CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

FACULTY OF ENVIRONMENTAL SCIENCES

CADMIUM AND OTHER TRACE ELEMENTS BEHAVIOR IN SOIL AMENDED WITH NANOIRON-BIOCHAR COMPOSITE

DIPLOMA THESIS

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PRAGUE 2019

CZECH UNIVERSITY OF LIFE SCIENCES PRAGUE

Faculty of Environmental Sciences

DIPLOMA THESIS ASSIGNMENT

Oluwasegun Israel Adeyemi

Environmental Geosciences

Thesis title

Cadmium and other trace elements behaviour in soil amended with nanoiron-biochar composite

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Objectives of thesis

The main objectives of the thesis are to assess (i) the efficiency of nanoiron-biochar composite for Cd and other trace elements stabilisation in soils, (ii) the spatial distribution of Cd in selected field area, and (iii) the mobility of Cd in soil profile.

Methodology

Based on recommended literature and other sources found by the student the theoretical part will be elaborated. It will include description of the nano zero-valent iron supported biochar and its role in metal sorption, the behaviour of cadmium in soils and related environmental and health risks, the role of soil organic matter in Cd mobility etc.

The practical part will include (i) basic soil properties characterisation, (ii) incubation of nanoiron-biochar composite in soil, (iii) soil extractions etc.

Sample preparation and treatment, laboratory experiments, and analytical data treatment will be performed by the student independently under control of the thesis supervisor.

The results will be presented in written and graphical forms. The discussion will be elaborated carefully based on the main results and with reference to relevant literature. The conclusion will be brief and concise. The text will be spell-checked and grammar checked before sent to the supervisor.

March-August 2018: Theoretical part preparation

May-June 2018: Sample preparation, basic characterisation and soil incubation

September-October: Extractions of incubated soils, data treatment

November 2018: Submission of the theoretical part

January 2019: Submission of the results and discussion

March 2019: Submission of FINAL VERSION of the thesis

The proposed extent of the thesis

50-60 pages

Keywords

soil contamination; metals; sorption; risk assessment

Recommended information sources

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Expected date of thesis defence

2018/19 SS – FES

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Electronic approval: 24. 3. 2019

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Dean

Prague on 04. 04. 2019

DECLARATION

I hereby declare that the present Diploma Thesis entitled "Cadmium and other trace elements behavior in soil amended with nano iron-biochar composite" is my own work and the literature and other sources, which I used, are stated list of references which are attached to this work.

In Prague, Tuesday, 4th of April 2019

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Oluwasegun Israel Adeyemi

ACKNOWLEDGEMENT

Many thanks to doc. Mgr. Martina Vítková, Ph.D. for her patience, guidance and advice prior and during different stages of the thesis. I also appreciate Dr. Václav Tejnecký, Dr. Ondřej Drábek and Karel Němeček for the tremendous work done in the field and for providing the samples, this thesis would not have been possible without their efforts. Thanks to Radim Vašát for sampling method optimization and David Stella, who kindly provided his private field for our research and information about the locality. Likewise, I thank Aikaterini Mitzia for her help with regards to preparing the samples. I give thanks to my family and friends for their constant support during the thesis. I ultimately give thanks to God almighty for his grace upon my life.

ABSTRACT

This study focuses on the application of nano zero-valent iron and biochar (nZVI-BC) composite on private field contaminated with cadmium due to former industrial activities in the area. Firstly, the spatial distribution of Cd and other elements was determined, and two contaminated samples were selected for further testing. The soil samples from 2 sampling points Cd6 and Cd14 were amended with powdered nZVI-BC, powdered BC, suspended nZVI-BC, suspended-BC, and a control (without amendment). The efficiency of each treatment on the immobilization of risk metals was evaluated through different extractions: demineralized water, $CaCl_2$ solution and acetic acid. Demineralized water and $CaCl_2$ mobilized Cd, Cr, Zn, As, Pb and Ni. Generally, trace elements in sample from site Cd14 was more mobilized than that from site Cd6. Total concentration and availability of trace elements in the soil profile of Cd14 and Cd6 was also evaluated; even though there were generally high total contents of trace elements (up to 93 and 82 mg/kg of Cd) in both soil samples, the mobility however was very low. There is no established pattern of distribution of Cd and other elements in both soil profile. Physical chemical properties of soil such as pH and organic matter also affect the mobility of Cd and other trace element in studied soil. Total concentration the trace elements in roots, shoot and rhizosphere were also analyzed, Cd was on found at a concentration up to 30 mg/kg. A slight difference was observed between both active and exchangeable pH values determined. This study will help select the appropriate amendment for remediating Cd and other trace element in area under study.

Keywords: soil contamination; metal sorption; risk assessment.

ABSTRAKTNÍ

Tato studie se zaměřuje na aplikaci nano-valentního železa a biouhlu (nZVI-BC). Nejprve bylo určeno prostorové rozložení Cd a dalších prvků a pro další testování byly vybrány dvě kontaminované vzorky. Vzorky půdy ze dvou míst odběru vzorků Cd6 a Cd14 byly modifikovány práškovým nZVI-BC, práškovým BC, suspendovaným nZVI-BC, suspendovaným BC a kontrolou (bez změny). Účinnost každého ošetření na imobilizaci rizikových kovů byla hodnocena různými extrakcemi: demineralizovanou vodou, roztokem CaCl2 a kyselinou octovou. Demineralizovaná voda a CaCl2 mobilizovaly Cd, Cr, Zn, As, Pb a Ni. Obecně byly stopové prvky ve vzorku z místa Cd14 více mobilizovány než ty z místa Cd6. Rovněž byla vyhodnocena celková koncentrace a dostupnost stopových prvků v půdním profilu Cd14 a Cd6; I když byl vysoký obsah stopových prvků vysoký (až 93 a 82 mg / kg Cd), půda byla velmi nízká. V obou půdních profilech není stanoven vzor distribuce Cd a dalších prvků. Fyzikální chemické vlastnosti půdy suché jako pH a organické hmoty také ovlivňují mobilitu Cd a dalších stopových prvků ve studované půdě. Rovněž byla analyzována celková koncentrace stopových prvků v kořenech, výhoncích a rhizosféře, zjištěná v koncentraci do 30 mg / kg. Byl zjištěn mírný rozdíl mezi hodnotami aktivního i vyměnitelného pH. Tato studie pomůže vybrat vhodnou změnu pro Cd a další stopové prvky ve studii.

Klíčová slova: kontaminace půdy; sorpce kovů; posouzení rizik.

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1. INTRODUCTION

1.1 BACKGROUND

Soils are the major sink for risk metals and metalloids released into the environment by anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation (Kirpichtchikova et al., 2006). Therefore, their total concentration in soils persists for a long time after their introduction (Adriano, 2003). The presence of risk metals in soils has mostly been due to metallurgical and smelting processes with high concentration in soils around the smelter (Rieuwerts, 1999). Depending on mobility rather than concentration, they may enter food chains and cause a negative effect on human health when they are taken up by agricultural crops (Vaněk et al., 2005).

Various techniques have been applied for removal and stabilization of contaminants in soil, the usage of nano zero-valent iron (nZVI) has been widely applied to water treatment; however, due to aggregation, poor transportability and reduced electron transfer, efficiency of nZVI can be inhibited. Recently, impregnation of biochar (BC) with nZVI has gained popularity because of the useful properties of BC such as high capacity to sorb contaminants and enhance nZVI reactivity. Biochar (i.e., pyrolyzed biomass) is rich in various functional groups and has high surface area, small pore sizes in the carbon skeleton and good electrical conductivity. These properties enable the optimal efficiency of the capacities of nZVI (Wang et al., 2019). Combined nZVI and BC was found to immobilize Cd and As better than single effect of BC and nZVI in immobilizing Cd and As (Qiao et al., 2018).

However, less work has been done in urban areas contaminated with Cd and other trace elements due to industrialization. This diploma thesis, therefore, focuses on the use of nZVI-BC treatment in soil to determine the behavior of Cd and other trace elements as a response to sorbent addition. Findings from this work will enable environment scientists apply the appropriate remediation procedure in soils of the study area and other location with similar contaminants.

1.2 AIMS OF THE STUDY

This study is focused to achieve the following objectives:

i. the assessment of the efficiency of nanoiron-biochar composite for Cd and other trace elements stabilization in soils,
ii. the assessment of the spatial distribution of Cd in selected field area, and
iii. the assessment of the mobility of Cd in soil profile.

2. LITERATURE REVIEW

2.1 RISK METALS AND METALLOIDS IN SOIL

According to Ross (1994) different sources of metals correspond to different sets of contaminants in soils. Agricultural soils often have elevated concentrations of Zn, As, Pb, Cd, Cu, Se, and U while metals like Cd, Pb, As and Hg coming from mining and smelting (Fig 2.1). Soils are the most important sink for the metals in the environment (Khalid et al., Soil contamination with metals poses environmental risks. It affects the human health via food chain (Yuan et al., 2017). Moreover, there is a possibility of accumulation in ground water, water bodies and sediments (Antoniadis et al., 2017). The rate of accumulation of metal in the food chain is determined by soil properties, metal amount and concentration and plants uptake rate (Yuan et al., 2017).

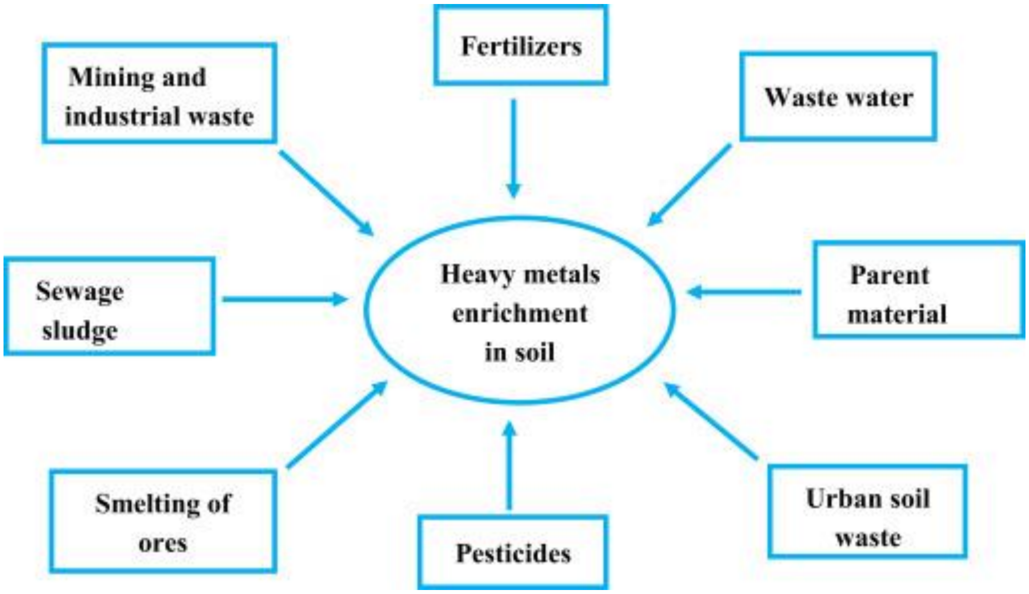


Fig 2.1: Major sources of heavy metals in soil. (Amanullah Mahar, 2016)

The retention of metals and metalloids in soils depends on the properties of soil such as pH, clay, Fe/Mn/Al oxides and organic carbon content. During the sorption process, charged metal ions are attracted by soil particles by electrostatic attraction and formation of chemical bonds (Xiao et al., 2015). Precipitation process is important at higher pH values, high amount of metal ions and high concentration of SO_4^{2-}, CO_3^{2-}, OH^-, and HPO_4^{2-} groups. Complexation of cation with inorganic and organic ligand ions is another important mechanism of metal retention in soil and these interactions are controlled by pH and the amount of ligands available. Volatilization takes place only when the element is able to form gaseous compounds, for instance As, Hg, and Se (Bolan et al., 2014).

Bolan et al. (2014) stated that soil chemical properties (pH, redox conditions, cation-exchange capacity, soil mineralogy, biological and microbial conditions, cation levels) could have effect on metal availability for plants in soils and define related environmental risks. Cationic heavy metals are more mobile under acidic conditions as their sorption increases at higher pH, while anionic elements are released under alkaline conditions. Soils rich in clay are able to retain higher amount of metals, hence, metals are more mobile in light-textured soil. The amount of adsorbed metal depends on cation exchange capacity (CEC) of clay minerals. Soils with high CEC retain both cations and anions. Soil organic matter favors metal retention as it adds the CEC to the soil. Especially, carboxylic and hydroxyl functional groups play an important role in metal sorption (Antoniadis, 2017). Yan et al. (2017) reported that some metals are adsorbed to soil particles; for instance, Pb mobility in the environment and in soils depends on the solubility of solid particles bearing Pb. The mobility of elements in soils depends also on the quantity and nature of these elements. Metals which form strong covalent bonds are more strongly adsorbed to soil (Hg>Pb>Cd>Co>Ni>Zn>Cu>Cr) (Antoniadis et al., 2017).

Turner et al., (2008) stated that metals in dissolved forms are more bioavailable and consequently constitute the greatest environmental hazard. Metals can be transported along the soil profile by colloids or in dissolved forms depending on the metal concerned (Zhao et al., 2009). In general, metal mobilization depends on the concentration of the parent metal in the soil solution, which in turn depends on the sorption and retention of the same metal in soil (Alloway, 1995; Sterckeman et al., 2000). As a rule, soil properties and composition change with depth. Consequently, the characteristics of subsoil could be different from those of the surface layer. The subsoil layer has been shown to be an important geochemical barrier against the migration of metals in the soil system, including penetration into groundwater (Sterckeman et al., 2000).

If subsoil has a high affinity for a metal, the retention of the metal leached from the surface soil is efficient and its further penetration to groundwater could be prevented. On the contrary, if the adsorption is low, subsoil is an inefficient barrier against groundwater contamination. Finally, if the adsorption capacity of both topsoil and subsoil is low, soil as a whole offers low protection against groundwater contamination by metals deposited to the soil surface from air pollution, fertilizer application, or other sources (Citeau et al., 2003).

2.2 CADMIUM AND SOIL CONTAMINATION

Cadmium (Cd) is a highly carcinogenic metal that can cause toxic reactions even in low concentration (Khan et al., 2015). It is a non-essential trace element and does not play any identified role in the growth and development of human, plants and animals. In comparison to other toxic elements for plants and animals, Cd is more toxic to a higher extent at lower concentrations than e.g Zn, Pb or Cu. (Zhang et al., 2014). Cadmium enrichment in soil occurs from both natural and anthropogenic sources and is considered to be of great environmental concern (Pan, 2016).

2.2.1 SOURCES OF CADMIUM IN SOILS

Cd is released to the environment in variable amounts from natural and anthropogenic activities. Volcanic eruptions, forest fires, windblown dust, and sea spray are among the natural sources of Cd to the atmosphere. Weathering of parent rocks also contributes to the release of Cd to the environment (Khan et al., 2010; Liu et al., 2013). Mafic and ultramafic rocks contain high amounts of Cd, and thus upon weathering, these rocks release significant quantities to soil (Shah et al., 2010). Black shales contain Cd up to 100 mg kg−1, and the soil derived from their deposits is enriched with Cd (He, 2005). Mean concentrations of Cd in mudstone and siltstone was 4.6 mg kg−1, while in carbonate rocks was 1.7 mg kg−1 collected from Three Gorges Region of Jianping (Liu et al., 2013).

Major forms of cadmium in soils and sediments are in the exchangeable fraction, followed by the Fe-Mn oxides and residual fractions. Several studies indicated the Cd in soils contaminated by anthropogenic activates such as mining and smelting, seem to be more bioavailable than Cd from anthropogenically unimpacted soils (Zhang et al., 2014: Chlopecka et al., 1996)

Over 90% (5.6–38 × 106 kg year^{-1}) of Cd is released into the environment from anthropogenic sources including the use of phosphate fertilizers, fossil fuel combustion, metallurgical works, wastes from cement industry, sewage sludge, municipal and industrial wastes, and mining, smelting and metals ore processing (Bi et al., 2006). It is also widely used in plastic stabilizers, pigments, solar panels, batteries, and steel plating to resist corrosion. Other sources of Cd may include polyvinyl chloride plastic manufacturing, alloys, fungicides, solders, motor oil, and rubber and textile manufacturing (Tamaddon and Hogland, 1993).

Mining activities release Cd to soil from mining sites to the nearby fields, since Cd occurs in all types of Zn ores as a gangue element due to geochemical similarity. Thus, substantial amounts of Cd are released to the environment during Zn smelting. In the production of Zn, Cd rich dust is released in to the atmosphere, has a short residence time and is deposited locally. (Khan et al. 2017)

2.2.2 CADMIUM TOXIC EFFECTS

Cadmium is a primary soil pollutant and is considered a major issue regarding human health after intake from contaminated rice caused Itai-Itai disease in Japan in 1970 (Kobayashi, 1978). The uptake of Cd by vegetables from soil is a major exposure pathway for humans (Franz, 2008; Kobayashi et al., 2008), and exposure through vegetables consumption accounts for approximately 70–80% of total intake in humans (Yang et al., 2017; Wang et al., 2016). Elevated intake by humans through contaminated food can cause severe damage to vital organs including lungs and liver and can cause cancer and other fatal health disorders (Adriano, 2001; Moynihan et al., 2017). Urban soil is mainly polluted with Cd from industrial processes and vehicular emissions (Khan et al., 2016). A large amount (67%) is used in the production of metallic Cd electroplate used in nickel-cadmium batteries (Greenwood and Earnshaw, 2001).

Cadmium is known to have longer biological half-life of 10–30 years in the human body when consumed, therefore the concentration in the body increases with age and continuously accumulating in the liver and kidney (JECFA, 2011). Long-term consumption of Cd contaminated rice causes severe health problems, notably increased risk of cancer in the lungs, endometrium, bladder and breast (Zhang et al., 2014)

In plants, accumulation of Cd causes a reduction in biomass, growth, a decrease in root growth chlorosis, and net CO_2 assimilation rate by reducing RUBISCO activity (Benavides et al., 2005). For example, increased Cd concentration caused a decrease of 30% in the strawberry plant growth and had a deleterious effect on the net photosynthetic rate in tomato seedling (Sanderson et al., 2019).

