arsine and elemental arsenic are present but even, limited under the natural conditions (Sharma and Sohn, 2009).

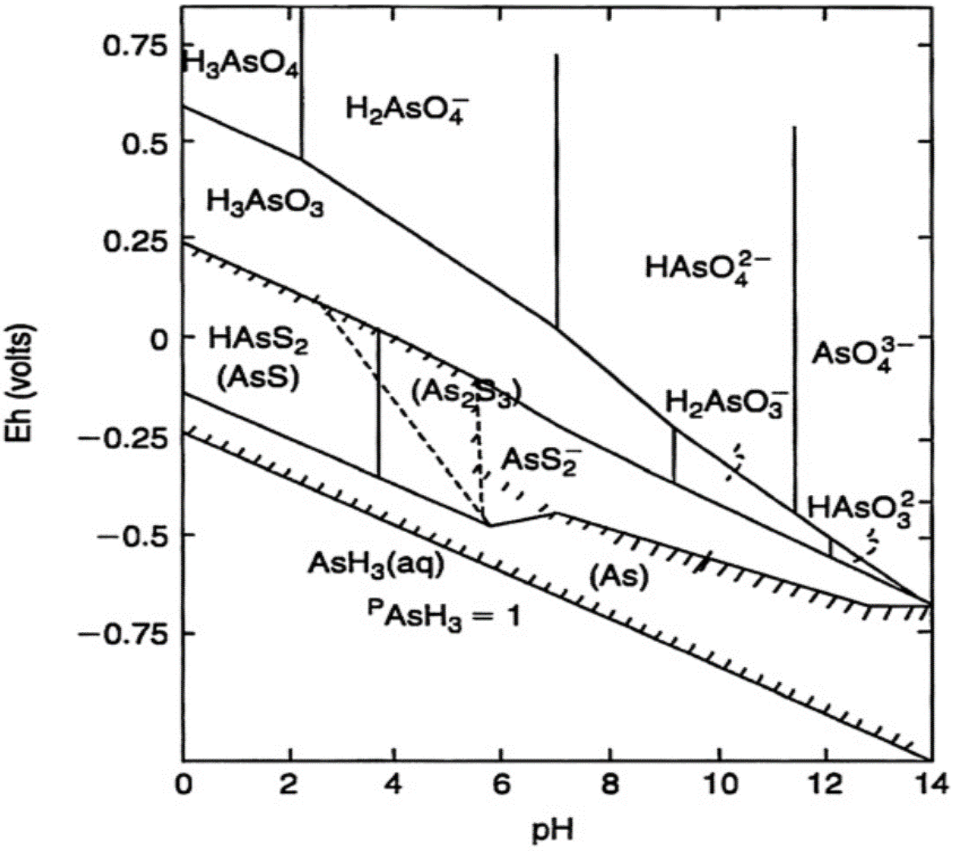


Fig. 4. The Eh–pH diagram for arsenic at 25 °C and 1 atmosphere with total arsenic10^{-5} mol L^{-1} and total sulfur 10^{-3} mol L^{-1}. Solid species in parentheses (Adopted from Ferguson and Gavis, 1972).

In supported, another Eh-pH diagram (Fig. 5) suggests that at pH < 6.9, $H_2AsO_4^-$ species is prevalent, whiles $HAsO_4^-$ dominates at higher pH (>6.9), at farthest acidic and alkaline environment, H_3AsO_4 and AsO_4^{3-} predominates respectively. Additionally, Hendricks (2006) stated that arsenite and arsenate occurs at same time in redox condition under the influence of slow kinetics. But, most H_3AsO_3 occurs at a vast range of pH from very low to nearly 9.2. Again, Smedley and Kinniburgh (2001) suggested increase in alkaline conditions assist the occurrence of $HAsO_3^-$ and AsO_3^{3-} in water.

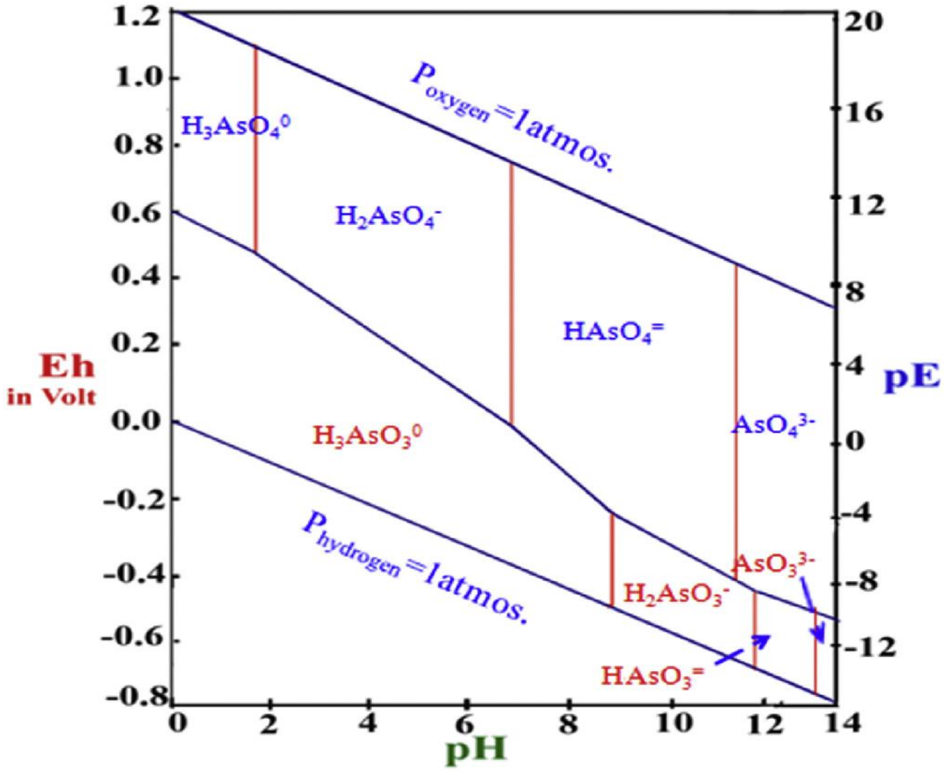


Fig. 5. Stability fields of dissolved As in water with respect to water pH and Eh at 25°C and 1atmospheric pressure (Welch et al., 1988, Smedley and Kinniburgh ,2001).

3.8 Various remediation techniques for metal(loids) in contaminated soil(As)

Techniques for remediation can be grouped namely, biological, or physical, chemical and which can be *ex situ* or *in situ*. However, for selection of a remediation technique, it must base on the cost, the intended result, and the long-term effects on the treated site. Undoubtedly, the type of contaminant, high concentration, soil properties at the area, and aftermath used of the site must be identified (Mulligan et al., 2001). Martin and Ruby (2004) suggested that soil remediation technique is to create an ultimate solution to protect human health and the atmosphere. Normally, remediation is applying different regulatory requirements and, even on assessments of human health and ecological danger where legislated standards and, or advisory standards can occur. The regulatory authorities accept remediation methods upon metal bioavailability reduction and even, over a long period (Martin and Ruby, 2004). The physical and chemical form of the metal(loid) pollutants in soil strongly determines the choose of the ultimate remediation treatment technique.

Among different methods for the remediation of metal(loid) contaminated soil, Gupta et al. (2000) have grouped remediation techniques of into three categories of hazard-alleviating measures: i) gentle in situ remediation, ii) in situ harsh soil restrictive measures, and iii) in situ or ex situ harsh soil destructive measures. Therefore the later, is to avoid hazards to mankind and plant, or animal whereas, the former is to conserve soil fertility, which permits a good use of the soil. However, USEPA (2007) has categorized remediation techniques for contaminated soils into two types, (i) source control and (ii) containment remedies. Source control deals with in situ and ex situ treatment methods for sources of pollutions. In situ or in place describes that the polluted soil is treated in its natural site; thus unmoved, unexcavated; remaining at the site or in the subsurface. In situ treatment techniques treat or remove the contaminant from soil without excavation or removal of the soil. Ex situ describes the polluted soil is moved, excavated, or removed from the site or subsurface. Certainly, ex situ remedies need excavation or removal of the contaminated soil. This include the building vertical engineered barriers (VEB), caps, and liners used to inhibit the transfer of contaminants. GWRTAC (1997) also grouped remediation techniques for metal(loids)-contaminated soils under five categories(Table 5): Isolation, immobilization, toxicity reduction, physical separation, and extraction.

Table 5: Techniques for remediation of metal(loids)-contaminated soils(source: GWRTAC,1997)

Category	Remediation techniques
Isolation	(i) Capping (ii) subsurface barriers
Immobilization	(i) Solidification/stabilization (ii) vitrification (iii) chemical treatment
Toxicity and/or mobility Reduction	(i) Chemical treatment (ii) permeable treatment walls (iii) biological treatment bioaccumulation, phytoremediation (phytoextraction phytostabilization, and rhizofiltration), bioleaching, biochemical processes.
Physical separation extraction	(i) Soil washing, pyrometallurgical extraction, *in situ* soil flushing and electrokinetic treatment

Moreover, this soil washing, phytoremediation, and immobilization techniques are described as, the best demonstrated available technologies (BDATs) for metal(loids)-contaminated sites (Wuana and Okieimen., 2011).