The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants. Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems (McLaughlin, 2000; Ling, 2007).

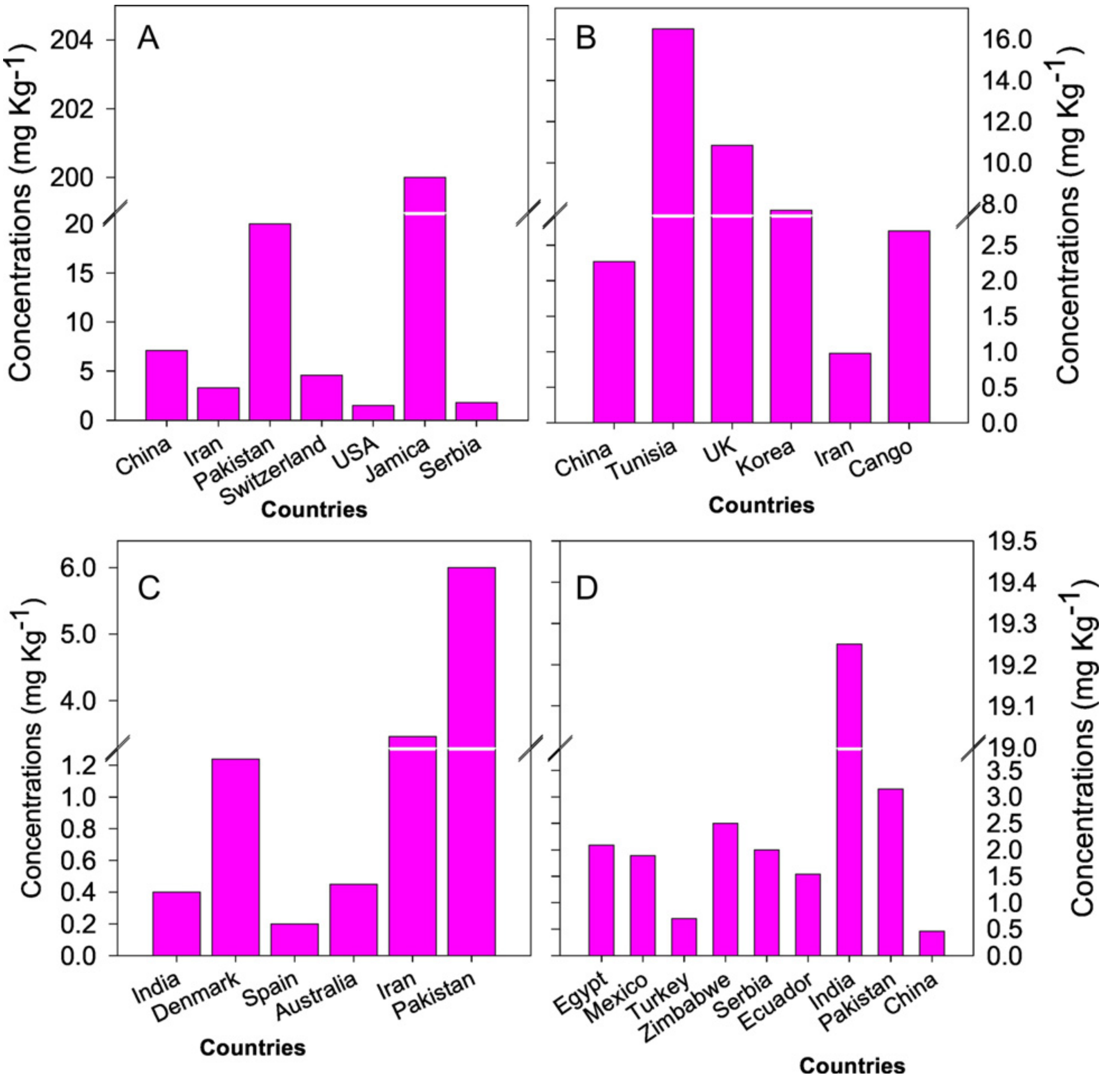


Fig 2.2: Cd concentration in soils of different countries. A: Natural/geogenic sources. B: Mine impacted soils. C: urban soils. D: irrigated by waste water (Khan et al., 2017).

2.2.3 SOIL CONTAMINATION WITH CADMIUM

The average content of Cd in soil varies between 0.06 to 1.1 mg/kg, whereas the global mean for surface soil has been estimated to be 0.53 mg/kg, and apparently all higher values may reflect anthropogenic influences. In industrialized countries, there is concern over anthropogenic accumulations of Cd in the environment, and it is classified as a potentially harmful element with respect to soil biological activity, plant metabolism and the health of humans and animals (Kabata-Pendias and Pendias 2001).

Jamaican soils are reported to have high level of cadmium majorly from natural sources, Cd concentration is found in the range of 0.3 mg/kg to over 400 mg/kg, although soils with concentration of over 400 mg/kg are rare (Lalor et al., 1998; Sanderson et al., 2019)

Chavez et al., (2015) measured Cd concentration at different soil depths in Ecuador, the total recoverable Cd ranged from 0.88 to 2.45 and 0.06 to 2.59, averaged 1.54 and 0.85 mg/kg, respectively in the surface and subsurface soils whereas the corresponding values for extractable Cd were 0.08 to 1.27 and 0.02 to 0.33 mg/kg with mean values of 0.40 and 0.10 mg kg. In general, the total concentration of Cd was found to be above the USEPA critical level of 0.43 mg/kg for agricultural soils, indicating that the subsurface soil is contaminated with Cd. Fig 2.2 above shows the concentration of Cd in soils of different countries.

2.3. BIOCHAR PROPERTIES AND APPLICATION

2.3.1 PROPERTIES OF BIOCHAR

According to Bashir et al., (2017) and Wang et al., (2017), biochar demonstrated good potential as a soil amendment favoring risk metal immobilization. Biochar is a product made after thermal decomposition of organic material under limited supply of oxygen and a temperature below 900°C (Lehmann and Joseph, 2009). It is obtained from pyrolysis of plant-derived biomass (wood bark, rice husk, pine wood and so on) or non-plant derived biomass (dairy and chicken manure) (Godlewska et al., 2017). Traditional source of biochar includes lump charcoal from primitive and modern kilns. Also, it can be produced in gasifiers, be co-product or by-product in retorts and bio-gas and bio-oil technologies (McLaughlin et al., 2009). Biochar is produced at various pyrolysis characteristics (heating rate, highest treatment temperature, pressure, reaction residence time, reaction vessel, pre-treatment, post-treatment). Temperature and feedstock are considered the most important factors affecting biochar properties. Biochar surface areas have numerous micropores with < 2 nm diameter, which gives adsorptive properties to biochar (Downie et al, 2009; Mendoza et al., 2006). The surface area and pore size grow with the temperature because of functional groups destruction (Angin and Sensöz, 2014).

At certain temperature, some deformations are found to occur and surface area starts reducing (Downie et al., 2009). Uchimiya et al. (2011) reported these changes at temperature above 700 °C, which was confirmed by the findings of Chun et al. (2004), at 700 °C surface area decreased. Pore size influence metal sorption as metals cannot be adsorbed by very small pores (Ahmedna et al., 2004). Ahmad et al. (2014) suggested that plant-derived biomass generally has higher surface area than biochar from manure or biosolids. Elemental composition of biochar mainly depends on pyrolysis temperature. Generally, biochar has been found to have high content of carbon with high amount of aromatic structures (Lehmann and Joseph, 2009). At higher temperatures carbon content normally increases and structure becomes more and exist in condensed form (Angin and Sensöz, 2014). Biochar pH depends on temperature and feedstock properties (Li, 2017). pH of biochar has alkaline values and rises with the pyrolysis temperature (Angin and Sensöz, 2014) because of the formation of ash. Moreover, the amount of base cations is higher at greater temperature, favoring pH increase (Yuan et al., 2011).

Keiluweit et al. (2010) reported that high temperatures favor depolymerization of biomass, but this process is not observed in the biochars from non-plant feedstocks because they do not have lignocellulosic molecules (Ahmad et al., 2014). After being added to the soil, biochar interacts and aggregates with mineral and organic matter. Possible degradation occurs due to biotic degradation of a labile biochar fraction, erosion, leaching, pedoturbation. However, biochar is very stable in the environment because of its organo-chemical and physical structure. Biochar from forest fires could be more than 10000 years old (Lehmann and Joseph, 2009). Kuzyakov et al. (2009) suggested that biochar residence time in soils of temperate climates is about 2000 years.

2.3.2 ENVIRONMENTAL BENEFITS OF BIOCHAR APPLICATION TO THE SOILS

Biochar application was reported to contribute in solving various environmental problems – greenhouse gases emissions, high CO_2 concentration in the atmosphere, managing organic waste. Biochar is also applied for soil improvement and energy production (Ahmad et al., 2014). It is considered as environmentally friendly ameliorant as local and renewable resources are used for its production. Various waste biomass including crop residue, manure and sludge are used for biochar production (Lu et al., 2017). Ahmad et al. (2014) stated that the usage of biochar favors managing this waste, and reduces pollution loading to the environment. During the process of charring the volume and weight of the waste is reduced. Another important benefit of biochar is decreasing methane emissions from landfill. Also, pyrolysis processes reduce pathogenic microorganisms from sludge or manure biochar. It also has the benefit of decreasing energy used in the long-distance transport of waste.

Biochar application to agricultural lands is able to sequester atmospheric carbon dioxide and mitigate climate change (Godlewska et al., 2017). It is very stable in soils due to its physical structure (Kuzyakov, 2009). This long-term stability plays an important role in reducing CO_2 emissions as it decreases the rate at which photosynthetically fixed carbon is transmitted to the atmosphere (Woolf, 2010). Biochar was suggested as a sink for atmospheric CO_2 by Glaser et al., (2002). Zweiten et al. (2009) also reported reduction of CH_4 emissions by biochar application. Globally, biochar implementation could reduce total greenhouse emissions by 12% annually (Woolf et al., 2010).

2.3.3 BIOCHAR EFFECT ON SOIL PROPERTIES

Biochar affects soils physical and chemical properties (ion exchange capacity, porosity, water holding capacity, retention of nutrients or microbial activity) positively (Godlewska et al., 2017). According to Glaser et al. (2002) and Verheijen et al. (2010), biochar addition to soil increases its cation exchange capacity and improves higher nutrient retention in comparison to untreated soil. Biochar has a low bulk density and its addition could reduce bulk density of soil and improve soil structure. Also, biogeochemical processes in soils are altered after biochar addition due to changes in microbial communities and changes in enzyme activities (Ahmad et al., 2014). All these processes improve soil fertility and provide better crop productivity after biochar addition (Glaser et al., 2002).

Al-Wabel et al., (2015) investigation showed that biochar application improved maize growth. Water retention of soil increases after biochar application (Downie et al., 2009) because net soil surface area increases. Glaser et al., (2002) suggested the increase of water holding capacity after biochar additions was because of high organic matter content in biochar. This effect is long-term because of biochar stability and recalcitrance. Due to additional water and nutrients in the micropores, biochar may improve plant water availability, especially for sandy soils during dry periods. However, in case of small pores, biochar particles can block soil pores, reducing the infiltration ability of soil (Verheijen et al., 2010).

Soils organic matter is significantly altered by the addition of biochar (Ahmad et al., 2014). It causes the positive priming effect (Zimmerman et al., 2011) by faster decomposition of soil native carbon by changing microbiological conditions (Kuzyakov et al., 2009). In other cases, the negative priming effect was observed due to the adsorption of dissolved organic carbon and its slower decomposition. Generally, the amount of mobile and resident organic matter, its sorption capacity affects the positive or negative direction of priming (Ahmad et al., 2014). In addition, positive priming effect is more pronounced in the case of application of biochar that are produced at lower temperature. Addition of biochar produced at higher temperature causes mostly negative priming effect. Over the long-term organic matter is strongly adsorbed to biochar causing carbon storage in soils. Because of its alkaline nature biochar has a liming effect on soil and the extent of this effect varies depending on biochar properties, its feedstock and temperature of production (Ahmad et al., 2014).

2.3.4 BIOCHAR USAGE FOR HEAVY METAL(LOID) IMMOBILIZATION

Biochar is considered as a soil ameliorant having a great potential for immobilizing risk metals (Al-Wabel et al., 2015). However, Ahmad et al., (2014) stated that the ability of biochar to adsorb contaminants varies depending on biochar physico-chemical properties and target pollutant.

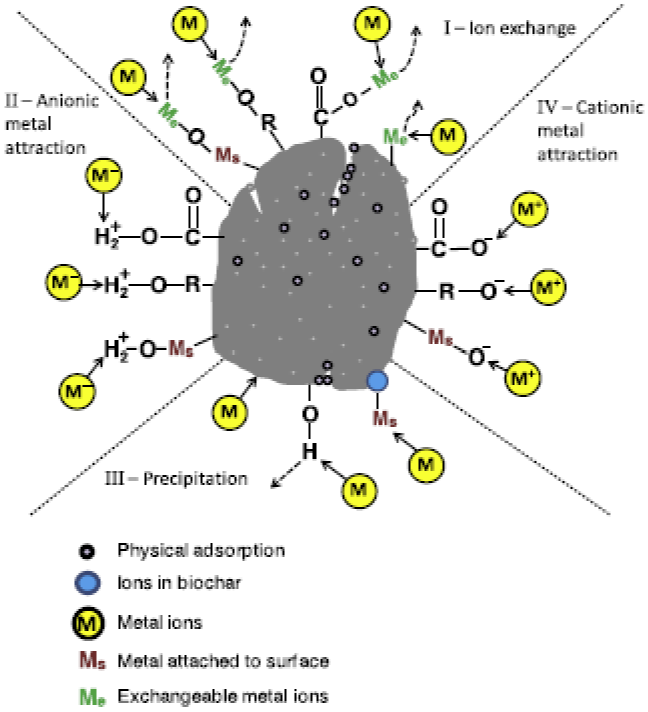


Fig 2.3: Mechanism of biochar interactions with inorganic contaminants. Circles on biochar particle show physical adsorption. I – ion exchange between target metal and exchangeable metal in biochar, II – electrostatic attraction of anionic metal, III precipitation of target metal and IV – electrostatic attraction of cationic metal. Extracted from Ahmad et al., (2014)

The most important properties are feedstock and pyrolysis temperature. The main mechanisms of reducing metal mobility include processes of complexation with functional groups, cation exchange with biochar surface, precipitation and formation of insoluble species, electronic attraction to biochar surface, reduction and further sorption of reduced compounds (Lu et al, 2017). Cation exchange capacity was found to predominate in cases of biochar having relatively high CEC and high amount of Ca, K, Mg, Na (Harvey et al., 2011). For biochars with low CEC other mechanisms (complexation with carboxylic surface functional group and precipitation) play an important role in Cd sorption. Uchimiya et al., (2011) observed the important role of carboxyl, hydroxyl, and phenolic functional groups for metal binding. Biochars derived from various feedstocks have different mechanism of metal sorption as in the case of manure biochar with high amounts of carbonate and phosphate. With this, precipitation is the main mechanism of Cd immobilization by manure biochar (Xu et al., 2013).

Cadmium and Pb are divalent cations and they have the same sorption behavior. Lead sorption is defined by the same mechanisms as sorption of Cd and depends on feedstock and pyrolysis temperature of biochar. Non-electrostatic mechanisms are considered as dominating for Pb (Lu et al, 2016). But Cao et al., (2011) reported immobilization of Pb by forming $Pb_5(PO_4)_3(OH)$ in soils amended with dairy manure biochar. Uchimiya et al., (2012) showed higher Pb immobilization performance in case of low pyrolysis temperature biochars. These biochars yielded O-containing functional groups playing an important role in altering the Pb mobility. Zinc immobilization by biochars is found to be controlled by complexation, electrostatic attraction, and precipitation. Moreover, Ca-oxalate (CaC_2O_4) crystals could be responsible for the increased ability of some biochars to remove Cd and Zn (Clemente et al., 2017). Lu et al, (2014) reported that reduction in biochar size could enhance the effectiveness of Zn immobilization illustrating biochar size also should be taken into consideration when in use as soil amendment.

Moreover, cation exchange capacity in soil increases after adding biochar amendment and soil pH range shifts towards neutral and alkaline range. Under these conditions metal mobility decreases and the mobilization of oxyanions increases (Al-Wabel et al., 2015). Ahmad et al., (2014) suggested that low temperature pyrolysed biochar with the high amount of O-containing functional groups generally show good efficiency for risk metals and metalloids stabilization. High surface area biochars with a high amount of pores produced under high temperature are more effective for organic contaminants (Ahmad et al., 2014).

Li et al., (2018) carried out a study to evaluate the effectiveness of four soil amendments (with main components being clay mineral, base mineral, humus and biochar, respectively) on reducing Cd availability and increasing Cd stability in soil in China. The maximum adsorption capacity of test amendments on Cd ranged from 7.47 to 17.67 mg/g. The characterizations of test amendments before and after Cd loading provided the evidence that surface precipitation and ion exchange were the main reasons for clay mineral and base mineral to adsorb Cd, and complexation was for humus and biochar. In addition, there was significant increase in the desorption percentages of Cd from amendments as pH decreased (from 7 to 1) or ion strength increased (from 0 to 0.2 M). Comparatively, humus and biochar could be more effective for in situ immobilization of Cd in contaminated soils, due to their high adsorption capacities (12.82 and 17.67 mg per g, respectively) and low desorption percentages (4.46–6.23%) at pH from 5 to 7 and ion strengths from 0.01 to 0.1 mol per L. The results obtained in this study could provide a guideline for in-situ remediation of Cd polluted field-soil in China.

In another study carried out by Wu et al., (2018) on investigating the adsorption of cadmium using batch methods of four degraded soils with different degrees of degradation were amended with maize-stalk-derived biochar. The maximum adsorption capacity of degraded soil was found to remarkably decrease in comparison with undegraded soil (5361 to 170 mg/ kg), and the maximum adsorption capacity of biochar increased with increasing pyrolysis temperature (22.987 to 49.016 g/kg) which was much higher than that of soil. The addition of biochar effectively improves the cadmium adsorption capacity of degraded soil (36–328%). The improving effect is stronger when increasing either the degradation level or the amount of added biochar, or the pyrolysis temperature of biochar. Contrary to the general soil–biochar system, adsorption of Cd was not enhanced but slightly suppressed (7.1–36.6%) when biochar was incorporated with degraded soils, and the absorptivity attenuation degree was found to be negatively linear with soil organic matter content in the degraded soil–biochar system. The results of the study suggested that more attention on the adsorption inhibition and acceleration effect difference between the soil–biochar system and the degraded soil–biochar system is needed.

Irhaa et al., (2009) investigated the sorption capacity of selected heavy metals (Cd, Pb, Cu, Cr) to five Estonian soils was evaluated using spiked subsoil samples in laboratory experiments. The experimental sorption data fitted well to the linear Freundlich isotherm. The sorption of metals in subsoil was found to depend on the soil type such as mineral composition. The results of the study indicate that the content of quartz and carbonates is important in affecting the metal sorption capacity of subsoil. On the basis of our data the possibility of penetration in depth and accumulation of mobile metals was evaluated. It was concluded that increase in dissolved Cd and accumulation of other metals in the subsoil of Podzol is expected. The accumulation of Pb could be the main process for soils with a high amount of dolomite.

In the study carried out by Kabała and Singh (2006) to determine vertical distribution and chemical forms of Cd using sequential extraction procedure in soil profiles exposed to smelter emissions in order to assess the potential Cd mobility. Four pedons were sampled near a copper smelter Głogów, in operation since 1972. A sequential extraction selected for this study separate metals into operationally defined fractions: water – soluble (WS), exchangeable (EX), specifically sorbed and carbonate bound (SSC), occluded on Fe/Mn oxides (OX), complexed by organic matter (OM), and residual (RES). Total Cd concentration does not depend on the distance to the smelter but correlates to clay content and CEC. Relative significance of fractions in non-contaminated soil horizons is as follows: RES >> OX > EX+SSC > OM >> WS. Increasing contamination of soils located close to the smelter manifests in a relative increase of non-residual fractions, the exchangeable Cd in particular. Cadmium mobility assessed both by single (in 0.01 M $CaCl_2$) and sequential extractions is relatively high in upper soil horizons. There is however little risk of groundwater contamination as the concentration of labile Cd in lower horizons is negligible.

Biochar possesses a good porous structure, a large specific surface area (<210 m^2/g), and various surface oxygen-containing functional groups (Bian et al., 2013; Peterson et al., 2012). The excellent physical and chemical properties of biochar contribute to the adsorption and immobilization of pollutants in soil. Adding a small amount (5.5%) of biochar (vinegar residue biochar; Maize stover biochar) to contaminated soil can effectively reduce the concentration of pollutants in the porewater of soil and decrease the migration of pollutants and its accumulation in plants and animals (Li, 2018). Bian et al., (2013) showed that the Cd content in rice from soils supplemented with wheat straw biochar was reduced by 20% to 90%, and the Cd content of rice was less than 0.4 mg/kg. Li et al., (2018) found that bioavailable Cd decreased most with 5% vinegar residue biochar application in soil. Liu et al, (2015) found that, when adding 5% (in mass) stalk carbon with particle size of 0.25 mm in paddy soil, available contents of Pb, Zn, and Cu in the soil were reduced by 52.5%, 52.1%, and 50.1%, respectively. Adsorption of heavy metals (such as Cd, Pd, and Cr) usually increased in soil–biochar system due to the increasing sorbed sites for heavy metals which was supplied by the coated DOM (dissolved organic matter) of soil onto biochar (Qu et al., 2017).

2.4 BIOCHAR AND NANOIRON COMPOSITE

Nanomaterials have high reactivity due to their unique surface properties, quantum size effects and macroscopic quantum tunneling effects, which play an important role in environmental fields such as catalysis, adsorption and degradation of pollutants. They are widely used in industrial and domestic sewage treatment, polluted soil and sediment treatment, air pollution control and other pollution remediation processes (Khin et al., 2012). Nanoiron is an effective material for groundwater remediation being environmentally friendly material. It has a low redox potential of -0.44 V, lower than that of common heavy metals (Pb, Cd, Ni, Cr) and organic pollutants (chlorinated hydrocarbons), and as such it is usually used as an electron donor during the remediation process (Li et al., 2006).

2.4.1 NANOIRON MODIFICATIONS

Iron nanoparticles are often surface modified because of their small particle size, large specific surface area, poor stability and easy agglomeration. There are four common surface modification methods: doping with other metals, surface coating, emulsification and solid-phase loading (Stefaniuk et al., 2016). These solid matrixes prevent nanoparticles from agglomerating by masking dipole interactions while the hydrophobic and inert coating of solid phase materials prolong the reaction activity of nanoparticles and promote the adsorption of hydrophobic contaminants on the surface of nanoparticles. The commonly used load matrixes are activated carbon, silica, montmorillonite, kaolinite, biochar etc. (Tomasevic et al., 2014; Wang et al., 2017). Solid-phase loading facilitates the reduction efficiency of nanoiron. In a study carried out by Huan et al., (2006) where they loaded nanoiron on exfoliated graphite, the results showed that nanoiron supported on exfoliated graphite had higher ability to reduce nitrate ions. Zhu et al., (2009) loaded nano iron on activated carbon, which showed that the adsorption capacity of iron on arsenate and arsenite reached 12.0 mg/g and 18.2 mg/g.

2.4.2 ADVANTAGES OF NAOIRON BIOCHAR COMPOSITE

Some of the advantages of biochar used as a nanoparticle loading matrix are: biochar has been used as an environmental remediation material with low environmental risk; it is prepared from a wide range of materials; the surface functional groups of biochar are abundant to provide the active sites for the loading of nanoparticles; it disperses and stabilizes the nanoparticles. Research carried out by Qian et al., (2017) showed that organic components and silicate particles within biochar served as additional reaction sites of nanoiron. Functional groups, such as C-O, O-H, aromatic C=C, aromatic C=O and aromatic O-H interacted with Fe^{3+}/Fe^{0} (Zhu et al., 2017). Moreover, biochar provides a large specific surface area for the efficient loading of nanoparticles. It has high stability, which can remain in the environment for a long time to reduce the risk of nanoparticles diffusion. During the remediation process, the function of nanoparticles is coupled with the adsorption of biochar, which promotes the interaction between nanoiron and pollutants. Zhu et, al (2017) showed that zero valent iron could help biochar improve efficiency in heavy metal (Pb^{2+}, Cd^{2+}, Cr^{6+}, Cu^{2+}, Ni^{2+}, Zn^{2+}) absorption, in which C-O/COOH groups of biochar were cracked with the formation of C=O/C=C during the loading process, and the C-O-Fe acted as an electron acceptor during the reduction reaction. Yang et al., (2018) synthesized biochar that composited with α- FeOOH nanorods, and believed that abundant oxygen functional groups, high surface area, and relative excellent slit-shaped pores improved the removal efficiency of Cu^{2+}. It could be deduced from the study that coupling between the surface properties of biochar and nanoparticles improve the remediation efficiency, indicating that some coupling mechanisms are occurring. These synergistic effects could be used for the removal of heavy metal in the aqueous solution.

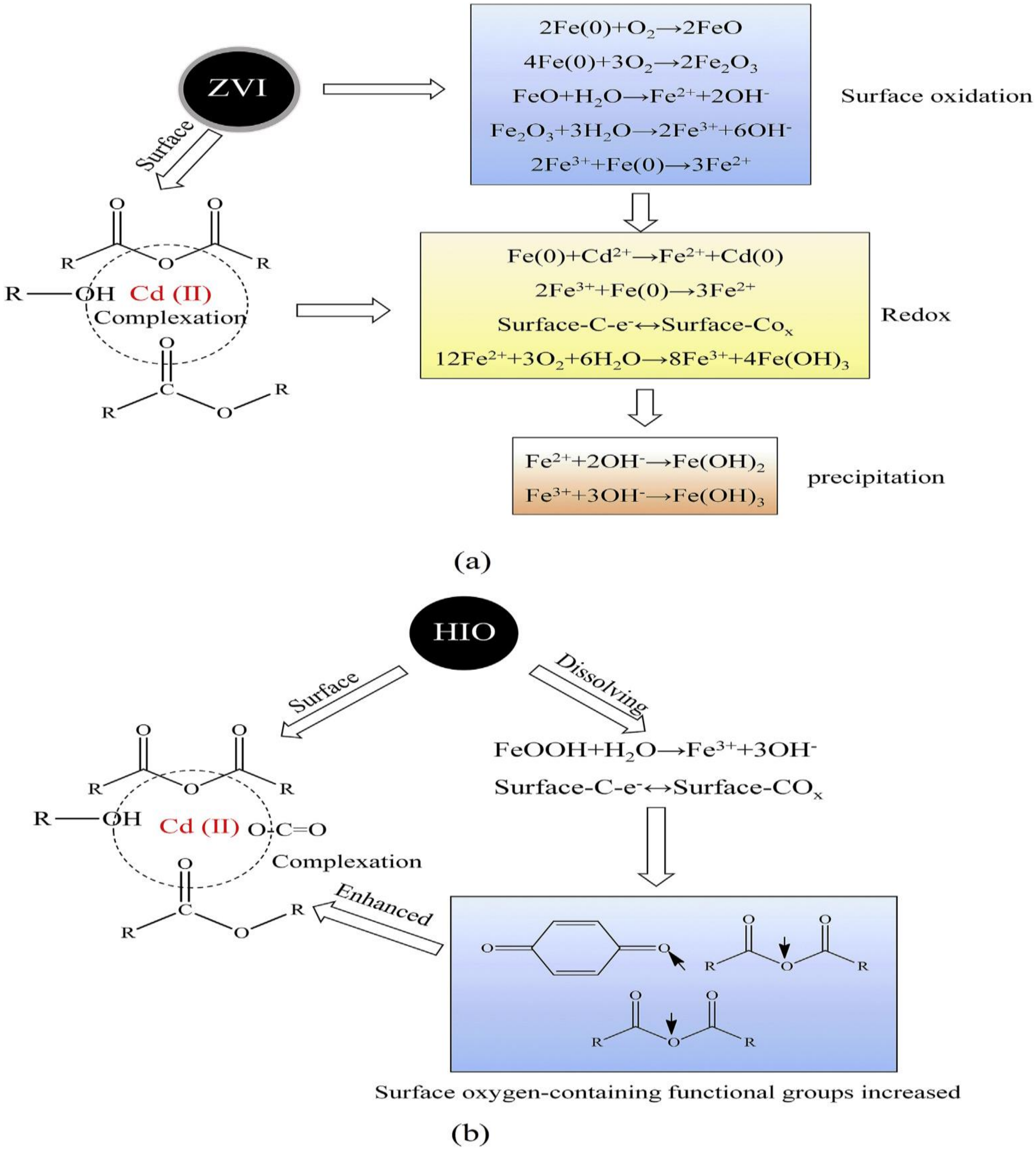


Fig. 2.4 The coupling adsorption mechanism of biochar and nZVI (α)/nHIO. Zhu et, al (2018).

According to the study carried out by Zhu et al. (2018) on the interaction between biochar materials and nanomaterials. Porous biochar activated by K_2CO_3 (KBC) loaded with nanoiron/nano-α-hydroxy-iron oxide (nHIO) was studied (Fig 2.3). The results showed a reduction in the specific area of nanoiron/nHIO to 178.6 m^2/ g and 272.2 m^2/ g, respectively, and Cd adsorption increased to 22.37 mg/g and 26.43 mg/g, respectively, which was more than three times that of KBC (7.02

mg/g). The interaction between nanoiron/nHIO and Cd was enhanced by the complexation of surface functional groups, but the coupling effects were different. The coupling mechanism of Cd on nanoiron with KBC was complexation - reduction. Cd was partly reduced in the removal process. Theoretical basis on the effective preparation of nanocomposite and their application in the field of environment effectively was provided by the interaction studied

3 MATERIALS AND METHODS

3.1 DESCRIPTION OF SAMPLING LOCATION

Vinoř is a city north of Prague, Prague-9 (Fig 3.1). The area was historically contaminated with Cd as a result of industrial activities, mainly production of motor components (PAL Kbely company). As a result, the Vinoř stream and several Vinoř ponds were contaminated. Later, in the 1980s the ponds were excavated, and the contaminated sludge was spread out over the nearby lands. The samples used for this study were collected at one of the affected private fields in our studied area.

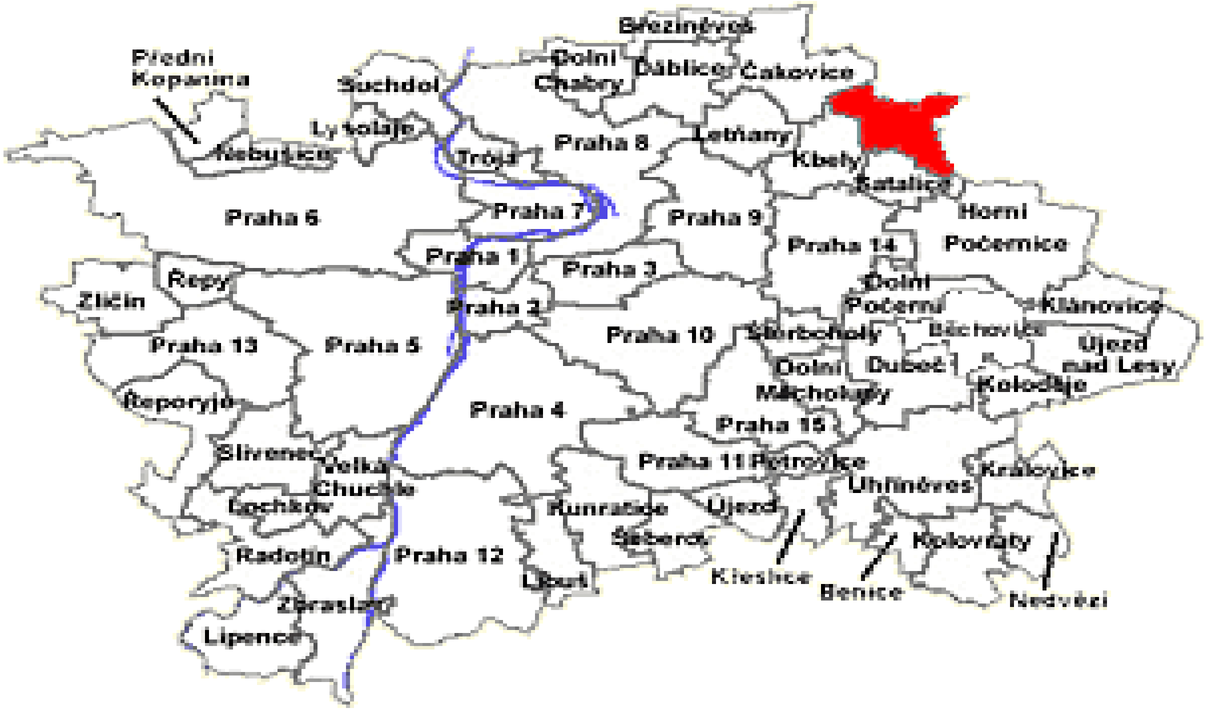


Fig 3.1: Map of Prague showing the study area of Vinoř in red. *Source: http://www.praha-vinor.cz/default_en.htm*

3.2 SAMPLING AND SAMPLE LOCATION

The sampling was performed in May 2018 in cooperation with the Faculty of Agrobiology, Food and Natural Resources, Department of Soil Science and Soil Protection. Spatial coverage sampling method was used to collect samples from the field because it optimizes the spatial distribution of the samples so that the sampling points are equally distributed in the given space

(Bruce et al., 2006). See Fig 3.2 below for the distribution of selected sampling points across the field under study.

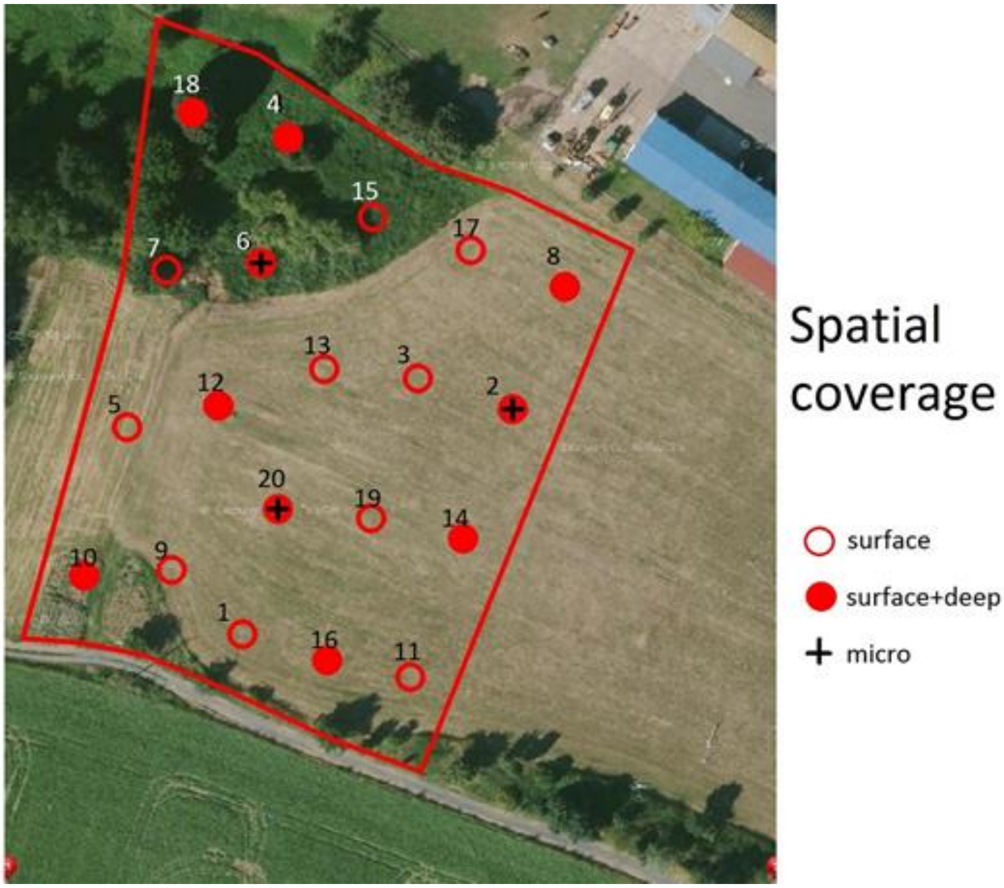


Fig 3.2: Photo of sampling points on the studied private field (performed and provided by Radim Vašát).