3.8.1. Soil Washing

Soil washing is defined as volume reduction/waste minimization approach process. Normally, soil is excavated (physically removed) (ex situ) or on-site (in situ). The technique uses physical and/or chemical procedures to eliminates metal(loids) pollutants from soils. For the physical soil washing, variations between particle grain size, settling velocity, specific gravity, surface chemical behaviour, and even, magnetic characteristic are employed to differentiate those “host” contaminant from the bulk which are contaminant-depleted. Standard mineral processing equipment for mining industry is used (Dermont, 2008).

For chemical soil washing, soil particles are washed by choosing and conveying the contaminants on the soil into solution. However, using only water would eliminate less cations in the leachates because metal(loids) are slightly soluble and exist mostly in a sorbed state, for that matter, extra chemical agents are applied to the water (Davis and Singh,1995).

As a result, Dermont (2008) suggested the following procedure for soil washing, (i) (physical separation) those soil particles which" host" the main contaminants are distinct from the bulk soil fractions, (ii) pollutants are evacuated from the soil by aqueous chemicals and eliminated from solution on a solid substrate (chemical extraction), or (iii) a combination of both. Moreover, separated pollutants are transported to dangerous waste landfill (or even further processed by chemical, thermal, or biological processes). However, after the removal, the existing bulk fraction can be (i) recycled on the site being remediated as partially inert backfill, (ii) applied on another site as fill, or (iii) discarded off as non-toxic substance.

The main advantages of ex situ soil washing are, (i) completely get ride off the contaminants and allows the fast cleanup of a contaminated place (Wood, 1997), in addition, (ii) meeting the specified criteria.

But, the most current soil washing involves soil flushing and in situ process where the washing solution is pump through the in-place soil matrix, whereas, ex situ extraction of metal(loids) from the soil requires soil heap leaching using acid and chelator (Peters, 1999). But the disadvantages include, the contaminants are moved to a different locality, there is risk of spreading contaminated soil and dust particles during removal and conveying of polluted soil, and the financial demands are high (removing large amounts of soil or disposal of at hazardous or toxic waste is needed (Wuana and Okieimen, 2011).

3.8.2. Phytoremediation

Phytoremediation, also termed green remediation, botanoremediation, agroremediation, or vegetative remediation, is described as an in situ remediation technique that deployed vegetation and related microbiota, soil amendments, and agronomic methods to eliminate, contain, or render environmental pollutants non-toxic (Cunningham and Ow,1999; Helmisaari, 2007). The usage of metal-accumulating plants to eliminate metal(loids) and other substances was dated back in 1983, nevertheless, the concept has been enacted 300 years ago on wastewater generated (Chaney et al., 1997; Henry, 2000). Moreover, plants can break down or degrade organic pollutants or remove and stabilize metal pollutants. For instance, Chinese Brake ferns (*Pteris vittta*) were used to eliminate more than 20 times the soil arsenic concentrations under field conditions (Salido et al., 2003). Moreover, Meharg and Macnair (1991), published As uptake reduction of 75% at 0.5 mM phosphate in a grass (*Holcus lanatus).* Furthermore, Arsenate concentrations in alfalfa (*Medicago sativa* L.) shoots has been reduced by phosphate (Khattak et al., 1991). Phytoextraction (phytoaccumulation), phytostabilization, and phytofiltration are techniques identified for remediation of metal(loids) contaminated soils (Garbisu and Alkorta., 2001).

3.8.2.1 Phytoextraction (Phytoaccumulation)

Phytoextraction is the process where plant roots uptake metal contaminants from the soil and transfer to their various plant tissues. For this reason, the plant used for this purpose must have certain qualities such as being metal(loids) tolerant, grow very fast a yielding high biomass, have high metal-accumulating capacity, have a profuse root system, and a high bioaccumulation factor (Scragg, 2006, Jadia, 2008). About 400 plant species have been identified as hyperaccumulators of metal(loids) (Lasat, 2000, Ghosh and Singh, 2000). Among them, is Brake fern (*Pteris vittata*) which is a native to South Africa, Madagascar, Asia, Japan, Malaysia, New Guinea, and Australia was reported to be the first arsenic hyperaccumulator (Ma et al., 2001). This fern can effectively accumulate As (up to 2.3% in its fronds) and yields a large portion of shoot biomass (up to 1.7 m in height), which potential makes it adapted for phytoremediation activities (Komar et al., 1998; Ma et al., 2001). Again, *Pteris vittata* has shown a shoot arsenic concentration more than 200 times higher than that of any other plant species tested (https://www.sbir.gov/sbirsearch/topic/current): (accessed 1/4/2018).

3.8.2.2 Phytostabilization

Phytostabilization, is also termed in-place inactivation, is simply using selected plants to stabilised soil sediment and industrial or refining liquid process (USEPA, 2000). Here, pollutants are absorbed and accumulated by roots, or adsorbed onto the roots, or precipitated in the rhizosphere. This certainly, reduce the concentration level of the contaminants, thereby preventing leaching into the groundwater or air and also, decreases the bioavailability/accesscibility of the pollutants and through the food chain (biomagnification) (Wuana and Okieimen, 2011). Furthermore, this method inhibits soil erosion and the spreading of harmful metal(loids) in the environment (Raskin and Ensley, 2000). However, is one of the best technique for eliminating, As, Pb, Cd, Cr, Cu, and Zn (Jadia and Fulekar, 2009). Again, is very productive to conserve ground and surface water (USEPA, 2000). However, a research conducted by Xinyu et al.,(2016) using Indian mustard, spinach and cabbage were proved to be good accumulators for translocation of As and Cs from plant roots to shoots by EKF (Electro-kinetic field). Also, the study produced 100 mg kg^{-1} loading levels, with As recording 20 and 5.75 mg kg^{-1} in SOL (water soluble) and EXC (exchangeable) fractions, respectively.

3.8.2.3 Phytofiltration

Phytofiltration is using plant roots (rhizofiltration) or seedlings (blastofiltration), to sheive or filter metal(loids), from groundwater and aqueous waste streams (GWRTAC,1997; Ghosh and Singh, 2005). For this, plants are (hydroponically) sowed in clean water instead of soil, to allow a large root system to develop, later transferred to polluted site where the roots absorb both the polluted water and contaminants as well (Wuana and Okieimen, 2011). Thus, saturated roots are gathered and disposed of saturated, they are harvested and discarded without any risk. However, the technique has been used in Chernobyl where sunflowers were pollutants (Scragg, 2006).

The following are some advantages of phytoremediation over typical remediation techniques i)economically feasible using the same tools and supplies as agriculture, ii) less disruptive to the environment, iii)it does not require disposal sites iv) it prevents excavation and transportation of contaminants hence decreasing the danger of transferring the pollutants. However, it has a lot of disadvantages such as: i) it needs the growing conditions the plant (i.e., climate, geology, altitude, and temperature), ii) it requires how tolerant the plant is iii) comparatively is time consuming to remediate the site, (iv) it increases solubility of pollutant resulting into environmental risk and mobility, hence it can be used alongside with other amendments.

3.8.3 Vitrification

Using high-temperature system to reduce the mobility of the contaminated metal(loids) in an area that leads to the formation of vitreous material, basically an oxide solid. Under this method, the high temperature volatilizes and/or destroy organic pollutants or volatile metal(loids) species (such as Hg) which is collected for treatment or discarded. Vitrification can be used to evaluate most polluted soils containing a lot of inorganic and organic contaminants (Wuana and Okieimen, 2011). Meanwhile, vitrification can undergo ex situ or in situ besides this, in situ processes are preferred because of less energy and cost demand (USEPA, 1992). Basic steps in ex situ vitrification processes include excavation, pretreatment, mixing, feeding, melting and vitrification, off-gas collection, and treatment, and forming or casting of the melted product. Hence, the amount of energy required for this melting, makes it expensive (Wuana and Okieimen, 2011).

Alternatively, the in situ vitrification (ISV) requires passing electric current through the soil using series of electrodes placed vertically into the contaminated area. The main key for in situ vitrification is the ability of the soil melt to transfer current and solidify as it cools (Buelt and Thompson,1992). Although, vitrification is not a classical immobilization approach, it has advantages like (i) it is usually used for reclamation of metal(loids)-contaminated soils (Pb, Cd, Cr, asbestos, and materials containing asbestos), (ii) the main contributing factor for using this method depends on how “hazardous to neutral” could be changed. The main drawback is that when the alkali content (as Na_2O and K_2O) of the soil is too high (1.4 wt %), the molten soil cannot allow conductance to transfer the current (Buelt and Thompson, 1992).

3.8.4 Immobilization Techniques

Immobilization technique involves applying organic and inorganic amendment/agent to speed up the attenuation of metal(loids) mobility and toxicity in soils. The main aim of immobilization amendment is to change the original soil metal(loids) to more geochemically immobile phases by sorption, precipitation, and complexation processes (Hashimoto et al, 2009). Clay, cement, zeolites, minerals, phosphates, organic composts, and microbes are the common amendments (GWRTAC,1997, Finzgar, 2006). Ex situ and in situ immobilization techniques are practical steps to remediation of metal(loids)-contaminated soils. However, in situ techniques are usually applied because low work-force and energy involvement, but even, it processes require specific area conditions. The ex situ technique is applied to highly polluted soil that must be removed from its natural place, and its storage is connected with a high ecological risk (such as, radionuclides). This method has the following advantages: (i) fast and easy use and (ii) comparatively low costs operation. But, it has disadvantages like (i) high risk to the surrounding, (ii) large amount wastes are produced (twice as large as volume after processing), (iii), risk of releasing of another contaminants to the environment, (v) continuous monitoring of the stored wastes.