Soil samples were taken at 20 selected points across the private field, at the upper soil horizon (0-20 cm) and a depth of 40-60 cm. Samples from points Cd6 and Cd14 (initially identified as the most contaminated with Cd) were sampled at different depths of the soil profile (80, 70, 60, 50,40, 35, 30, 25, 20, 15, 10, 5 cm). In addition, about 2 kg of the surface layer of the Cd6 and Cd14 samples was collected for further testing of Cd immobilization using amendments. The soil samples were air-dried and sieved through a 2-mm stainless steel before use and transferred to labeled polyethylene bag and kept in room temperature until analysis.

Additionally, rhizosphere soil was separated from the roots and analyzed accordingly. Also, both the shoots and roots from point Cd 14 and Cd 6 were collected. Shoots and roots were carefully washed with deionized water and dried using an oven set at 60 °C for 24 hours. The samples were then analyzed accordingly.

Table 1: List of samples without amendments.

Sample No	Location	Depth	Remark	Sample No	location	remarks	
1s	s	surface	s=0-20cm	14, 70	70cm	soil profile	
2s	s	surface		14, 60	60cm	soil profile	
2d	d	deep	d=40-60cm	14, 50	50cm	soil profile	
3s	s	surface		14, 40	40cm	soil profile	
4s	s	surface		14, 35	35cm	soil profile	
4d	d	deep		14, 30	30cm	soil profile	
5s	s	surface		14, 25	25cm	soil profile	
6s	s	surface		14, 20	20cm	soil profile	
6d	d	deep		14, 15	15cm	soil profile	
7s	s	surface		14, 5	5cm	soil profile	
8s	s	surface		6, 80	80cm	soil profile	
8d	d	deep		6, 70	70cm	soil profile	
9s	s	surface		6, 60	60cm	soil profile	
10s	s	surface		6, 50	50cm	soil profile	
10d	d	deep		6, 40	40cm	soil profile	
11s	s	surface		6, 30	30cm	soil profile	
12s	s	surface		6, 25	25cm	soil profile	
12d	d	deep		6, 20	20cm	soil profile	
13s	s	surface		6, 15	15cm	soil profile	
14s	s	surface		6, 10	10cm	soil profile	
14d	d	deep		6, 5	5cm	soil profile	
15s	s	surface		Cd6 B			
16s	s	surface		Cd14 B			
16d	d	deep		Cd6 Rh		Rhizosphere	
17s	s	surface		Cd14 Rh		Rhizosphere	
18s	s	surface		Cd6 root		roots	
18d	d	deep		Cd14 root		roots	
19s	s	surface		Cd6 Shoot		shoots	
20s	s	surface		Cd14 Shoot		shoots	
20d	d	deep					

3.3 TREATMENT OF SOIL SAMPLES WITH BIOCHAR AND nZVI

The selected soil samples (denoted as Cd14 and Cd6, respectively) were amended with 2 wt.% of a sorbent, i.e., woody biochar (BC), composite of nano zero-valent iron - biochar (nZVI-BC) both prepared by pyrolysis at 700°C. Two variants were prepared - powder sorbents and water suspension of sorbents (more details in Table 2 below) to see if activation of the sorbents in water is favorable for further immobilization of risk elements. The amended soils and control non-amended soil were kept under 60% of water holding capacity (WHC) for 3 months to ensure the equilibrium conditions after the addition of amendments.

Table 2: Table showing details of amendment used and preparation of amendment.

Sample location	**Sample number**	**Amendment**	**Preparation of wet sorbent**	
Cd14	Cd 14 ,1	98 g soil + 2g nZVI-BC		
	Cd 14, 2	98 g soil +2g BC		
	Cd14, 3	Control, 100 g of soil		
	Cd14, 4	98 g soil + wet 2 g nZVI	2 g of nZVI-BC + 35.5 g of demineralized water, carefully shaken, covered with parafilm and kept for 24 hours standing	
	Cd14, 5	98 g soil + wet 2g BC	2 g of BC + 35.5 g of demineralized water, carefully shaken, covered with parafilm and kept for 24 hours standing	
Cd 6	Cd6, 1	98 g soil + 2 g nZVI-BC		
	Cd6, 2	98 g soil + 2 g BC		
	Cd6, 3	Control, 100 g of soil		
	Cd6, 4	98 g soil + wet 2 g nZVI	2 g of nZVI-BC + 35.5 g of demineralized water, carefully shaken, covered with parafilm and kept for 24 hours standing	
	Cd6, 5	98 g soil + wet 2 g nZVI	2 g of BC + 35.5 g of demineralized water, carefully shaken, covered with parafilm and kept for 24 hours standing	

3.4 ACTIVE AND EXCHANGEABLE SOIL pH

Determinations of pH were done in batches and triplicates. A mass of 6 grams of each soil sample was placed into labeled plastic tube (50 ml) and a volume of 20 ml of 0.01M of freshly prepared calcium chloride solution was added. Tubes containing samples were arranged on the agitator and shaken thoroughly for 3 hours at a 250 rpm. pH probes were calibrated at pH values of 4, 7, and 10 while agitating the samples. Agitated samples were allowed to settle for 30 minutes, the pH values were measured with pH meter as shown in Fig 3.3. This procedure was performed on both surface (s) and deep (d) samples, i.e, Cd1 – Cd20 (Table 3.1).

In the same procedure, active pH values were derived for all samples using demineralized water.

Fig 3.3: Photo of pH meter used for pH measurement (WTW, photo taken in august 2018).

3.5 SIMPLE EXTRACTION

Determination of the availability of various elements was done using 0.01M of $CaCl_2$ (Quevauviller, 1998). Simple extraction was performed on all the samples in batches. Firstly, all the surface (s) and deep (d) samples Cd1 – Cd 20 were tested. A mass of 2 g was measured in to a tube in duplicates, 20 ml of 0.01M of $CaCl_2$ was added. Tubes containing sample and solution were then agitated for 3 hours in the agitator at a speed of 250 rpm to allow complete extraction of the ions. After that, the tubes were centrifugated at a speed of 5000 rpm for 10 minutes. The leachates were then filtered using 0.45-µm pore sized filter in to labeled clean tubes. Finally, the samples were diluted 10 times in to 10 ml tubes, 2-3 drops of HNO_3 was added to each extract solution to keep it acidified before they are finally passed for ICP-OES analysis.

In the same manner, soil profile samples Cd14 (70- 5cm) and Cd6 (80 – 5cm) (shown in Table 1 above) were analyzed following the above described procedure. Rhizosphere samples taken from the sampling points Cd6 and Cd14 were also tested following the same procedure described above.

Soil samples amended with biochar and nZVI-BC composite were tested using both demineralized water and 0.01M of $CaCl_2$. Compared to the standardized procedure, wet soil sample was extracted in order to keep the conditions as close to reality as possible. For this purpose, the corresponding mass of samples was calculated with respect to the water content (according to the WHC). In particular, 5.4 g was weighed, and 38.6 ml of solution was used to keep the liquid to solid ratio of 10 since demineralized water was already added during the process of amending the soil samples. The experiment was run in triplicates and the samples were all agitated for 3 h, centrifuged and filtered before passing for ICP-OES analysis. Additionally, pH, Eh and EC was also measured in the sample solution.

3.6 AQUA REGIA EXTRACTION OF SOIL AND PLANT SAMPLES

The total concentration of metals and metalloids was determined by weighing 0.25 g of each soil samples into acid washed Teflon tubes. Aqua regia solution prepared from 2.5 ml HCl and 7.5 ml of HNO_3 was successively added to the sample and left open for at least 15 minutes for initial reaction with the soil sample (Fig 3.4), they were then carefully arranged inside a rotor of a microwave digestion program system as shown in Fig 3.5 and finally submitted to a microwave digestion program. Method 3501A was chosen at 170 degrees 175 and dropped to 70 degrees after 15 minutes. The extract of this procedure was carefully filtered using 0.45 μm into 50 ml tubes. The tube containing the filtered extract was finally diluted with demineralized water to the 50 ml mark. Diluted filtered samples were passed for ICP-OES analysis. Samples prepared for the total elemental composition were diluted 10 times. The same procedure was followed to analyze the total elemental composition of the root and shoots samples taken from the sample location. Likewise, the procedure was also used to analyze the total elemental composition of soil samples amended with biochar and nZVI-BC composite.

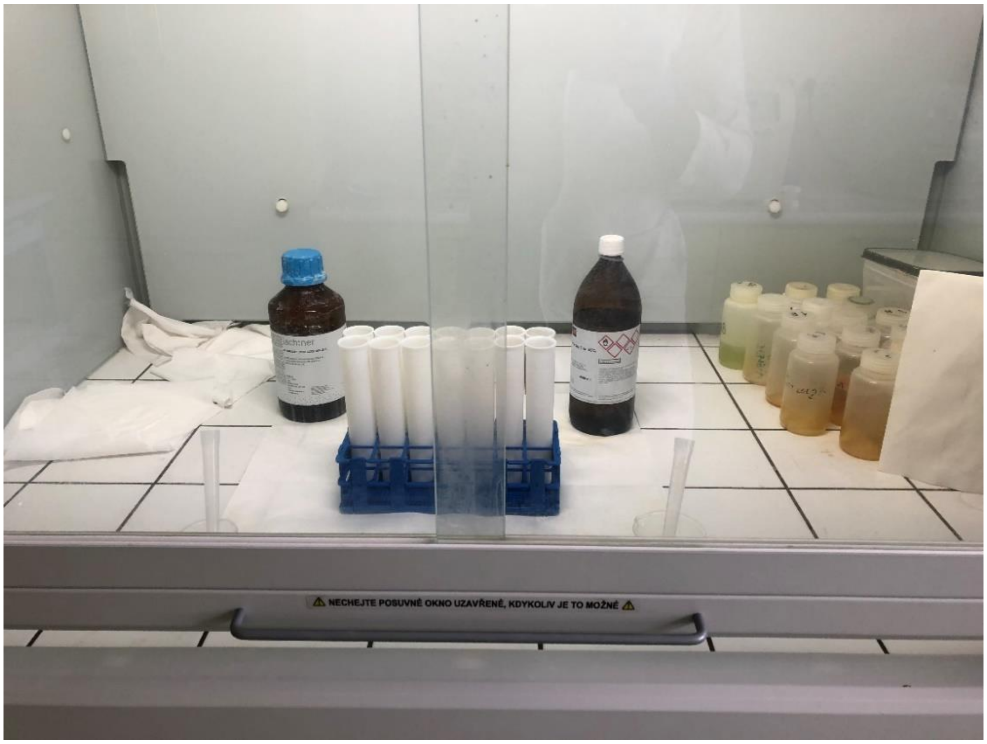


Fig 3.4: Photo of samples and aqua regia solution in fume chamber, left for initial reaction.

Fig 3.5: Photo of Microwave digestion system.

3.6 ACETIC ACID EXTRACTION

Acetic acid extraction was applied for the (non)amended soil samples. Determination of the concentration of metals and metalloids in the bound to carbonates in soil were dissolved with acetic acid which represent the first fraction of sequential extraction.

A mass of 1.35 g of amended soil samples Cd14,1 were placed in the labeled tubes in triplicates and 39.65 ml of 0.11M acetic acid was added. The solution was shaken for 16 hours at 200 rpm using the agitator. The shaken solution was centrifuged at 9000 rpm for 10 mins, the supernatant was afterwards filtered using 0.20 µm pore sized filters into cleaned 10 ml test tubes. The solution was diluted 10times. The solution to be tested were then kept in the fridge until they were passed for ICP-OES analysis.

3.7 IONIC CHROMATOGRAPHY

The means of ionic chromatography was used to determine NO_3^- and SO_4^{2-} in selected water extracts. The samples were diluted thus:

- 1ml of sample + 9ml H2O (10x dilution) for CD14 samples
- 0.5ml of sample +9.5ml H2O (20x dilution) for Cd6 because of higher Electrical conductivity values of above 300us/cm.

kept in the fridge until they were passed for ionic chromatography analysis.

3.8 DISSOLVED ORGANIC AND INORGANIC CARBON CONTENT

The determination of carbon content in the soil solution samples was carried out on samples amended with nZVI/Biochar. The samples were diluted in the following proportions:

- 2ml sample + 18ml H2O + 2-3 drops of HNO3 (x dilution) for Cd14 samples.
- 1ml sample + 19ml H2O +2-3 drops of HNO3 (20x dilution) for Cd6 samples.

Finally, TOC bottles containing solution to be analyzed were covered with aluminum foils and kept in the fridge until they were passed for analysis.

3.9 INSTRUMENTAL ANALYSIS

All sample were analyzed at the analytical laboratory of the Department of Environmental Geosciences at the Faculty of Environmental Sciences (FES) at the Czech University of Life Sciences (CULS) Prague.

Filtered samples were appropriately diluted and acidified with 2 – 3 drops of 2% HNO_3 and passed to the laboratory for bulk concentrations of major and trace elements using inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 730, Agilent Technologies, USA).

In the same manner samples carbon analyzer TOC- CPH (Shimadzu, Japan) was used to determine both dissolved organic matter (DOC) and total dissolved carbon (TC) in the samples. Dissolved inorganic carbon (DIC) was recalculated from the TC and DOC results. The inorganic ions were detected by the use of Dionex ICS-2000 ion chromatography system (Dionex, USA).

4 RESULTS

4.1 SURFACE AND DEEP SAMPLES

4.1.1 pH VALUES

The exchangeable pH values obtained using 0.01M of $CaCl_2$ is presented in Fig 4.1. The pH values for both surface and deep samples ranged from 6.98 to 8.23, with mean pH value of 7.41. Sample 9s was found to be most strongly alkaline (with pH value of 8.23 for surface sample) as seen as Fig 4.1. Most of the samples were found to be slightly alkaline except for sample 10s, which was nearly neutral. pH values for deep samples tend to be higher than the values for the surface samples as shown in Fig 4.2. Sample 16d has the highest pH of 7.80 while the 10d has the lowest value of 7.09. Both 4s and 4d have similar values of 7.39.

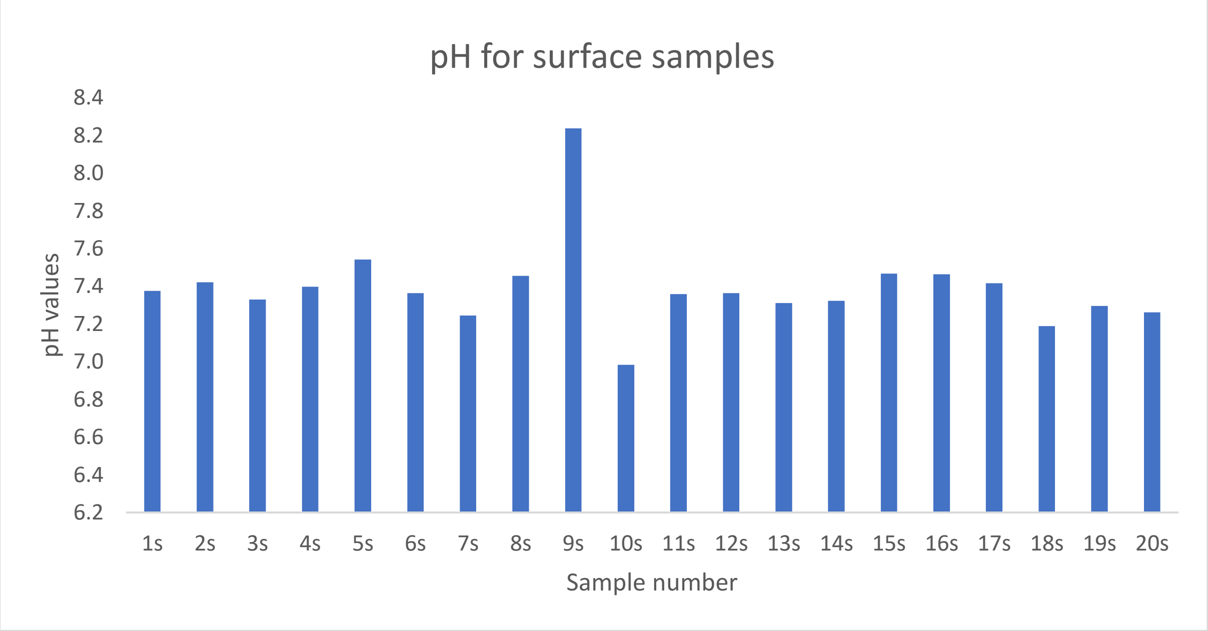


Fig 4.1: Plot of pH values for the surface samples (0-20 cm depth).

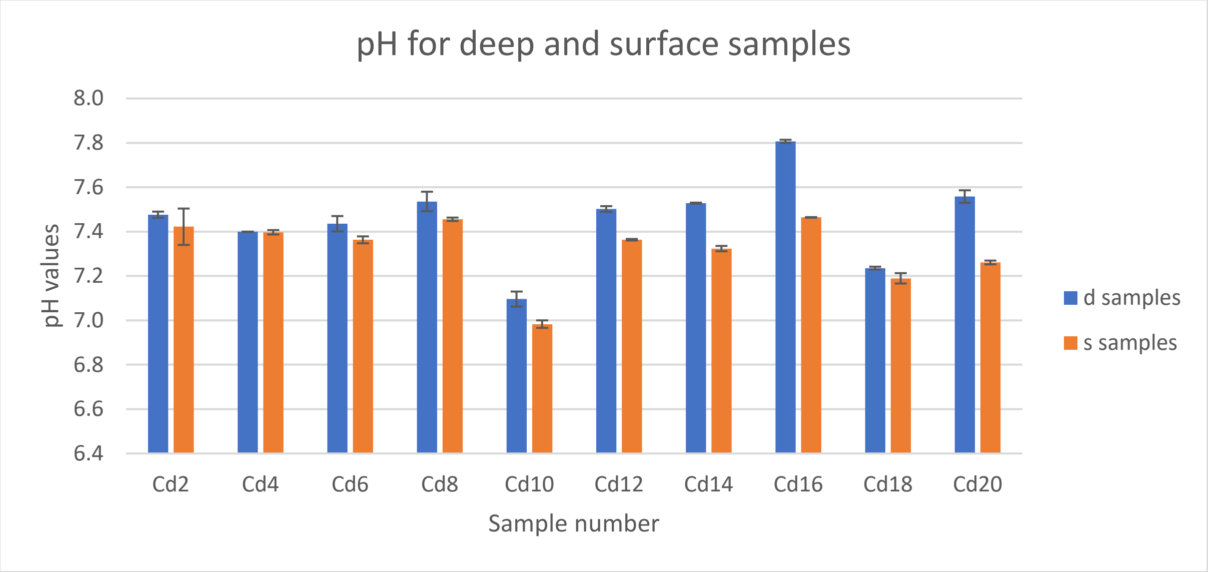


Fig 4.2: Plot of pH values of both surface (0-20 cm depth) and deep (40-60 cm depth) selected samples.

4.1.2 AQUA REGIA EXTRACTION

Pseudo-total concentrations of trace elements in the sample points across the study area are presented in plots below Fig.4.3a and Fig 4.3b. Zinc was observed to have the highest concentration of all the trace metals determined, the highest concentration of 193 mg/kg at point 12s and lowest concentration of 73 mg/kg at point 20d, although there is no particular trend observed in the distribution across the sampling points just as observed for all other trace elements. Concentration of Cd was found at the highest 27 mg/kg at point 12s and lowest 1.2 mg/kg at point 10s. Arsenic distribution across the field ranges between 24 and 6 mg/kg in both surface and deep samples. Generally surface samples. Significant standard deviation (SD) was observed for Pb, As and surface and deep samples (Fig 4.3b). Distribution of the trace elements shows no particular trend across the sampling points as shown in Fig 4.3a and Fig 4.3b.

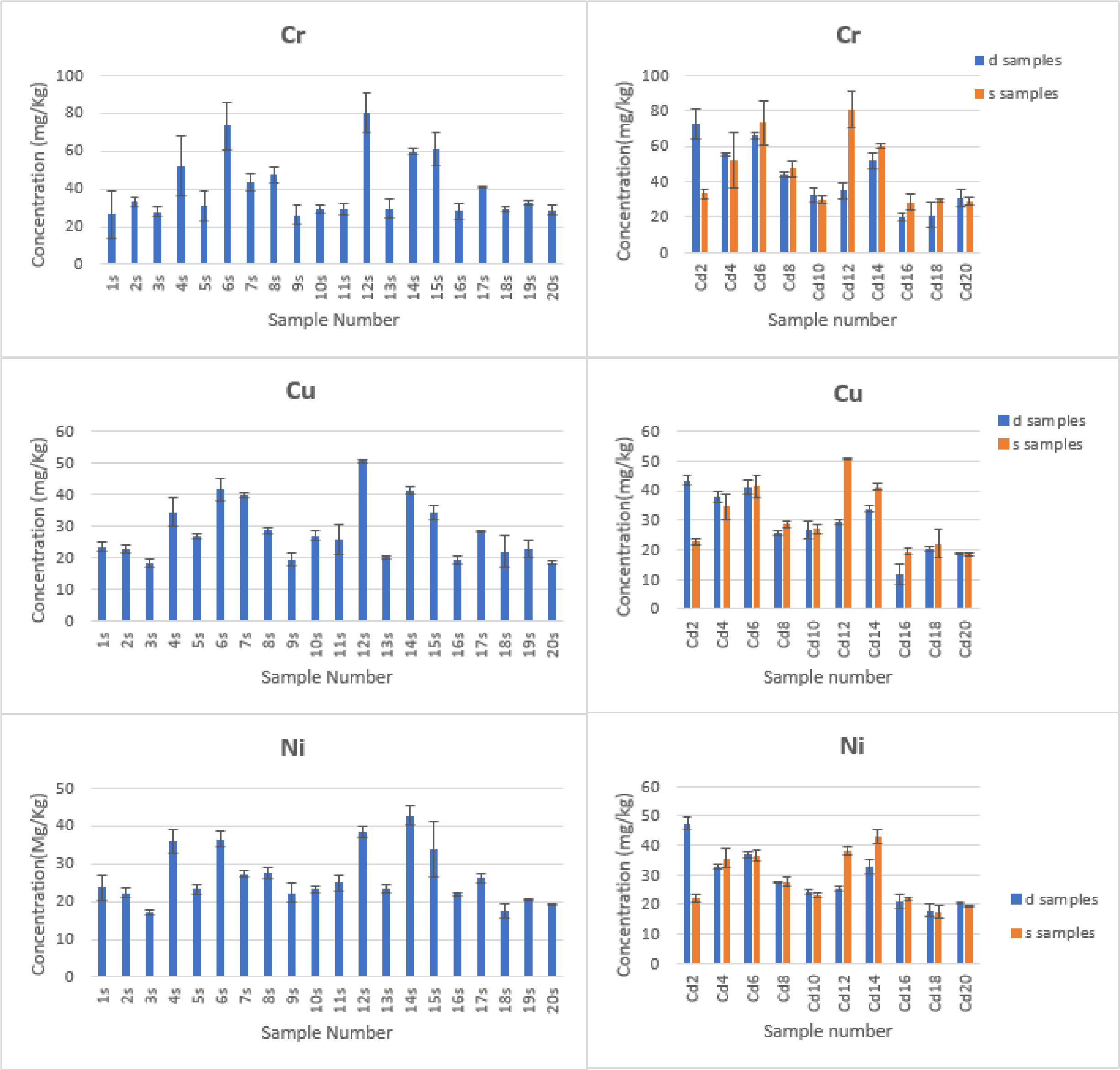


Fig 4.3a: Pseudo-total concentration of trace elements in surface (0–20cm) and deep (40–60cm) samples.

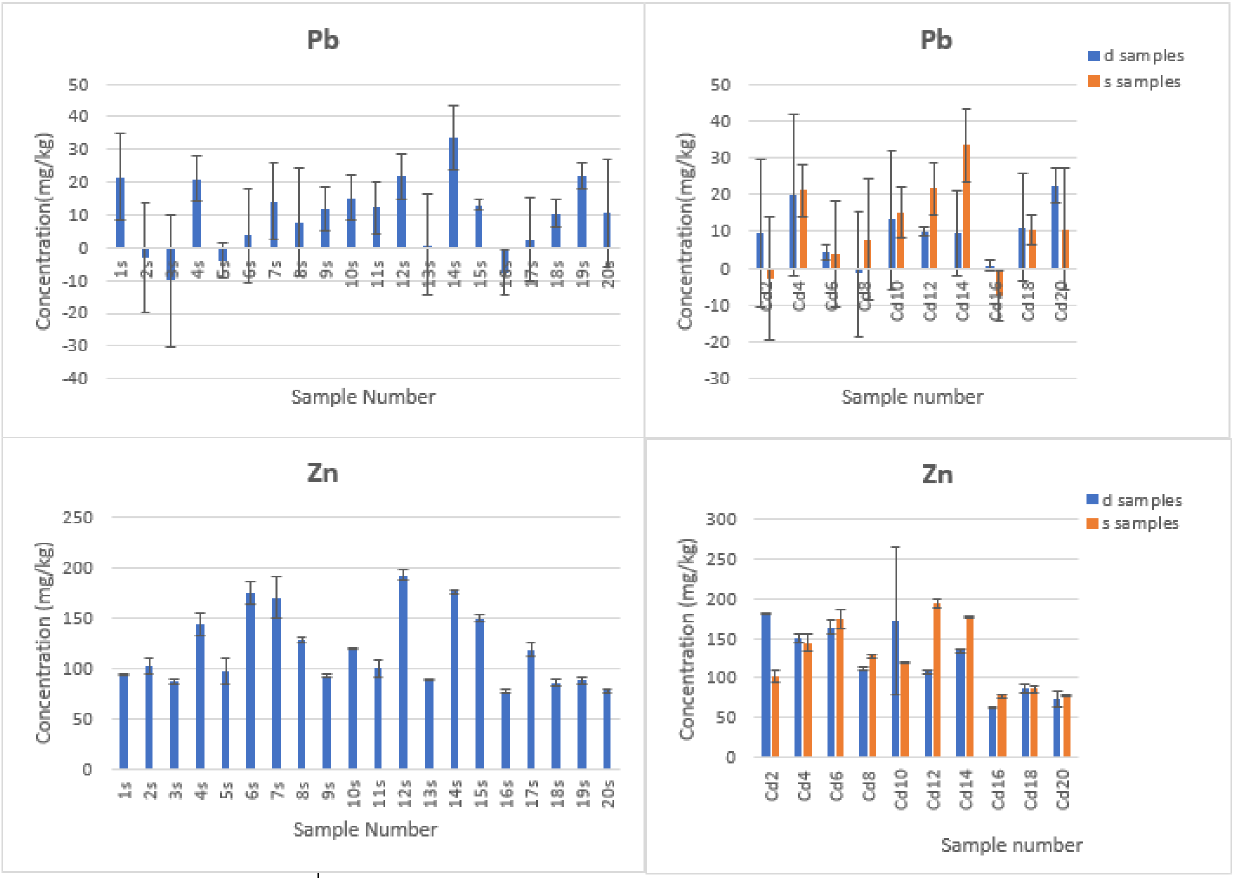


Fig 4.3b: Pseudo-total concentration of trace elements in surface and deep samples.

4.1.3 $CaCl_2$ EXTRACTION

Fig 4.4 shows the concentration of selected trace elements in both surface and deep soil samples. The results of Cd are not presented since they were found below the ICP-OES detection limits (additional ICP MS analyses will be necessary to perform). Therefore, nickel (Ni) and lead (Pb) are presented here to illustrate trace metal distribution. Concentration of extracted Ni ranges between 2.29 and 1.35 mg/kg, at points 18s and 5s. Concentrations of Ni at the surface doesn't show much difference. At point 18, concentration at the surface was higher than the concentration of deep sample with a difference of 0.8 mg/kg, the contrary was observed at point 2 where concentration at deep was higher than concentration at surface with a difference of 0.55 mg/kg.

Concentration of Pb was generally less than 1 mg/kg with the exception of point 14s at 1.11 mg/kg. Pb at the surface ranges between 0.17 – 1.11 mg/kg at 11s and 14s respectively. The range of Pb observed in deep and surface samples was 0.28 -0.89 mg/kg. Concentration of surface sammples was significantly higher at point 2 and 14 for both surface and deep samples. The trends of distribution is shown in Fig 4.4.

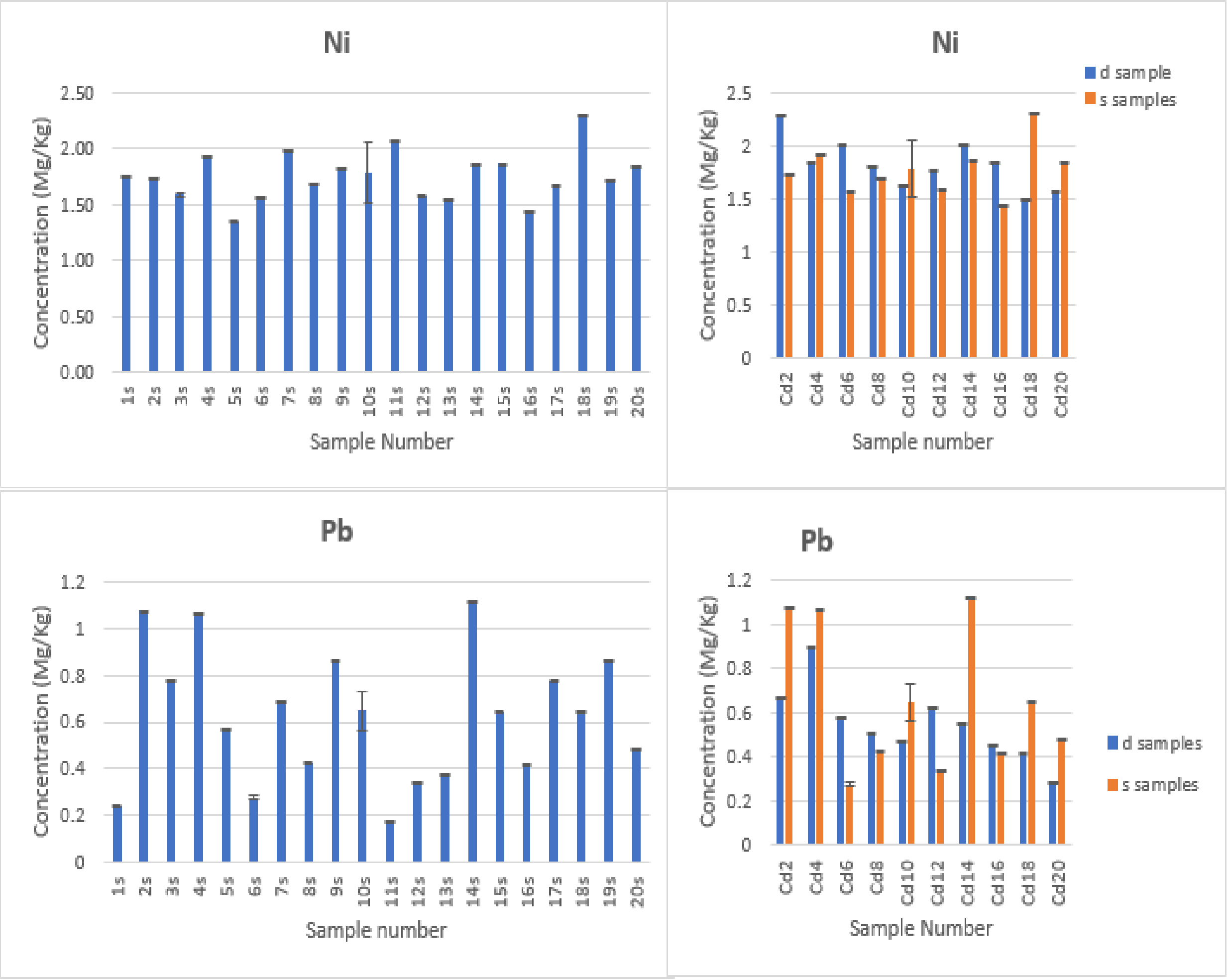


Fig 4.4 Concentration of Ni and Pb, plots shown on the left provides a comparison between both surface and deep samples.

4.2 Cd14 AND Cd6 PROFILE SAMPLES

4.2.1 pH VALUES

In Cd14 and Cd6 profiles, all the pH values obtained were found to be alkaline. Generally, pH values of Cd14 was found to be higher than Cd6 profile (Fig 4.5). The highest value for Cd14 profile was observed at 35 cm was7.60 and lowest value of 7.38 at 5cm. For Cd6 profile, samples at 60 and 50 cm both have pH value of 7.49 and the lowest of 7.34 was observed at 15 cm. pH values tend to decrease upwards.

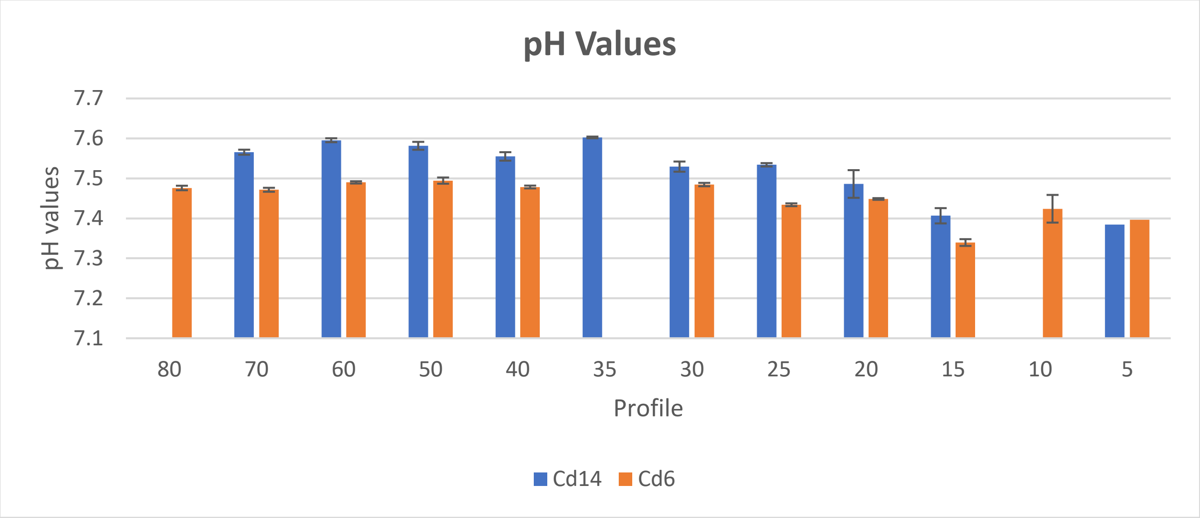


Fig 4.5: pH values for the soil profile from sampling point Cd6 and Cd14

4.2.2 AQUA REGIA EXTRATION

The determination of the pseudo-total concentration of Cd and other trace elements in the profile was observed and presented in Fig 4.6a and Fig 4.6b. The concentration of Cd observed ranges between 93.25 – 30.49 mg/kg for Cd14 profile at 35cm and 15 cm respectively. A decrease in concentration towards the surface was observed, although concentration at 5 cm was slightly higher than at 15 cm. The range of concentration of Cd in profile Cd6 was observed to be between 82.15 – 18.94 mg/kg at 50 cm and 5cm respectively. The highest concentration for any trace elements recorded for Cd14 profile is Zn at 35 cm with a value of 435.09 mg/kg, likewise for Cd6, the highest concentration is for Zn at 50cm, a value of 361.15 mg/kg.