For drawbacks in situ immobilization: (i) it is only a temporary measure (contaminants are still in the environment) and, (ii) the reclamation approach is done to the surface layer of soil within a range of (30–50 cm), and (iii) constant monitoring is required (Martin and Ruby, 2004; USEPA, 1997). As mentioned before, immobilization techniques involve: (i) Solidification/stabilization, (ii) vitrification, (iii) chemical treatment.

3.8.5 Solidification/Stabilization (S/S)

Solidification is a process of introduction stabilizing reagents to a contaminated material to influence physical/dimensional immobility to contain contaminants, in order to decrease any external agents either, by a combination of chemical reaction, or encapsulation, and permeability/surface area (Wuana and Okieimen, 2011). In support, Evanko and Dzombak (1997) stated that, S/S is an international enacted remediation technique for polluted soils and hazardous wastes in the globe. A simple method by introducing required amount of regents/ chemicals into contaminanted soil. Ling et al. (2007), Fawzy (2008), Wuana and Okieimen, (2011), mentioned inorganic agents as clay (bentonite and kaolinite), cement, fly ash, blast furnace slag, calcium carbonate, Fe/Mn oxides, charcoal(biochar), zeolite whiles, Farrell (2010) stated organic stabilizers as bitumen, composts, and manures or an integration of organic-inorganic amendments.

3.8.5.1 Stabilization technique application

However, the expensive nature of traditional soil remediation techniques (excavation and landfilling) and limited resources given to remediate polluted areas distract the success of other techniques that are cost-effective and environmental friendly like soil stabilization (Kumpiene et al, 2008, Komarek et al, 2013). In addition, Mulligan et al. (2001) reviewed the correlations of soil stabilization with other frequently used soil remediation techniques as a promising alternative. The technique relates to element fractions, even small interference under soil conditions, can be liberated and percolate into ground/surface water or absorbed by soil organisms (Kumpiene et al, 2008). Because it involves the reduction of contaminant mobility only by chemical means can be called chemical stabilization.

3.8.5.2 Chemical stabilization

Chemical stabilization is a soil remediation method based on the application of various inorganic and organic amendments to polluted soils. Moreover, these stabilizing agents lower the mobility and bioavailability of metal(loids) in soils. As mention above, stabilization can be reached through several physico-chemical processes, such as adsorption, complexation, precipitation, and co-precipitation. For this reason, the technique is not an innovation, as soil amelioration adding, like; organic matter, lime, phosphates, has been used for long time with the aim to promote plant growth, alter a depletion of nutrients (e.g. Ca and Mg) and lower soil phytotoxicity (Bolan et al., 2003). Nevertheless, the technique appears to derive from the study of agriculture with crops being the target. Further, contaminants bioavialability can be decrease through the process of precipitation and complexation. However, there are many factors that influence sorption/dissolution processes such as, pH, redox potential, type of soil constituents, cation exchange capacity (Kumpiene et al, 2008). Therefore, the key question is, ‘which agent to select’? Recommended amendment must have affinity for metals, for instance, metal oxides, phosphates, sulfides, others. Because, to select an appropriate amendment for soil treatment is determined by the type of pollutant. For that matter, chemical stabilization (the introduction of various stabilizing amendments, which by chemical means reduces pollutants mobility, bioavailability and bioaccessibility) has shown to be possible less destructive alternatives to conventional remediation option.

Hence, the mobility of As in soil is mostly controlled by adsorption/desorption processes and co-precipitation with metal oxides. Therefore, my study discussed AMOChar (amorphous Mn oxide-biochar composite) and AMO (Amorphous Manganese oxide) amendments for As immobilization.

3.9 Behavoir of manganese oxides (MnO) as stabilizing amendments

MnO are group of secondary minerals usually found in soils as scavengers of metal(loid)s (Manceau et al., 2002). MnO exist as fine-grained coatings on soil particles and nodules (Post, 1999, Essington, 2004). They often occur as amorphous materials (Sparks, 2003).

However, there are still only a limited number of studies done with Mn oxides as stabilizing amendments for As in available literature, but, the most common investigated reagents for As stabilization are oxides of Fe (Kumpiene et al., 2008). Despite their important sorption properties, Mn oxides efficiently changes the speciation of redox-sensitive elements (e.g., As, Co and Cr) and even, alter their dissolved concentrations in water and soil solution (Molar/mass concentration) (Manning et al., 2002a). The capacity of Mn oxides to effectively adsorb metals/metalloids has been examined in environmental sites, such as contaminated water treatment (Chang et al., 2008, Han et al., 2006, Liu et al.,2009, 2016; Ocinski et al., 2016) and even, used in chemical stabilization of metal(loids) in polluted soils (Ettler et al., 2015; Chen et al., 2000; Komarek et al., 2013; McCann et al., 2015; Michálková et al., 2014, 2016a). Even though, the oxidation of As(III) decrease its mobility and toxicity, the oxidation of Cr(III) point to production of high poisonous and reactive Cr(VI) species (Kumpiene et al., 2008). Also, Feng et al. (2006) argued that Mn oxides can firmly oxidize Cr(III) at less pH values whiles, even no Cr(III) precipitation is formed, but As(III) and Cr(III) strongly dissolve Mn oxides via these oxidation/reduction processes (Tournassat et al., 2002). According to, Manning et al. (2002a), Feng et al. (2006) these processes are termed as As(III)/Cr(III) oxidation associated with reductive dissolution of the Mn oxide at reduced pH, as shown below (Equation:1).

$MnO_2 + H_3AsO_3 + 2H^{2+} \rightarrow Mn^{2+} + H_3AsO_4 + H_2O$

$3MnO_2 + 2Cr(OH)_2^{+} + 2H^{+} \rightarrow 3Mn^{2+} + 2HCrO_4^{-} + 2H_2O$ (Eq: 1)

(Adopted from Komarek at al., 2013)

Primarily, the As(III) species can produced inner-sphere complexes with the birnessite surface and the resulted As(V) can be released with the reduced Mn(II) into the solution. Moreover, an identical pattern is produced during Cr(III) oxidation to Cr(VI) but, the degree of oxidation changes for various Mn oxides. Additionally, Tan et al. (2005); Feng et al. (2007) reviewed that the Mn oxides show effective oxidative characteristics.

However, Manning et al.(2002a) mentioned that this process, interferes with the oxide surface, generating new binding spots for As(V) adsorption onto hydroxyl groups of the Mn oxide surface (Mn-OH) as shown in (Equation; 2)

$2Mn\text{-}OH + H_3AsO_4 \rightarrow (MnO)_2 + AsOOH + 2H_2O$ (Eq: 2)

(adopted from Komarek et al 2013)

Again, As(V) can co-precipitate with hydrous Mn oxides and/or dissolved Mn^{2+} (Masscheleyn et al., 1991; Moore et al. 2000, Tournassat et al.,2002, Komarek et al., 2013) (Eq. 3) (via the following reactions:

$3MnOOH + 2HAsO_4^{2-} + 7H^{+} \rightarrow Mn_3(AsO_4)_2 + 6H_2O$

$Mn^{2+} + H_2AsO^{4-} + H_2O \rightarrow MnHAsO_4.H_2O$ (krautite) + H^+ (Eq: 3)

Nevertheless, Mn oxide, oxidizes at higher Eh values with respect to Fe oxides and for that matter, can evolve As before Fe oxides get dispersed. Furthermore, Mn can stabilize As via formation of a highly insoluble mineral $Mn_3(AsO_4)_2 \cdot 8H_2O$ with lowest solubility around pH 6 and Eh 6 (Porter et al., 2004) (Eq.3).

According to Sun and Doner (1998), birnessite has proven significantly to reduce arsenic levels in environmental toxicity in contaminated soils.

3.10.Advantages of amorphous manganese oxide (AMO) as amendment

The amorphous manganese oxide is basically formed by poorly crystalline/amorphous grains (Ettler et al., 2014). The new amorphous Mn oxide (AMO) has been manufactured and examined as a potential amendment for chemical stabilization of metal(loids) in soils because of its strong adsorption behavior and easy production (Della Puppa et al., 2013; Ettler et al., 2014). In support, Della Puppa et al. (2013), Ettler et al. (2015). Michálková et al. (2014) reported that the affinity by cationic and anionic pollutant was also established by adsorption experiment giving adsorption capacities of 2.24, 0.52, 4.02 and 0.46 mmol g^{-1} for Cd, Cu, Pb and Zn, in orderly manner. However, Mn oxide as a soil reagent often has the capacity to form inner-sphere complexes with As(III) and Cr(III), oxidizing them to As(V) and Cr(VI) accordingly (Komárek et al., 2013).

. Furthermore, the AMO was able to reduce effectively content of many selected metal(loids) in soil solution after the application to contaminated soils. Moreover, experimental study of chemical stabilization of Cd, Cu and Pb in polluted soils using AMO identified that, the adsorption capacity of AMO was in an ascending order than those reported for selected Fe-nano oxides (nano-maghemite, Fe_2O_3 and nano-magnetite, Fe_3O_4) (Michálková et al., 2014). Despite the high efficiency, the disadvantage of this agent is its lower stability, often at lower pH values (acidic conditions), which is connected with dissolution of soil organic matter (SOM) and eventual release of potentially phytotoxic Mn^{2+} (Ettler et al., 2014; Michálková et al., 2014). Hence, adsorption capacity of the AMO in soils is significantly dependent on the pH and time factor.

Therefore, AMO seems to be a suitable amendment for neutral and slightly alkaline soils. As one of the aims of the current study was to evaluate the stabilizing potential and stability of prepared AMO particles with respect to changing redox conditions.

3.10 Biochar (BC) as a perspective amendment for stabilization of As

Biochar is a carbon-rich product prepared by heating biomass in a closed system under limited supply of oxygen (Xiaokai et al, 2013). Biochar (BC) is manufactured by high-temperature, low-oxygen pyrolysis of wood, rice husks, crop residues, and other forestry wastes (Fig. 6) and enhance soil functions and decrease greenhouse gaseous emissions attained from organic materials (Brewer and Brown, 2012, Glaser and Birk, 2012, Beesley et al., 2011). To date, there are many thermochemical technologies such as pyrolysis, gasification, and hydrothermal conversion to produce biochar (Wang et al., 2010). Pyrolysis involves the heating of organic materials in the absence of oxygen to yield a series of bioproducts: biochar, bio-oil, and syngas. Pyrolysis is simple and cheap process which has been used to obtain charcoal for thousands of years. Biochar is added to a soil as a means of sequestering carbon and enhancing soil quality. As reviewed by Lehmann et al. (2006) and Lehmann (2007), biochar improves soil properties such as; soil fertility and increasing soil pH, increasing moisture holding capacity, engaging more efficient fungi and microbes, supporting cation exchange capacity (CEC), and maintaining nutrients in soil as a soil amendment. In addition, biochar has the capacity to sequester carbon from the atmosphere-biosphere pool and transform it to soil (Winsley, 2007; Lehmann, 2008; Laird, 2008). Biochar can raise the soil pH, which may increase the mobility of As and cause plants to uptake As more easily (Joseph et al., 2010). Moreover, a normal biochar has both high pH value and cation exchange capacity, and even, support soil fertility (Jeffery et al. 2011; Kookana et al., 2011). Most importantly, it is one of the best reagents for pollutants immobilization due to its very high surface area, high cation exchange capacity, high pH and reactive functional groups, enhancing stabilization via precipitation, ion exchange, surface complexation and adsorption (Beesley et al., 2011).

Again, some researchers have documented that biochar has a potential to adsorb contaminants in soils (Beesley et al. 2011; Yuan and Xu 2011). For this reason, the combination of BC with Mn oxides to aid the immobilization of As in soils can be a preferred choice, as Mn oxides can reduce As mobility via anion exchange in soils.

Undoubtedly, biochar is quite stable in soils due to its persistence to microbial decomposition and mineralization. This property of biochar depends mostly on its behavior, the pyrolysis nature and the kind of feedstock used in its preparation (Fig. 6). Woolf et al. (2010) suggested that a bioenergy method that intends use biochar in soil does not only leads to a total sequestration of CO_2 but rather, reduce outflow of greenhouse gases such as N_2O and CH_4 (Spokas et al., 2009).

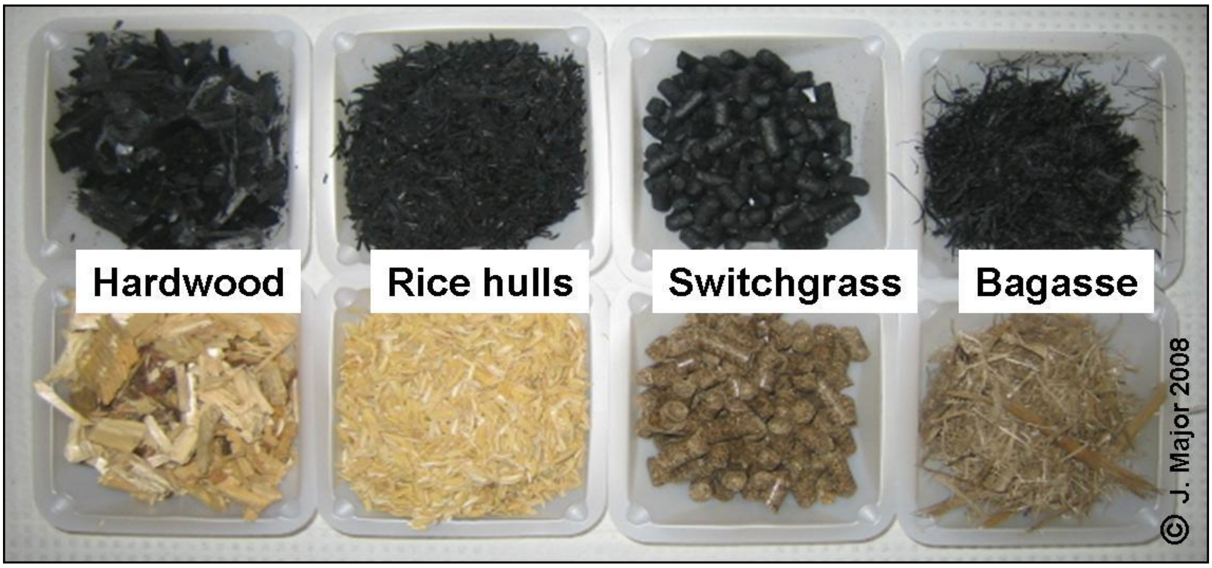


Fig. 6 Types of feed stock used in biochar production (http://www.biochar-international.org/technology/feedstocks, accessed, 23/3/2018)

However, biochar has currently been modified using several secondary oxides (e.g. magnetite) in order to improve its sorption efficiency. As observed by Trakal et al. (2016), metal sorption of the biochar's with effective structure was remarkably refined after the modification. In support, Mohan et al. (2015); Han et al. (2015); and Yan et al. (2015) reported the same effect.

Also, biochar is very efficient for several metal(loid)s removal like As(V) (Wang et al., 2015a; 2015d), Cd(II) (Wang et al., 2015b) and Pb(II) (Wang et al., 2015b; 2015c)..

Certainly, biochar has more merits than other known type of stabilization, such as physical barriers, cementation, addition of lime or clay, phosphate etc. due to the fact that, it increases the organic matter in the soil thereby enhancing nutrient cycling and even, the potential support to plant revegetation at polluted areas (Beesley et al., 2011).

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4. MATERIALS AND METHODOLOGY

This section explains about the site selection and techniques applied in the project.

4.1 Description of Sample Site/area

Location: Smolotely, CZ

The study area is located in a village Smolotely in central bohemian region, about 60 km south-west from Prague. This zone is heavily contaminated with arsenic from natural sources (Fig. 7).

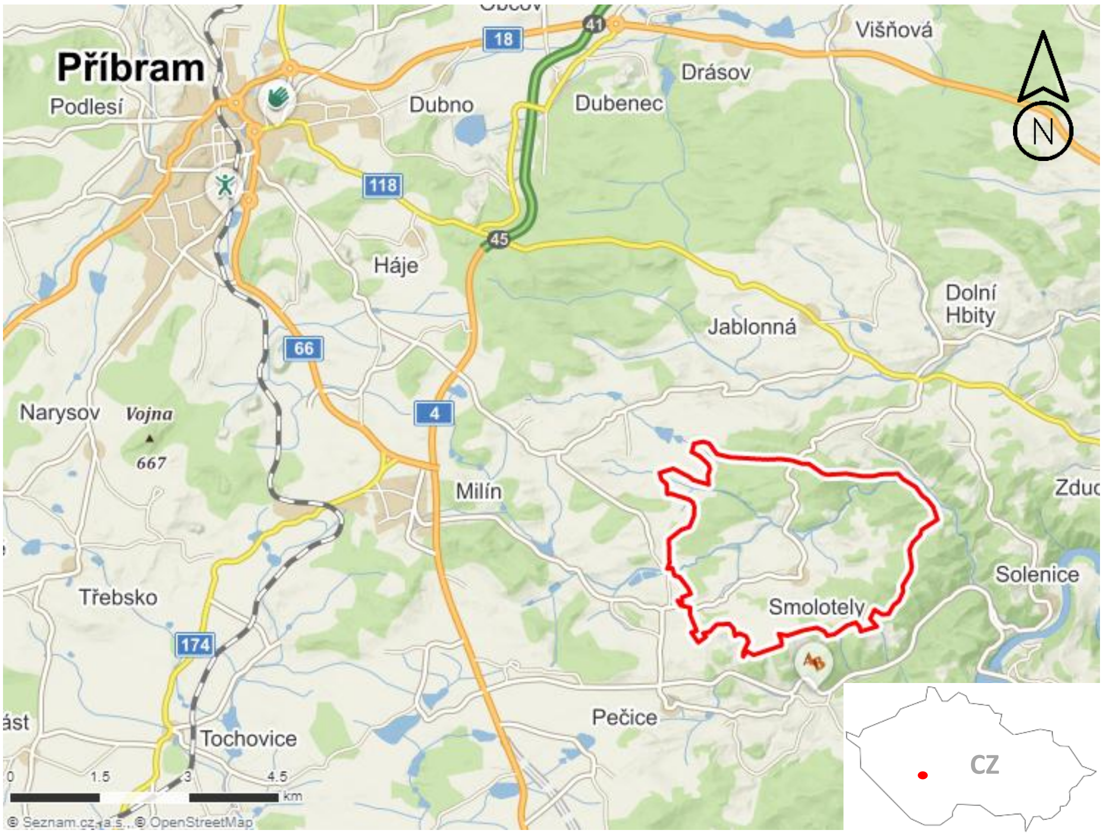


Fig. 7 A map of the soil sampling location at Smolotely village, Czech Republic.