A trend peculiar for Cd and other trace elements was a spike in the concentration of the elements at 35 cm for Cd14 profile, at that depth, Cd is 93.25 mg/kg, Cu is 126.66 mg/kg, Cr is 218.93 mg/kg, Ni is 92.15 mg/kg, Pb is 44.98 mg/kg and Zn is 435.09 mg/kg. The same trend can also be observed in Cd6 profile, the concentration of cadmium and other trace elements has a sharp increase at 50 cm, Values for Cd is 82.15 mg/kg, Cr is 179.20mg/kg, Cu is 105 mg/kg, Ni is 67.61 mg/kg, Zn is 361.15 mg/kg and Pb which is the only exception to this trend has the highest concentration of 46.20 at 80 cm, however, the value at 50 cm is closer at 41.78 mg/kg.

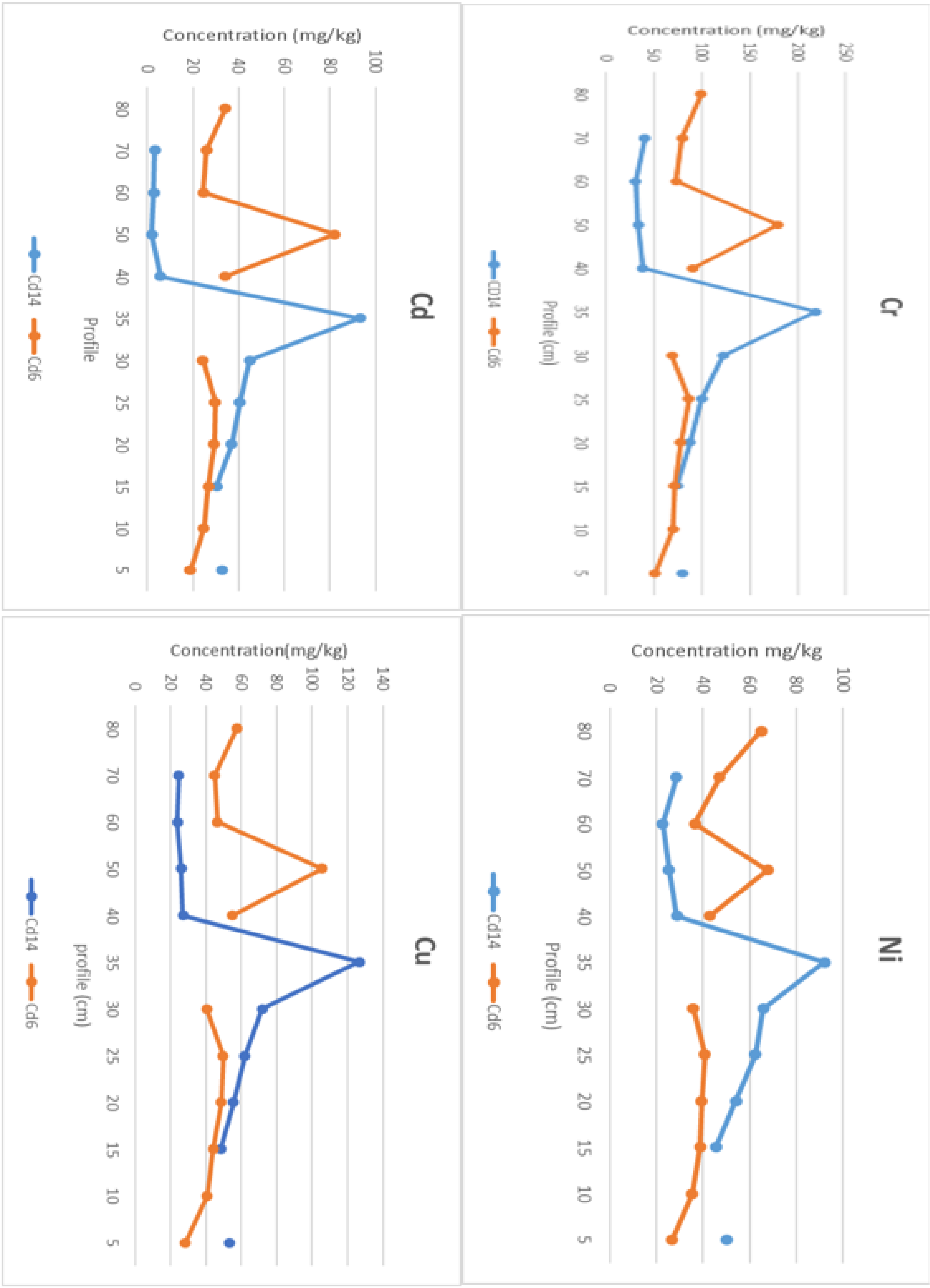


Fig 4.6a: Pseudo total concentration of Cd, Cr, Cu and Ni in Cd14 and Cd6 profiles.

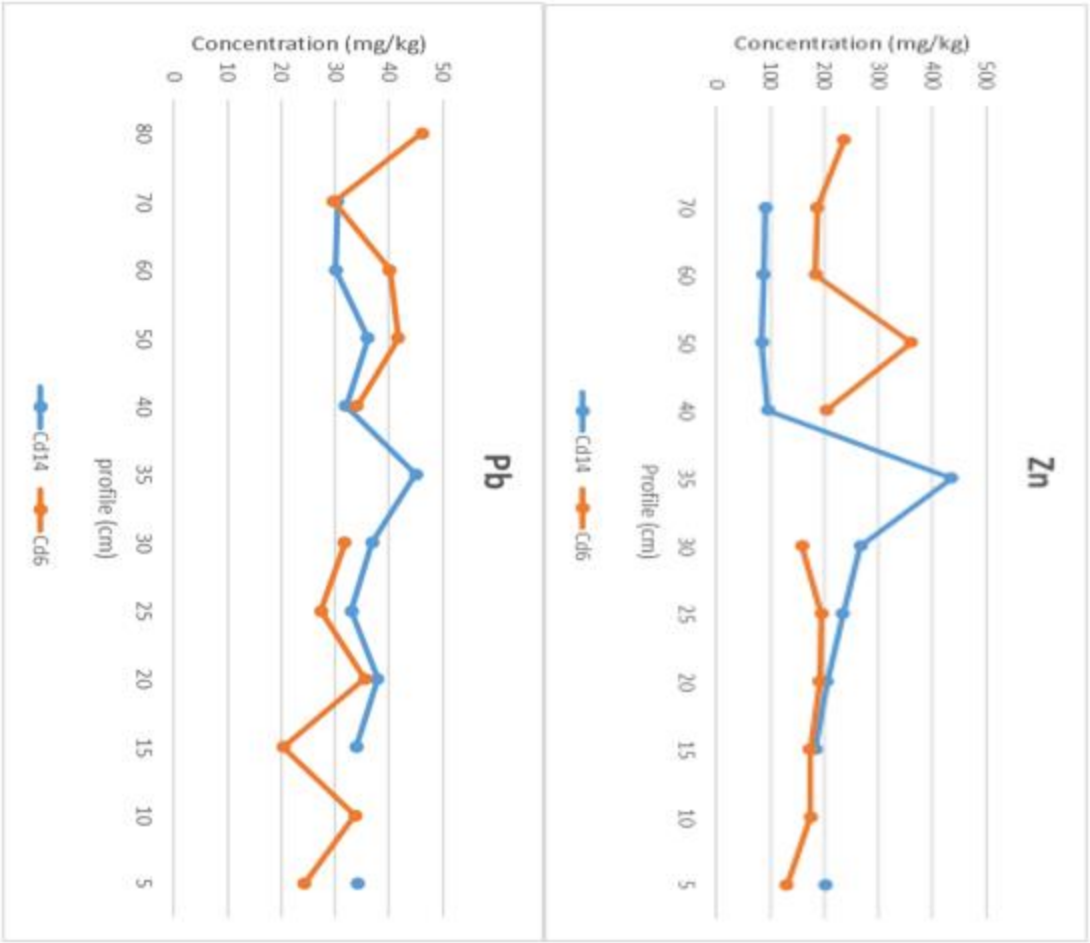


Fig 4.6b: Pseudo-total concentration of Pb and Zn in Cd14 and Cd6 profiles.

4.2.3 $CaCl_2$ EXTRACTION

The concentration extracted by $CaCl_2$ was for all the trace elements was below the detection limit of ICP-OES.

4.3 ROOT, SHOOTS AND RHIZOSPHERE SAMPLES

The concentration of Zn in roots at sampling point 14 was found to be that highest at a value of 82.2 mg/kg followed by Cd at a value of 39.05 mg/kg and Cu with a concentration of 15.08 mg/kg. the only element detected for Cd6 roots is Zn with a concentration of 45.26 mg/kg.

Concentration of Cd in rhizosphere soil was observed to be 15.24 and 24.81 mg/kg at points Cd6 and Cd14 respectively. Higher concentration was detected for Zn for all the samples, it was found to be highest in rhizosphere at point Cd6 with value of 370.99 mg/kg. see Fig 4.7a and 4.7b.

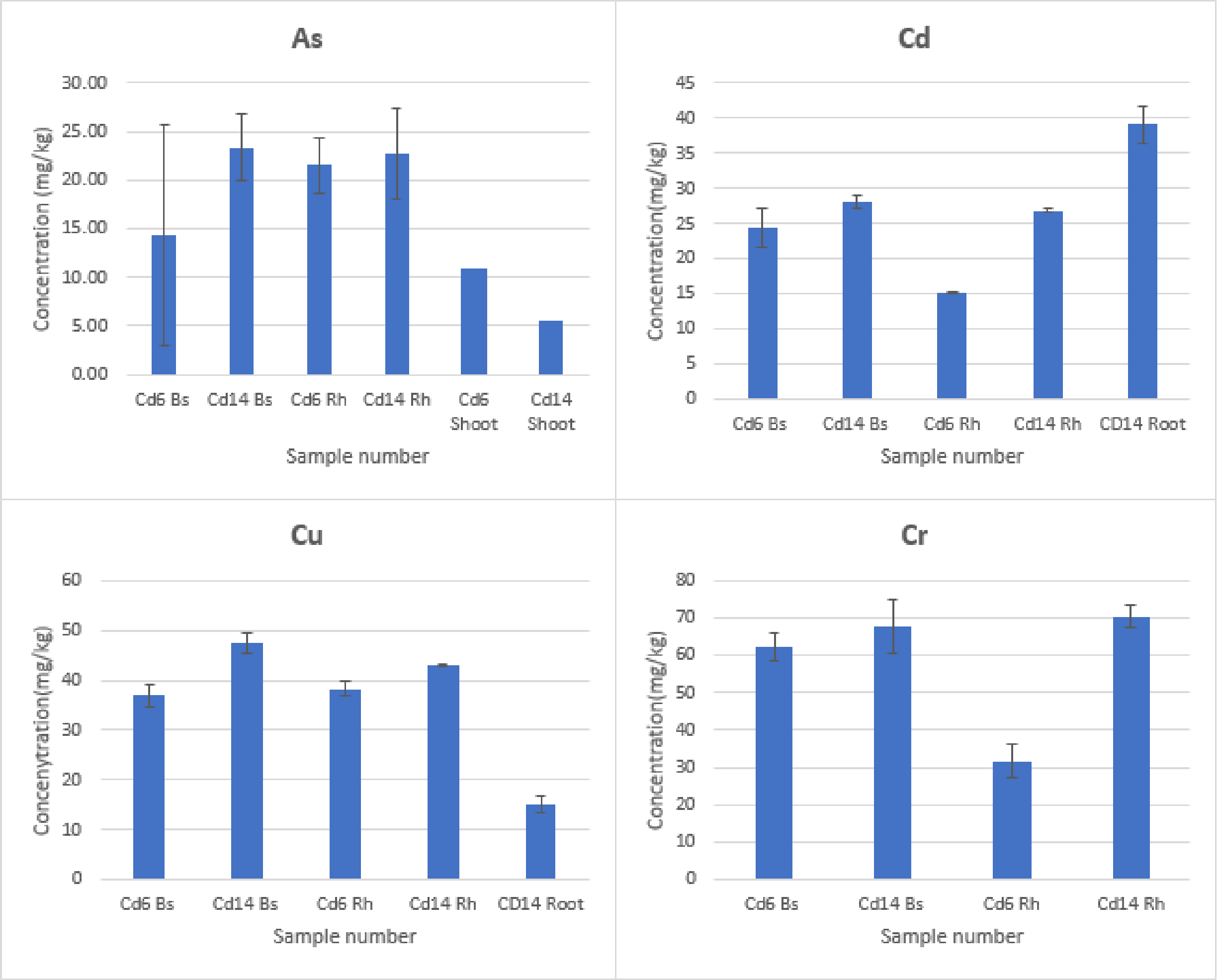


Fig 4.7a: Pseudo-total concentration of As, Cd, Cu and Cr in roots, shoots and rhizosphere samples

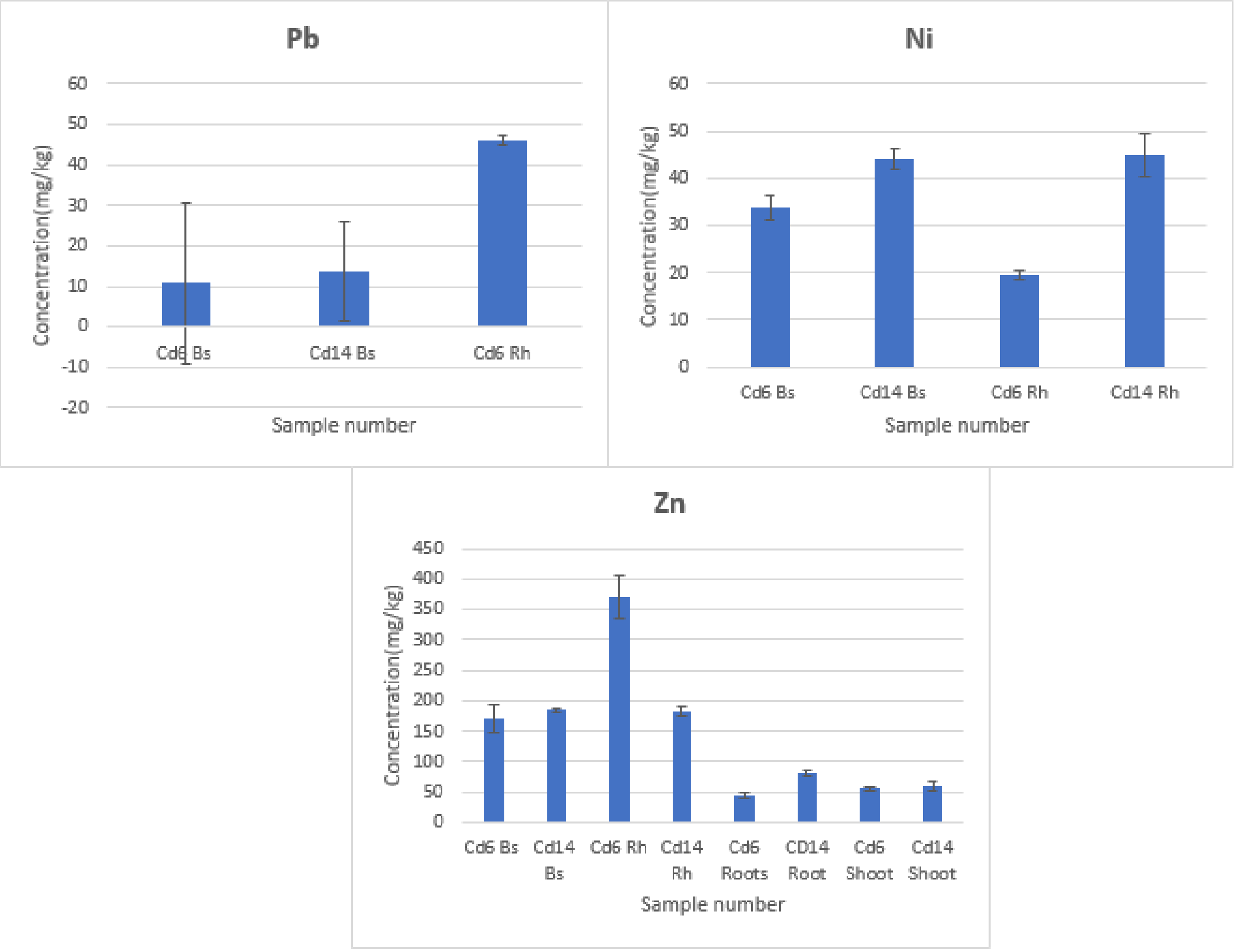


Fig 4.7b: Pseudo-total concentration of Pb, Ni and Zn in roots, shoots and rhizosphere samples.