(Source: http://www.mapy.cz)

In this research, the goal was to test the sorption efficiency of AMO and AMOchar with soils that have been contaminated with Arsenic under different redox conditions. For that matter, model soil contaminated with As was used. The soil (Leptosol) was sampled at Smolotely village, in Příbram district (Czech Republic), where As occurs naturally in extremely high concentrations due to the presence of As-bearing minerals.

4.2 Characterization of sampled soil

Soil samples were collected from the superficial layer (0-20 cm), air dried, homogenized, and sieved through a 2-mm stainless sieve. The particle size distribution was determined using the hydrometric method (Gee and Or, 2002). Soil pH was recorded in suspension using a 1:2.5 (w/v) ratio of soil/deionized water or 1 M KCl (ISO 10390:1994). The carbon analyzer TOC-L CPH was used to find the total organic carbon content (TOC) (Shimadzu, Japan). The cation exchange capacity was determined using the 0.1 M $BaCl_2$ extraction method (Carter and Gregorich, 2008). The pseudo total concentrations of elements were assessed using the US EPA *aqua regia* extraction method (US EPA method 3051a) with microwave digestion (SPD-Discover, CEM, USA) and ICP-OES analysis (Agilent 730, Agilent Technologies, USA). The fractionation of metals was determined using the BCR sequential extraction procedure by Rauret et al. (2000) and the fractionation of As was determined according to Wenzel et al. (2001). The standard reference materials 2710a Montana Soil I (NIST, USA) and CRM 483 (Institute for Reference Materials and Measurements, EU) were used for QA/QC. All chemicals used in the experiments were of analytical grade.

4.3. Preparation of AMO and AMOchar

Firstly, the amorphous manganese oxide used in this study was synthesized at the Czech University of Life Sciences Prague according to a modified sol-gel procedure, which is often used to manufacture birnessite (Ching et al., 1997) based on Della Puppa et al. (2013). The two amendments were synthesized in order to determine their ability to immobilize As in the studied soil: (i) Amorphous Manganese Oxide (AMO) and (ii) Amorphous Manganese Oxide/Biochar Composite (AMOchar).

A measured volume of 0.5 L of a 1.4 M glucose solution was added to 0.5 L of a 0.4 M KMnO4 solution. The suspension was homogeneously mixed and allowed to settle for 30mins. The subsequent gel was filtered, washed with 2 L of deionized water to eliminate unwanted reactants, and dried at room temperature. Then it was milled in agar mortar into fine powder to increase its surface area. The final crystallization step (heating) to 600°C was excluded to maintain the amorphous structure of the material.

The pH of the AMO prepared was determined after 24-hour shaking in deionized water (1:10, w/w)

AMOchar which was second amendment was subsequently prepared to compare its immobilzing efficacy to AMO. The AMOchar was prepared subsequently, the same grape stalks biochar used by (Trakal et al., 2014) was also chosen for this research because of its highest metal sorption efficiency. Specifically, biochar was initial mixed with 0.5 L of a 1.4 M glucose solution and subsequently, 0.5 L of a 0.4 M $KMnO_4$ solution was added (Trakal et al., 2018).

The resulting gel was filtered later and washed several times with deionized water. Lastly, dried at laboratory temperature and milled in agar mortar. The overview of the AMOchar synthesized used for this study is illustrated below (Table: 6).

For the sorbent characterization, the pH value (at 1:10 (w/V) using inoLab® (pH 7310, WTW, Germany), pHzpc using immersion technique (IT) by (Fiol & Villaescusa 2009) and cation exchange capacity (CEC) of AMOchar were measured according to Trakal et al. (2018). For characterization, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS: Omicron Nanotechnology, Ltd.) and SEM (Scanning Electron Microscope) were analysed in the study of Trakal *et al*. (2018) was employed to identify the structure of the AMOchar.

Table 6: Composition of used sorbent (adopted by Trakal et al. 2018)

Composition of used sorbent			
Symbol	component (%)		Reference
	Biochar	*Mn-oxide*	
AMO	0	100	Synthesis according to Della Puppa et al. (2013)
AMOchar	33	67	Application for the BC during the actual synthesis of the AMO, Trakal et al. (2018)
BC	0	100	Pyrolysis of grape stalk, Trakal et al. (2014)

AMO: amorphous manganese oxide, BC: pristine biochar

4.4. Incubation batch experiments

Incubation batch experiments were performed to evaluate the stability and transformations of the AMO and AMOchar particles in contaminated soils with respect to changing redox conditions and the mobility of contaminating metals/metalloids. The experiment was conducted in 18 variants in triplicates using Leptosol soil (Table 7). Firstly, 150 g of soil samples were mixed with (i) AMO and (ii) AMOchar at a concentration of 1% (w/w) and placed into plastic pot with a rhizon sampler as shown below (Fig.8).. In total, 54 pots representing two different incubation conditions (i.e., standard soil moisture ~70% water holding capacity (WHC) and fully saturated (with water) ~90% were prepared. Situated approximately 3cm from the bottom of the pot were the rhizon samplers (mean pore volume size 0.15 mm; Rhizosphere Research Products, Netherlands), enabling the collection of the soil solution. A control (C) variant without any amendment was included. All pots were watered with specific mass of deionized water to maintain the water holding capacity mentioned above. The experiment was performed in separate pots for time intervals of 1, 4 and 10 weeks. Anaerobic conditions were simulated by oversaturating the soil with water, so that the soil surface was nearly about 0.5 cm under the water level. After the set periods, the soil solution was collected for analysis(Fig.9). The content of metals/metalloids and DOC (dissolved organic carbon) was determined using ICP-OES and a TOC/DOC analyzer, respectively. The pH and Eh of the soil solutions were all measured immediately after collection.

Table 7: Experiment time (weeks) that each sampling period was carried out.

Oxic conditions (70% WHC- water holding capacity)				**More Reducing conditions (soil oversaturated with water)**		
Amendments	Time interval (week)			Time interval (week)		
	1	4	10	1	4	10
Control						
AMOchar						
AMO						

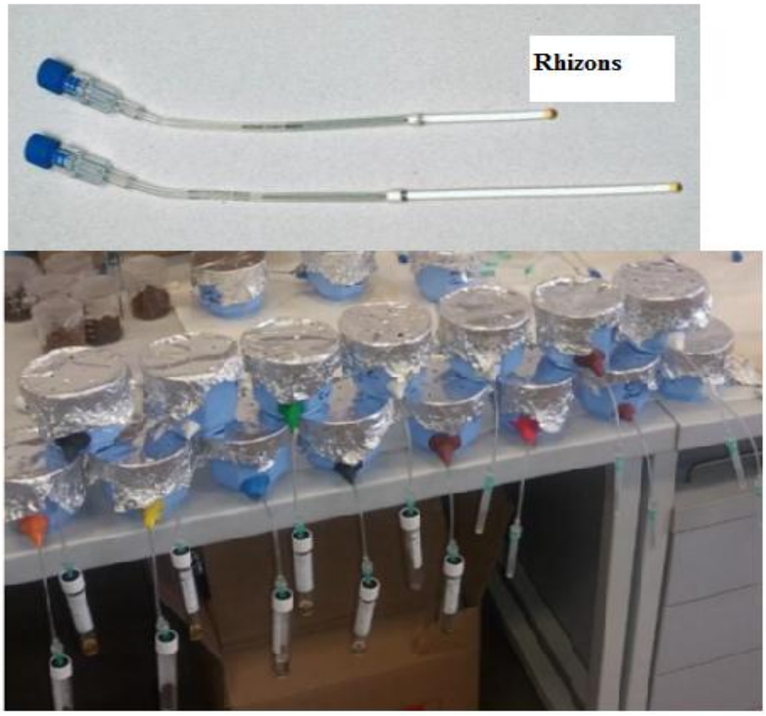


Fig. 8. Pore water collection with rhizon samplers or/suction cups carried in Laboratory of Environmental Geochemistry.

Fig. 9 Pore collection with rhizon samplers or/suction cups ready for analysis .

4.5 Statistical analysis

All statistical analyses were conducted using SigmaPlot 14.0 software (StatSoft Inc., USA). The experimental data were assessed using analysis of variance (ANOVA) at $P < 0.05$ using the Tukey test.