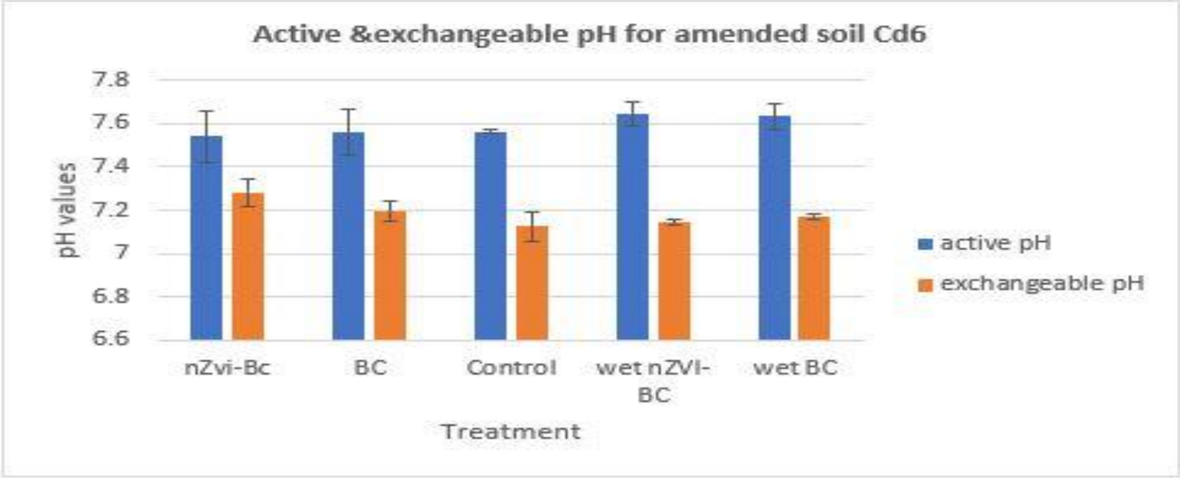
4.4 AMENDED SAMPLES

4.4.1 pH VALUES

In Cd14, wet nZVI-BC had the highest active pH value of 7.91 and the lowest was observed in Control sample 7.64. Likewise, wet BC has the highest pH value of 7.10 and the lowest was observed in BC at a pH value of 7.0, although there is only a slight difference between the exchangeable pH values observed in nZVI-BC, BC, Control and wet nZVI-BC at 7.04, 7.00, 7.04, and 7.06 respectively.

In Cd6 the highest active pH was observed in both wet nZVI-BC 7.64 although wet BC has a value of 7.63, the lowest was observed in Control sample with a value of 7.56 however, the values for nZVI-BC and BC is 7.54 and 7.55 respectively. This can be visualized in Fig 4.8 below.

Exchangeable pH value was observed as highest in nZVI-BC at value of 7.28 and the lowest was in Control at value of 7.12. In all the 5 samples, the difference in exchangeable pH was only 0.16.



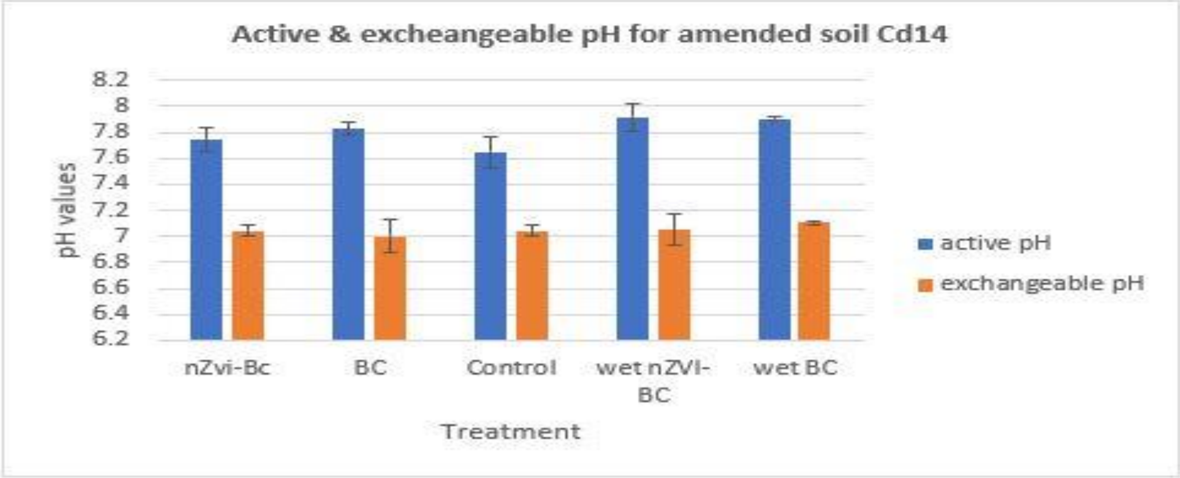


Fig 4.8: pH values for active and exchangeable values for Cd6 and Cd14 amended soils

4.4.2 EC AND Eh VALUES

Eh was measured in both demineralized and $CaCl_2$. The highest Eh value for Cd14 in demineralized water (DEMI) at a value of 431 mV was observed in nZVI-BC and the lowest was 383 mV in wet nZVI-BC. The highest Eh values in $CaCl_2$ was observed in Control at a value of 485 mV and both wet BC and nZVI-BC both have values of 422 mV, see Fig 4.9 below.

Meanwhile in Cd6, the highest value of Eh in demineralized water was found in nZVI-BC at value of 452 mV and the lowest was observed in wet nZVI-BC at a value of 430 mV. In $Cacl_2$ solution, the highest and lowest value was observed in Control and BC at values of 454 and 427 mV respectively.

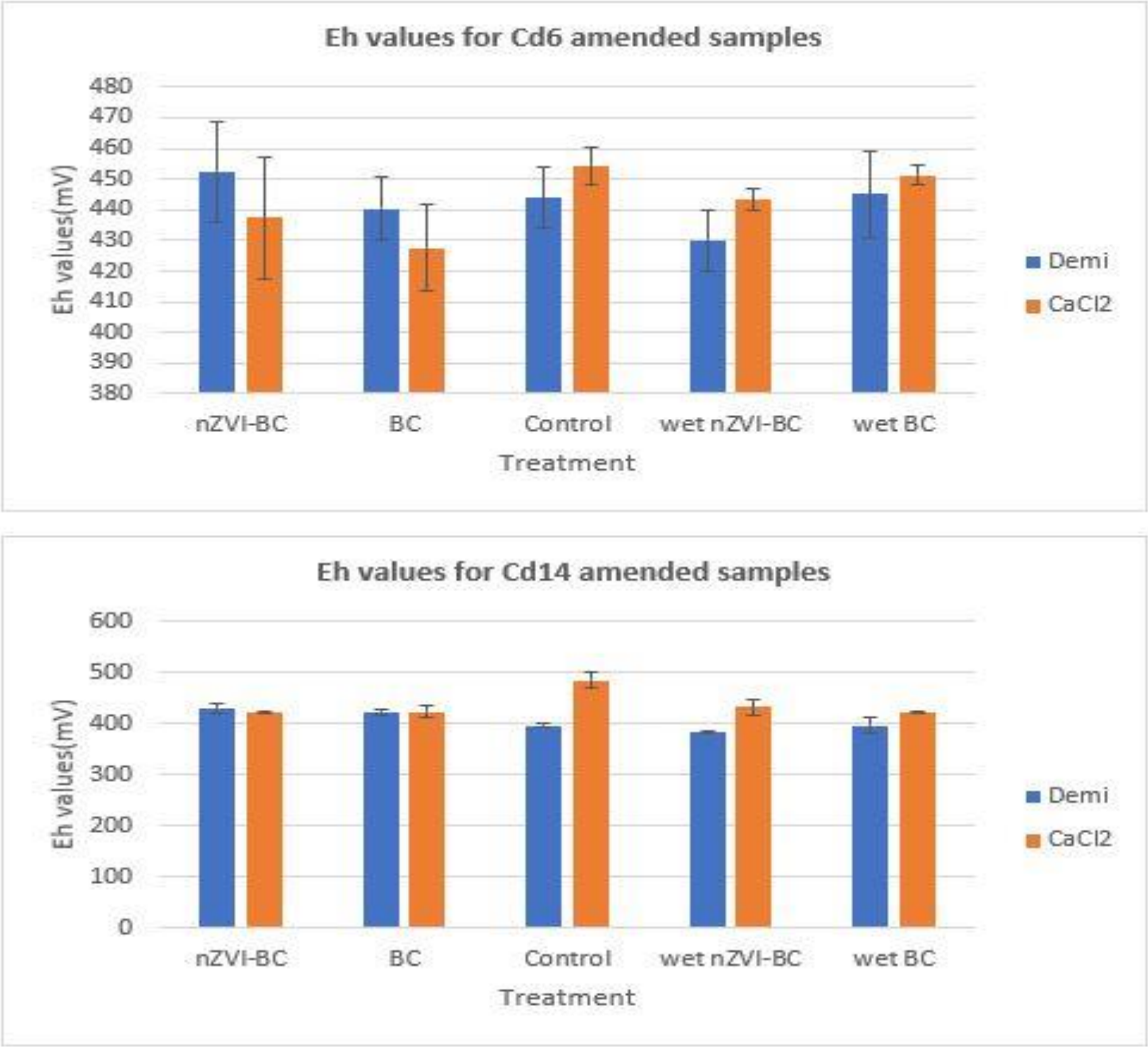


Fig 4.9: Plot of Eh for Cd6 and Cd14 for amended samples using demineralized and $CaCl_2$.

Electrical conductivity (EC) values measured for both Cd14 and Cd6 amended samples shows that Cd6 has higher values than Cd14 amended samples as seen in Fig 4.10. The highest EC value was observed in wet nZVI-BC, a value of 331 µs/cm and the lowest in BC at a value of 273 µs/cm. in Cd14, the highest and lowest EC value was observed in wet nZVI-BC and wet BC at values of 235 and 128 µs/cm respectively.

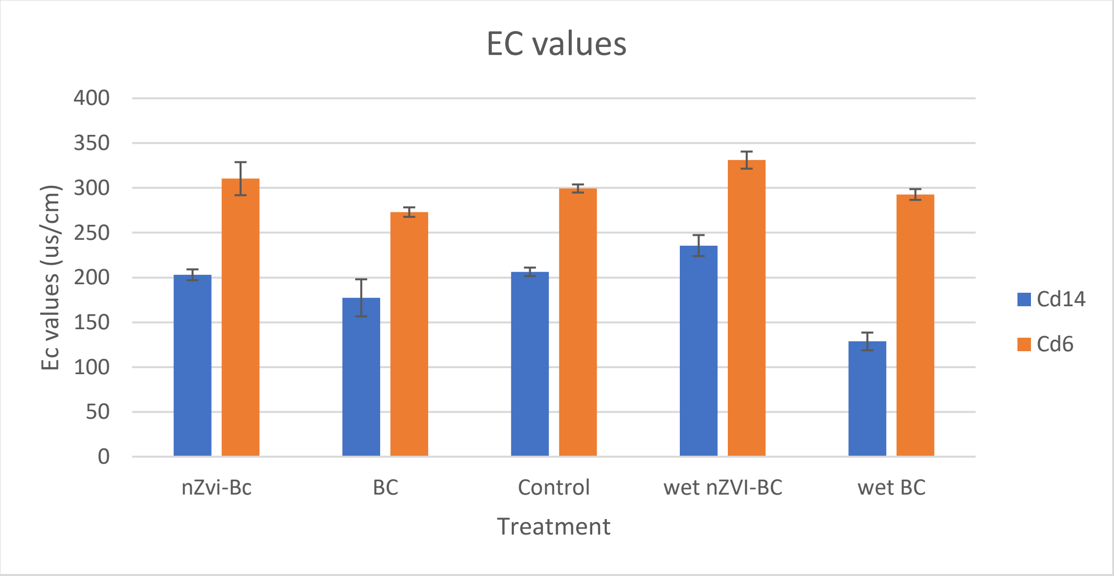


Fig 4.10: Plot of EC values for Cd14 and Cd6 amended samples.

4.4.3 DEMINERALIZED WATER EXTRACTION

In general, Demineralized water was able to mobilize Cd and other trace elements. The highest element mobilized with DEMI in Cd14 and Cd6 is Zn, the highest concentration was observed in wet BC for at concentration of 0.62 and 0.35 mg/kg respectively. Result for Cd, Cr, As, Cu, Ni shows higher concentration of the elements for wet BC with values of 0.05, 0.14, 0.17, 0.15 and 0.14 mg/kg respectively in Cd14 amended soils. However, the amendments show different concentration in Cd6 samples. The concentration of Cd in wet nZVI-BC was the lower than other amendments with a value of 0.016 for both Cd14 and Cd6 samples. Cd14 shows higher concentration for Cd and other trace elements for all amendments then the concentration seen in Cd6 samples as seen in Fig 4.11a and Fig 4.11b.

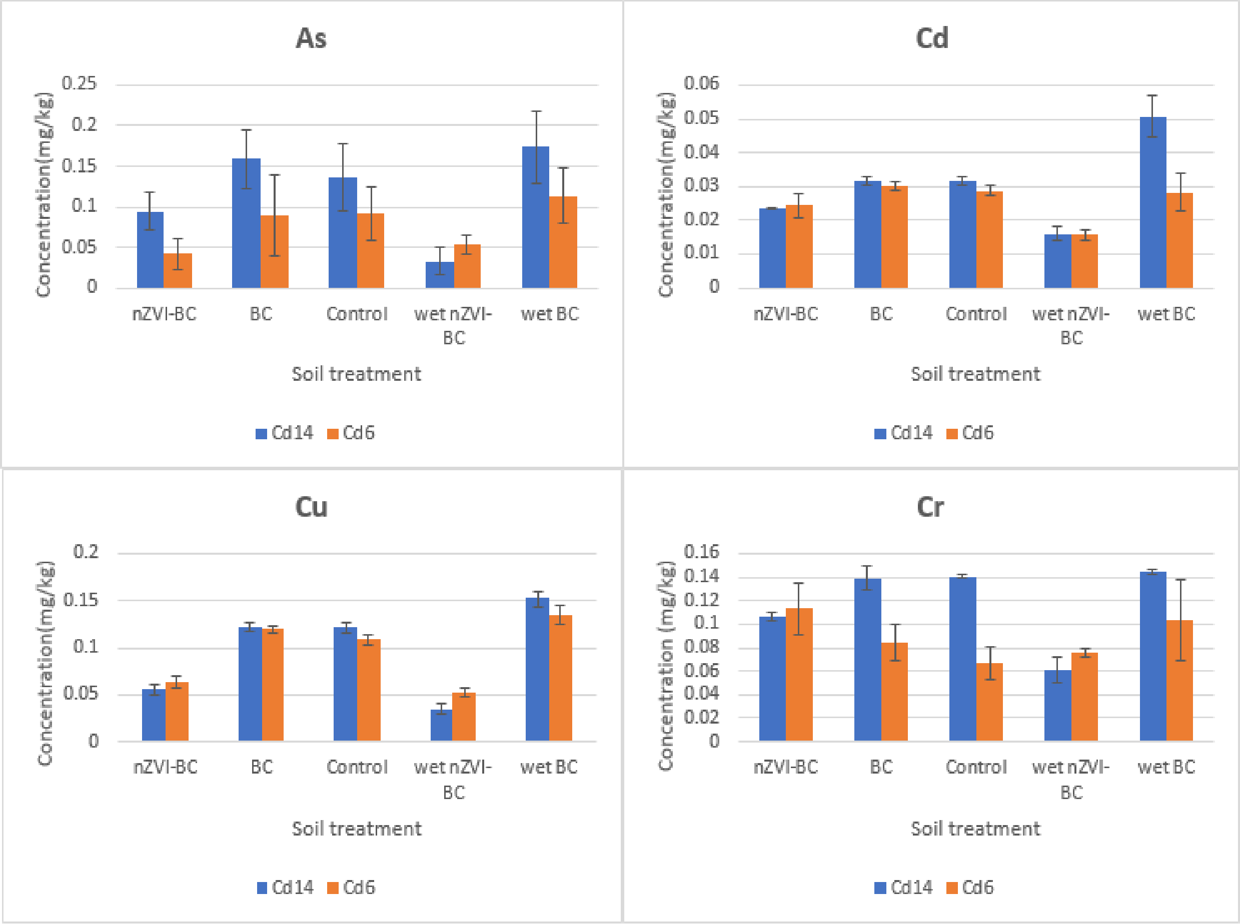


Fig 4.11a: Concentration of As, Cd, Cu and Cr mobilized by demineralized water for the amended samples

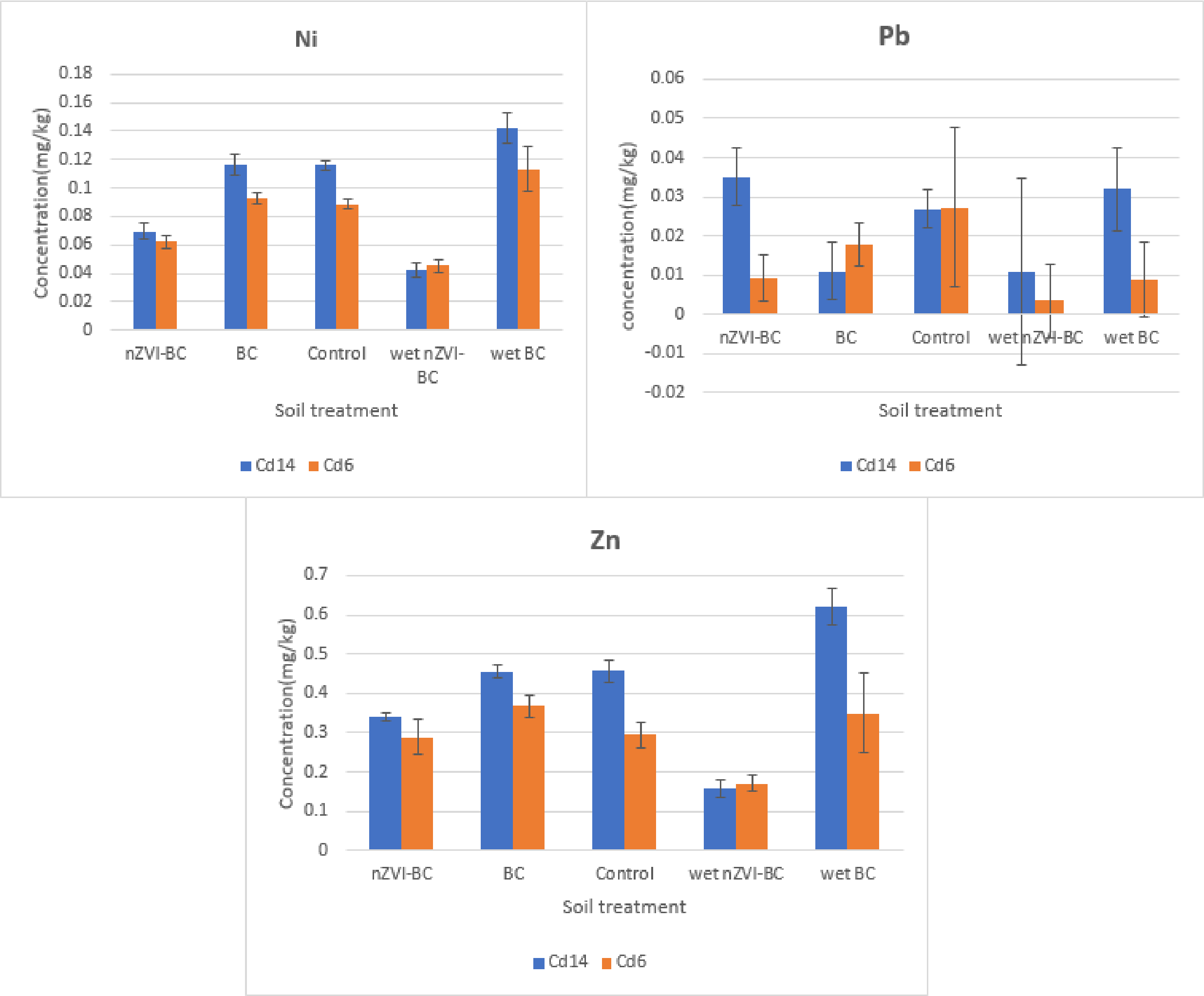


Fig 4.11b: Concentration of Ni, Pb and Zn mobilized by demineralized water for the amended samples.