5. RESULTS

5.1 Characterization of sampled soil

The fundamental physico-chemical properties of the studied soil are summarized in Table 8. The soil is slightly acidic with active pH value 6.09 ± 0.03. It has low organic matter content (SOM), with a coarser texture due to high content of sand particles amounting to 87%. Leptosol showed a high cation exchange capacity 15.85 cmolkg^{-1}, mainly due to high content of Fe oxides present. The limit values set for metals/metalloids in agricultural soils by the Ministry of the Environment of the Czech Republic (Act No. 13/1994) (Table 8) were exceeded for As. Moreover, high As concentration in the Leptosol was originated from the bedrock rich in As-bearing minerals.

Table 8: Basic physico-chemical characteristics of the studied soils (Leptosol) <DL: below detection limit.

pH H_2O	6.09 ±0.03
pH KCl	4.89 ±0.04
CEC (c mol kg^{-1})	15.85± 0.54
TOC (%)	1.16 ±0.14
Particle size distribution (%)	
Clay (%)	6
Silt (%)	7
Sand (%)	87
Texture	Loamy sandy

Pseudo total metal concentration (mg kg^{-1}) (n-3)		Limit concentration (mg kg^{-1})
As	17563 ± 2798	30
Cd	<DL	1
Cu	51 ± 5	100
Fe	68910 ± 4274	no limit
Mn	1096 ± 124	no limit
Pb	73 ± 12	140
Zn	193 ± 12	200

The Table 9 shows results obtained using sequential extraction procedures for As fractionation in the studied soils. The non-specifically sorbed As fraction bound in outer sphere complexes amounted to 64 ± 3 mg kg^{-1} whiles, that of specifically sorbed As fraction bound to inner sphere complexes represented 1516 ± 96 mg kg^{-1} which was potentially stronger structure than the outer sphere complexes. However, large fractions of As bound to amorphous and poorly crystalline hydrous oxides of Al, Fe and Mn and crystalline hydrous oxides of Al, Fe and Mn represented 11 777 ± 1968 mg kg^{-1} and 5753 ± 537 mg kg^{-1}, respectively, which was still very high due to the extreme As concentrations in the parent soil. Nevertheless, residual phase was relatively negligible.

Table 9: Fractionation of As (sequential extraction by Wenzel et al, 2001) (mgkg^{-1}) (n=3)

	FA:	**FB:**	**FC:**	**FD:**	**FE:**
	non-specifically sorbed	**specifically absorbed**	**bound to amorphous and poorly crystalline hydrous oxide of Fe, Al, and Mn**	**bound to well-crystalline hydrous oxide of Fe, Al and Mn**	**Residual phase**
Leptosol	**64 ± 3**	**1516 ± 96**	**11 777 ± 1968**	**5753 ± 537**	**-**

5.2 Physico-chemical properties and characterization of AMO and AMOchar

The Table 10 shows basic physico-chemical characteristic of the AMO and AMOchar as extrated from Trakal et al. (2018) for this study. On the one hand, the pHzpc and BET of AMO was higher than of AMOchar (Table 10). But there was no much difference between the pH values obtained from the two amedments which ranges from 8.47 to 8.10 (alkaline) for both AMOchar and AMO respectively (Trakal et at., 2018). However, the specific surface area (BET), pHzpc and CEC parameters of the two sorbents were different. The specific surface area for the AMO is 134 m^2/g which is higher than that of AMOchar figure of 44 m^2/g. Again, the pHzpc of AMO was higher than AMOchar with values of 8.30 and 7.88 respectively. But, the CEC of AMOchar was higher than AMO.

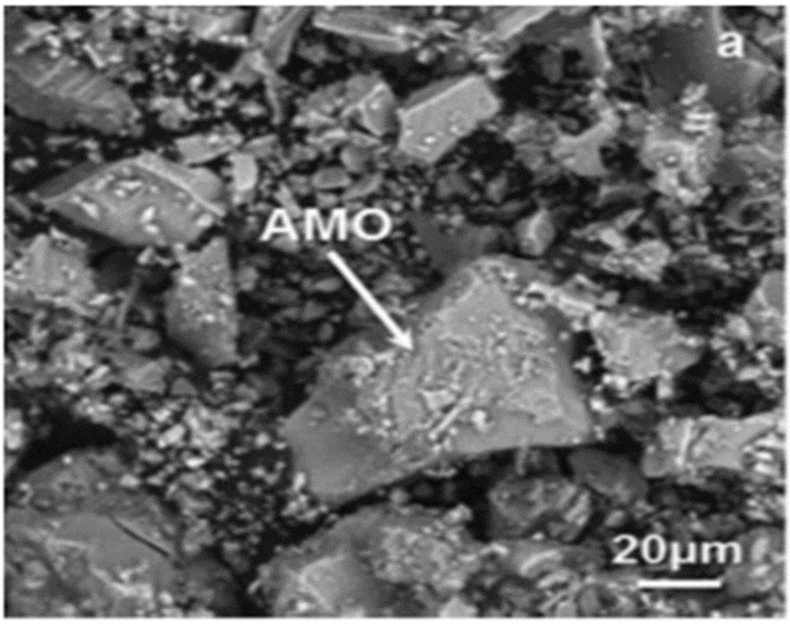
The AMO XRD results in this study were adopted from Michalkova et al. (2016a). The freshly synthesized AMO (Fig. 10) and AMOchar were investigated using XRD and SEM/EDS. Amorphous structure was confirmed by XRD (Ettler et al.,2014). Additionally, according to Michalkova et al. (2016a), Mn-oxalate was also another mineral phase identified with the AMO, which is consistent with the findings of Ettler et al. (2014) and Trakal et al. (2018). The SEM results reinforce the presence of the above mentioned mineral phases.

However, AMOchar XRD charaterization results were adopted from Trakal et al. (2018) for this research. The XRD pattern of the AMOchar shows Mn-oxalate hydrate ($C_2MnO_4.H_20$) as the predominant peak representing as by-product of AMO synthesis. Additionally, the XRD pattern shows carbon due to presence of the biochar skeleton. The SEM images of AMOchar (figure11) (Trakal et al., 2018), revealed that AMO coated surface of the biochar.

Table 10: The basic physico-chemical properties of the amorphous manganese oxide (AMO) and its AMO + biochar (AMOchar) (adopted from Trakal et al., 2018).

Sorbent	**Ph**	**pHzpc**	**CEC**	**BET(m^2g^{-1})**
AMO	8.10 ± 0.30	8.30 ± 0.10	60.8 ± 1.0	134
AMOchar	8.47 ± 0.03	7.88 ± 0.10	78.9 ±1.0	44.0

et al., 2018)



AMO: amorphous manganese oxide

Fig. 10. A SEM image of original AMO particles(a) (adopted from Michalkova et al., 2016a)

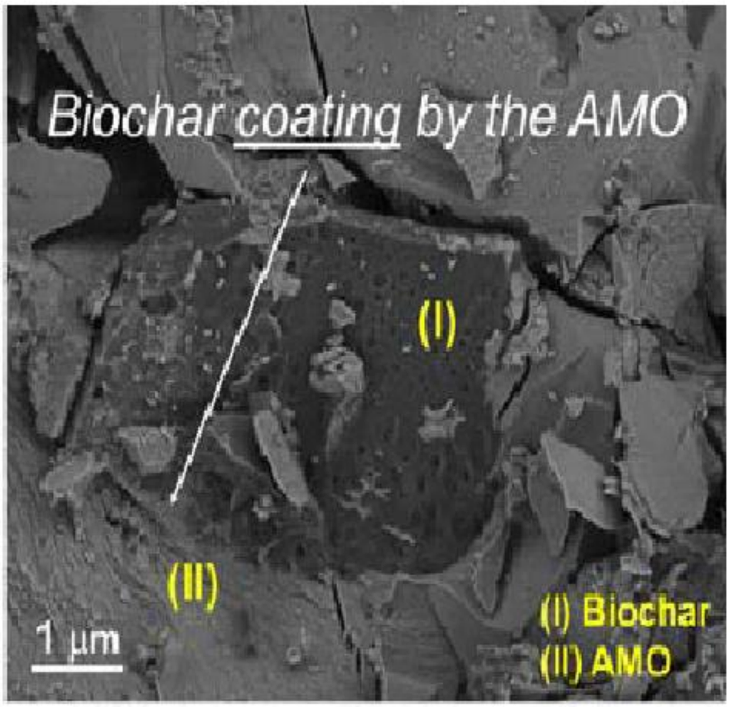


Fig 11: A SEM image of biochar coating by amorphous manganese oxide (AMO) (adopted by Trakal et al., 2018)

5.3. Incubation batch experiment

The AMO and AMOchar amendments caused an increase in soil pH relative to the control values (figure.12). But the highest pH of the amended soil was recorded in week 1 under oxic conditions. That corresponded to pH increase from 5.62 ± 0.2 in the control to 7.93± 0.02 in the AMO amended soil and 7.39 ± 0.15 in the AMOchar amended soil. After which the pH decreased in the soils of week 4 and further decreased in week 10. Meanwhile, the controls for the oxic conditions remain fairly stable with time.

However, the over-saturated conditions results show increasing pH for both the controls and amended soils with time. The highest pH for the both controls and amended soils was recorded after 10 weeks.

Meanwhile, the Eh results of the control and amended soils are shown in figure 13. Generally, the Eh values for both oxic and oversaturated condition depicted an inverse relationship with that of the pH.

Undoubtedly, the Eh-result verifies a decrease/falll of Eh in the amendments specifically in the over-saturated condition than that of oxic condition (figure 13). However, another trend was detected in both regimes (oxic and oversaturated condition), where there was drop in all the amendment applied (AMO and AMOchar) from the week 1 to week 4. But it started rising just after the week 4, which was significant.

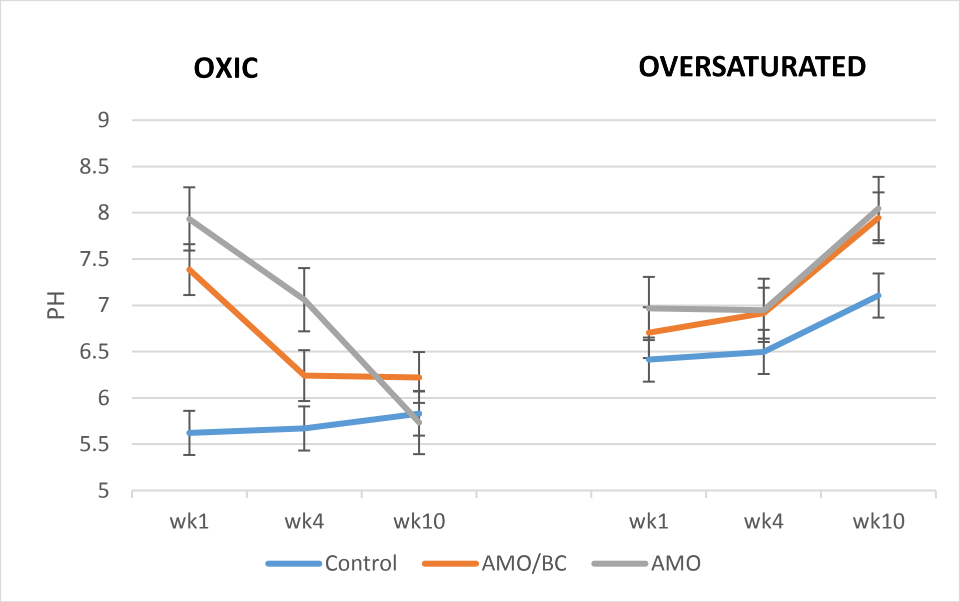


Figure 12: pH of soil solution from incubation experiment for both redox regimes. AMO: amorphous manganese oxide (1%, w/w), AMOchar (AMO/BC): amorphous manganese oxide/biochar (1%, w/w), (n=3).

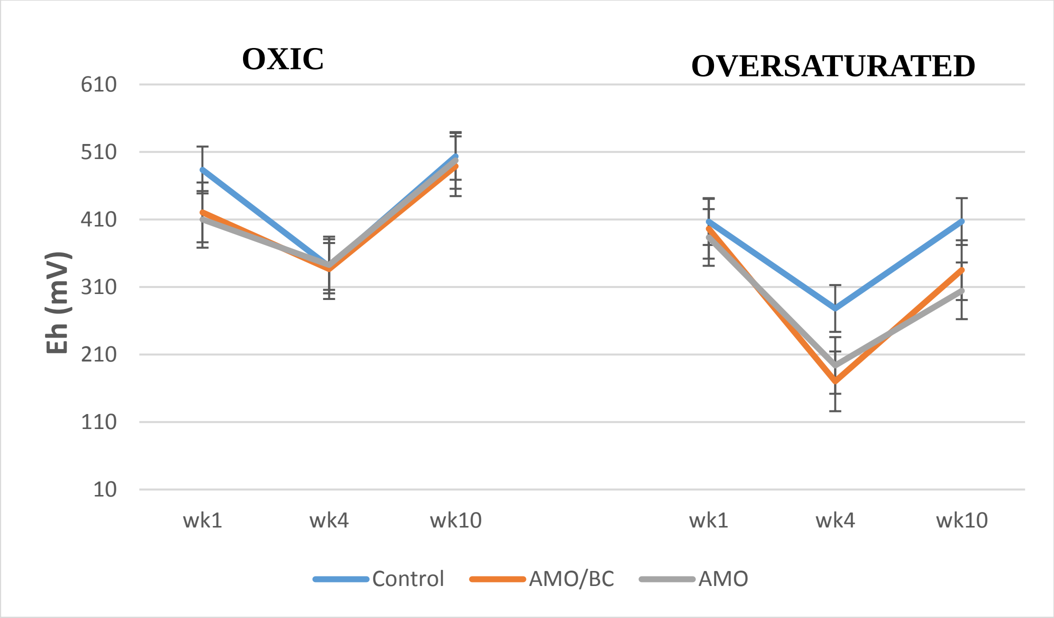


Fig.13: Eh of soil solution from incubation experiment. AMO: amorphous manganese oxide (1%, w/w), AMOchar (AMO/BC): amorphous manganese oxide/biochar (1%, w/w), (n= 3).

With respect to the immobilization of As in the amended soils, AMO proved more efficient stabilizing agent for the stabilisation and immobilisation of the metalloid under oxic condition. As shown in figure 14b1, under oxic condition in the week 1, AMO decreased the concentration of dissolved As by 92% of the control. At the same week under oxic conditions, AMOchar decreased As concentration by 59% of the control**.** The amount of As from the week 1 of the oxic condition, then began to increase with time towards the control with the week 4 of the oxic condition recording an increament of As in the AMOchar amended soil by 59% over the control (figure 14b1). Generally, the concentration of As in the control variant under the oversaturated conditions was relatively the same throughout the incubation period (14.78 ± 1.05 mg $kg^{-1)}$ whiles, the concentrations of As in the amended soils showed significant difference under the same conditions ranges from 84.41 ± 17.4 mg kg^{-1} to 184.25 ± 8.06 mg kg^{-1} for AMOchar and AMO respectively (fig.14b2). However, the largest increament of As of the amended soil compared to the control was recorded in the week 10 of the oversaturated condition by 92% over the control in AMO amended soil (figure 14b2). Overall, the concentration of dissolved Mn in the amended soil (both AMO and AMOchar) under oversaturated conditions was higher than the oxic conditions (fig.14a1, a2). But, the Mn concentration in the week 1 of the oxic condition was 99% increase in the AMO amended soil as compared to the control, whiles, that of AMOchar was satistically insignificant from the control.

Generally, in the entire incubation period and conditions (both oxic and oversaturated), the concentration of the Mn decreased rapidly beween both amended soils as shown in figures 14 a1, a2. But there was no statistical difference recorded between the two amended soils in the oversaturated condition.

However, concentration of all the variants were increased throughout the period, apart from Mn under weeks 10 of both oxic and oversaturated conditions but with different orders of magnitude. However, both Mn and DOC were prominent in the first two weeks (week 1 and weeks 4) under over- saturated conditions (figures 14a2 and c2), but eventually decreases rapidly in the 10 weeks, and was consistent.

DOC concentration was significant throughout the period, exept the week 10 under saturated condition, where it reduced drastically as compared with weeks 1 and 4 respectively (fig. 14 c2). Hence, the control variant recorded the lowest concentration throughout the entire peroid. Moreover, no significant difference was recorded between the immobilizing capacity of both AMO and AMOchar in weeks 1, 4 and 10 under oversaturated conditions. But, As dissolution was more pronounced in over-saturated conditions than oxic conditions. Comparatively, the AMO had more DOC concentration than AMOchar in entire incubation time, but in contrast for As.

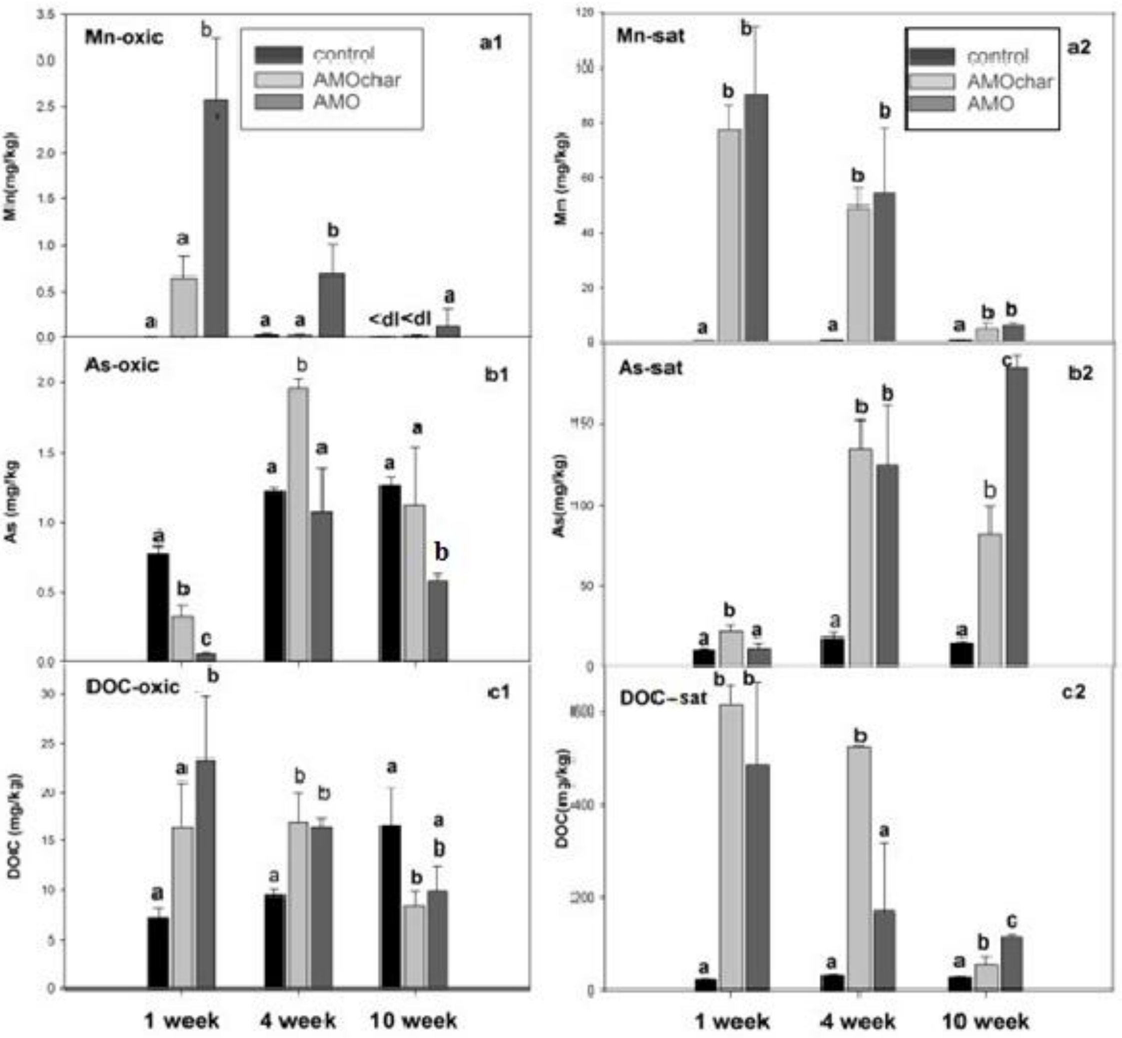


Figure 14: Metal(loids) and DOC concentrations obtained after amendment application against time interval in differnet humidity conditions: concentrations of Mn (a1), As (b1) and DOC(c1) solutions under oxic conditions, concentrations of Mn (a2), As (b2) and DOC(c2) solutions under over-saturated conditions (n = 3); C: control, AMO: amorphous manganese oxide (1%, w/w), AMOChar: amorphous manganese oxide/ biochar (1%, w/w), <dl: values below the limit of detection. Statistical evaluation was performed to compare data for various variants in each time interval separately, data with the same letter represent statistically identical values ($P < 0.05$).

6. DISCUSSION

6.1 Characterization of sampled soil

The soil was slightly acidic and with quantities of metal(loid)s. Large propotions of metal(loid)s and more avialable fractions can cause high total concentration of metal(loids) (Ehlers and Luthy, 2003). Consequently, high level total concentration of As was observed. This is as a result of As occurring naturally in extreme concentrations due to the presence of As-bearing minerals (Michálková et al, 2016a). Moreover, large proportions of As fraction bound to amorphous and poorly crystalline hydrous of Al, Fe and Mn oxides.

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6.2 Incubation batch experiment

6.2.1 Stabilization of arsenic (As) by AMO and AMOchar under various redox condition.

In this study, oxic conditions and oversaturated conditions were used to show the influence of different redox conditions on the stability of AMO and AMOchar, and also their immobilizing potential towards As in contaminated soil. The Eh values recorded in this study showed increasing and decreasing values.

Obviously from the results obtained from the As immobilization as shown in figures14 b1 and b2, the two amendments were effective only under oxic conditions but showed downward trend with incubation time. However, under oversaturated conditions, their immobilising efficiency was comparatively low, rendering them ineffective. AMO proved more effective than AMOchar with respect to immobilization and stabilization of As under oxic conditions. In the week 1 of incubation period, under the oxic conditions, AMO reduced the concentration of As by 92% of the control, whilest, AMOchar decreased the concetration of As by 59% of the controls. The immmbolization efficiency of AMO was further increased because week 1 under oxic condition resulted in high pH in alkaline range. This is consistent with Michalkova et al. (2016a), whose research finding came up with the conclusion that adsorption of As onto AMO generally increases with increasing pH. But this is inconsistent with studies of Dixet and Hering (2003), whose result indicated that AMO adsorption of As increased at lower pH values. From Michalkova et al. (2016a); Trakel et al. (2018), AMO dissolves at lower pH. This then, explains why AMO immobilizing efficiency decreased drastically at lower pH in this study (from 7.93 to 5.73). Certainly, the ability of a material to undergo adsorption depends on large surface area (Frost et al., 2007).

The immobilizing efficiency of the AMO was enhanced by its higher specific surface area over the AMOchar. The higher specific area leads to higher reactivity, subsequently translating to higher adsorption capacities (Hongbo et al.,2017). However, this is in contrast with Li et al. (2017), who posited Mn oxides in AMOchar serves as the adsorption sites which appears to command adsorption in AMOchar more than specific surface area. The adsorption efficiency of AMOchar can be reduced during preparation. This can lead to release/dissolution of critical constituents such as Mn and DOC (Trakal et al., 2018). Under oxic conditions, As usualy appears as less mobile As(V), mainly as the negatively charged $HAsO_4^{2-}$ and H_2AsO^{4-} oxyanions (Satiq, 1997,; Mandel et al., 2002) as compared to oversaturated condition, whereas As appears as the mobile As(III) predominantly as neutral H_3AsO_3 (Mandel et al., 2002).

The negatively charged As(V) oxyanions in oxidizing conditions therefore form strong inner-sphere complexes with the sorbents, whiles under reducing conditions, weak outer-sphere complexes are formed with the sorbents (Samsuri et al., 2013,: Mandal et al., 2002). Hence, adsorption and speciation can determine As availabilty in soil solution. This is collaborated by Michalkova et al.(2016b), who opined that speciation can lead to sorption differences.

The stability of the AMO and AMOchar under oxic and oversaturated conditions was estimated based on the concentrations of Mn released into soil solutions.

From the XRD analysis, AMO showed amorphous structure and carbonate mineral phase of rhodochrosite ($MnCO_3$). According to Michalkova et al. (2016a,), $MnCO_3$ peaks appeared after one week of AMO incubation in soil. On the other hand, XRD analysis on AMOchar showed Mn oxalate as a by-product of AMO, with carbon as the reflection of biochar skeleton (Trakal et al., 2018).

The controls for both oxic and oversaturated conditions showed insignificantly lower concentrations of Mn in solution throughout the incubation period, compare to other variants. For example, week 10 under oxic condition recorded Mn concentration below the detection limit. The oxic conditions generally recorded lower concentrations of Mn in the amended soils as compared to the oversaturated conditions (Sparkes, 2003). Mn(III/IV) oxides appeared in soils as suspended particles coating clay minerals and soil organic matter. However, under saturated conditions these oxides under reductive dissolution through the action of reducing agents such us dissolved organic matter and micro organism, releasing Mn(II) in solution.This then, explained why the low amount of DOC recorded under oxic conditions compared to the oversaturated conditions, that increasing pH promotes DOC dissolution under reducing conditions.

From Tokarz and Urban (2015) and Yu et al. (2007), a decrease of soil organic matter contration results in a high oxidation- reduction potential (Eh) and low pH of the soil which reduce microbial activity and vice versa. This is because microorganism and organic matter are known reductants of oxides and hydroxides. The microorganism and soil organic matter can cause the reductive dissolution of Mn (III) and Mn (IV) oxide to Mn (II) which is highly soluble and mobile.

Moreover, oxalate and pyruvate, two metabolites from microorganisms reduced and dissolve Mn(III/IV) oxide particles (Stone, 1987). Comparing the leaching of Mn from AMO and AMOchar, more Mn was leached from AMO than from AMOchar in all the incubation periods and time. This can be linked to their Mn content during their preparation prior to their applications to the soil. According to Trakal et al.(2018), AMOchar composites demonstrated low Mn leaching compared to AMO. In his view, total amount of Mn in all the AMOchar composites was lower than that of AMO. Also, he indicated some Mn was leached during the stirring process of AMO and biochar composites.

7. CONCLUSION

To assess the influence of different redox conditions on stabilization of arsenic (As) in contaminated soil using AMO and AMOchar.(1% wt.) was analysed for time interval of 10 weeks using tthe incubation batch experiment.

Leptosol of slightly acidic pH from Smolotely (Czech Republic) with high As content mainly from geogenic source was studied in this work. Amorphous manganese oxide (AMO) and amorphous manganese oxide combined with biochar(AMOchar) was used to immobilise As under oxic and oversaturated conditions, which resulted in different redox conditions. Results showed that AMO was capable of removing 92% of As dissolved in soil solution, whereas AMOchar removed 59% of amount of As content of the control, all under oxic condition.

However, the immobilising efficiency of the two amendments were comparatively low under oversaturated conditions, thus the two amendments were ineffective as such. Mn leaching into soulution was used to assess the stability of the two amendments. Comparing results, AMO leached more Mn than AMOchar in all incubation periods and time. Implying that AMochar was more stable than AMO.

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