4.4.4 ACETIC ACID EXTRACTION

Acetic acid mobilized Cd and 3 other trace elements in Cd14 and Cd6 samples for all the amendments (Fig 4.12). It was observed that all amendment used mobilized more concentration of Cd in Cd14 than in Cd6 samples. The highest concentration of 9.49 mg/kg of Cd was mobilized in wet BC amended sample, the lowest was for 8.41 mg/kg was the lowest observed in nZVI-BC. In Cd6, the concentration extracted by acetic acid ranges between 7.55 and 6.36 mg/kg of Cd observed in BC and control respectively. The extracted concentration of Cr for control sample in Cd 14 showed a large difference in the concentration extracted between both soil samples, 0.24

mg/kg in Cd6 and 0.07 mg/kg in Cd14. The values of concentration extracted for nZVI-BC, control and wet mZVI-BC was below the detection limit of ICP-OES therefore, the results were excluded.

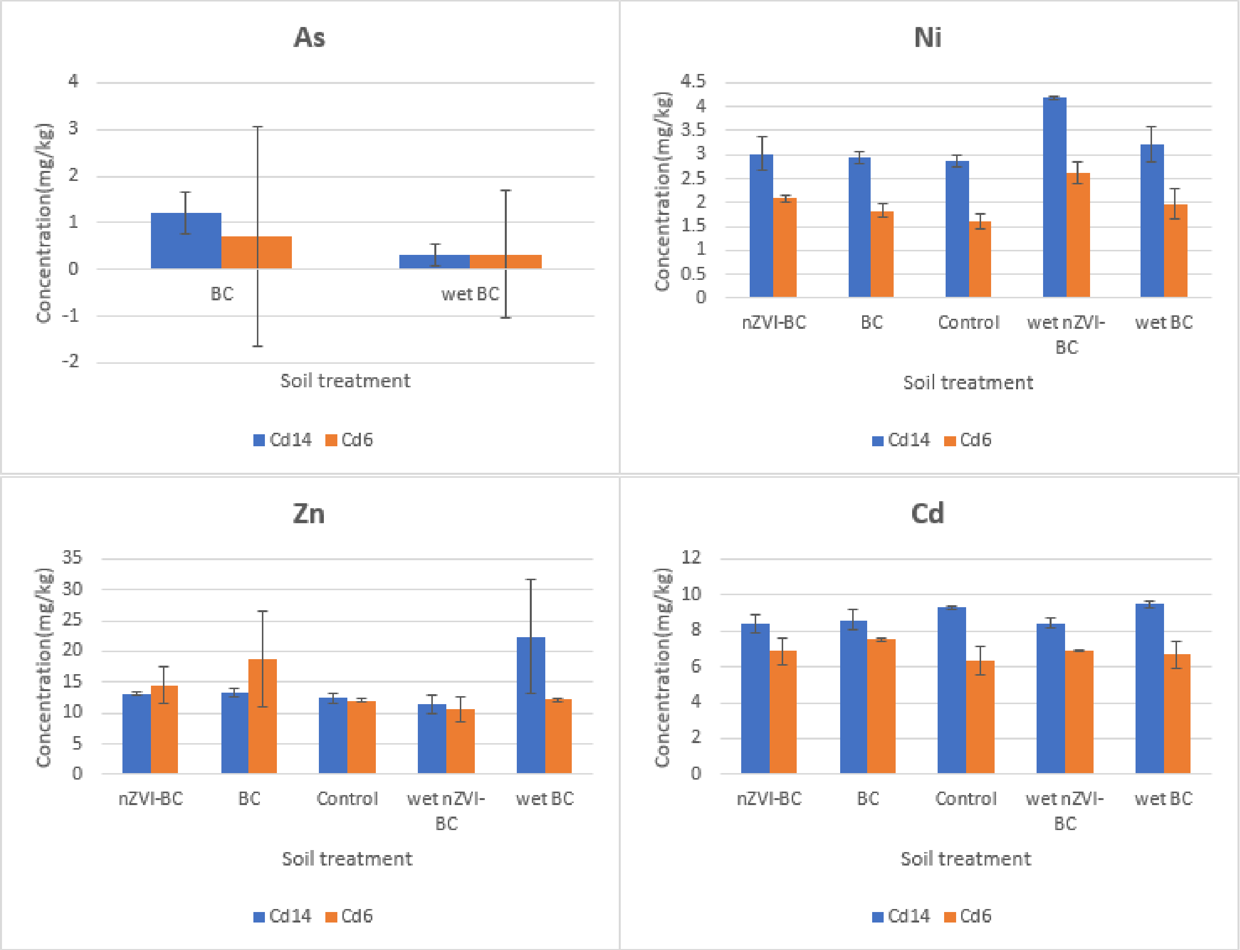


Fig 4.12: Concentration of metals extracted by Acetic acid solution for Cd14 and Cd6 samples.

4.4.5 $CaCl_2$ EXTRACTION

The results for the concentration mobilized by $CaCl_2$ were not presented as the values were below the detection limit of ICP-OES.

4.5 TOTAL ORGANIC CONTENT (TOC)

The general trend observed for the concentration of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) in Cd14 and Cd6 amended samples was that concentration of both DIC and DOC was higher in Cd6 than in Cd14 as seen in Fig 4.13, the only exception was the value of DIC where value for Cd14 was higher than the value of Cd6. The highest DOC content for Cd14 was observed in sample amended with wet BC with a value of 99.45 mg/kg and the lowest was observed in sample amended with wet nZVI-BC with a value of 27.83 mg/kg. For Cd6, the highest value of 148.89 mg/kg and the lowest value of 90.24 mg/kg observed in wet BC and nZVI-BC respectively. The DIC content for Cd14 amended samples was found to be highest for wet BC at a value of 124.22 mg/kg and the lowest for wet nZVI-BC with a value of 100.62 mg/kg.

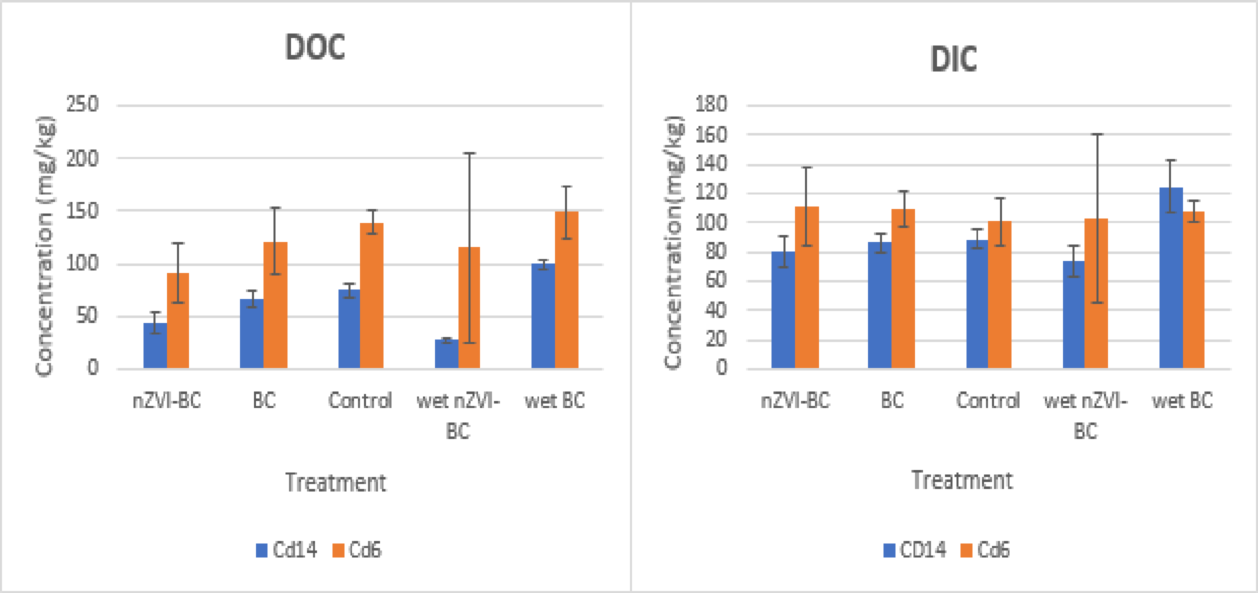


Fig 4.13: Dissolved organic and inorganic carbon content in Cd14 and Cd6 amended soil.

4.6 IONIC CHROMATOGRAPHY

Result for both Nitrate (NO^{3-}) and sulphate (SO$_4^{2-}$) ions were presented in Fig 4.14 below. The values of NO^{3-} for Cd14 ranges from 415.14 and 66.26 for wet nZVI-BC and wet BC respectively. The value of NO^{3-} for Cd6 is from 699.78 and 572.81 for wet nZVI-BC and BC respectively.

For SO$_4^{2-}$, the values range from 62.19 and 34.46 in BC and nZVI-BC respectively for Cd14 samples. The range for Cd6 is from between 95.87 and 78.19 in wet nZVI-BC and nZVI-BC respectively.

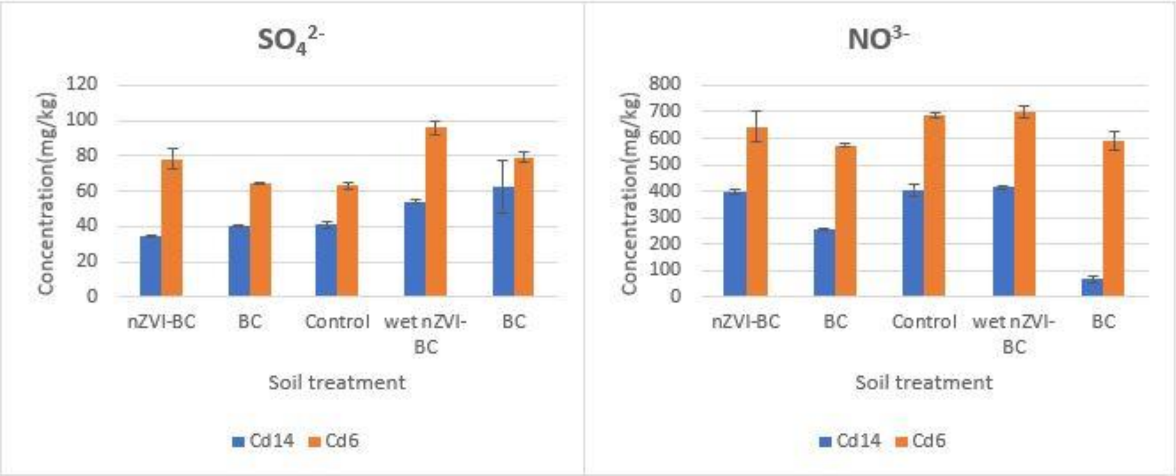


Fig 4.14: Nitrate and sulphate concentration from the soil samples with amendments.

5 DISCUSSION

5.1 PHYSICO-CHEMICAL PROPERTIES

Soil Ph determines the acidity or alkalinity of soil solution, basically, the concentration of Hydrogen ions (H^+) in the soil water together with its dissolved substances.

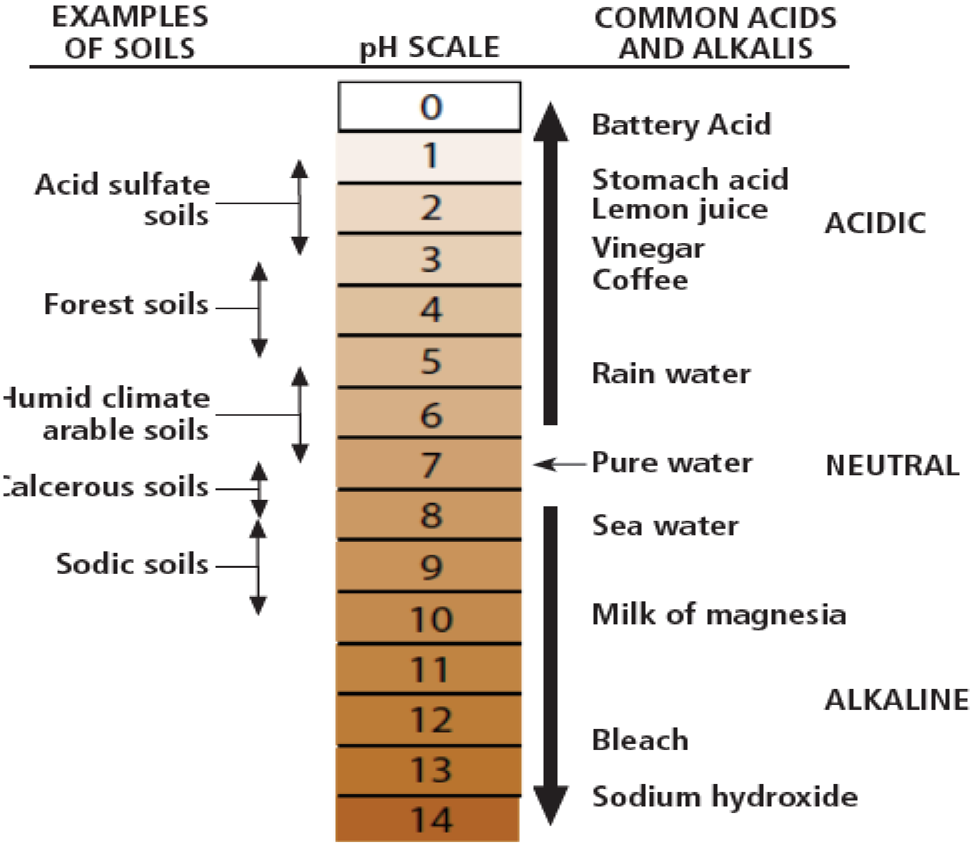


Fig 5.1: pH scale with categorizing common acids/alkalis and examples of soils. Extracted from McCauley et.al (2017).

The pH values of Surface (s) and deep (d) samples ranges between 8.23 to 6.98 with a mean pH of 7.41, this indicates that the soil pH is slightly alkaline to neutral, the exception to this is at sampling point 10s exhibiting a slightly acidic pH (6.98) and this is the lowest pH recorded for both surface and deep samples. Since soil pH is mostly dependent on common acid forming (H^+, $Al3^+$, and Fe^{2+}/Fe^{3+}) and base forming cations (Na^+, Ca^{2+}, Mg^{2+}, K^+) (McCauley et al., 2017), therefore the soil of the study area constitutes moderate amount of base forming cations to keep the pH values slightly above 7 for both surface and deep soil. Considering the Ph scale and soil examples in Fig 5.1, both s and d samples can be said to be between humid arable climate soil and

Calcerous soil. Likewise, soil profile Cd6 and Cd14 showed no significant difference from the surface and deep samples as they both have pH value ranging between 7.3 and 7.6. Generally, soil pH changes with depth due to leaching of ions of metals in soil, however this was not observed in the study area, therefore the soil may not be a source of pollution for underlying water sources.

The effect of the amendments on the soil samples did not result to a significant change in the soil pH. values of active pH were still in the range of 7.9 -7.5 for both Cd6 and Cd14 samples. As expected, exchangeable pH showed slightly lower pH values, ranging between 7.2-7.0 for all the amendments applied on Cd6 and Cd14.

The application of the amendments can further reduce the amount of acid cations leached in the soil under study. It can be said that Cd and other trace metals exhibit a strong bond to the soil organic matter. According to McCauley et al., (2017) the higher the soil organic matter and clay content, the higher affinity to bind with ions of metals and metalloids in soil, this reduced the bio availability of Cd and other trace elements for plants in the study area. Although roots of plants analyzed at sampling Cd14 without any amendment showed a total concentration of Cd up to 39 mg/kg, although uptake of metals and metalloids also depends on the plant system but since addition of biochar can increase organic matter in soil (Glaser et al., 2002) with the addition of the amendments used, the rate of Cd and other trace element uptake by plants is expected to reduce.

5.2 MOBILITY OF CADMIUM AND OTHER TRACE ELEMNTS IN THE SOIL PROFILE

The concentration of Cd and other trace elements after extraction by $CaCl_2$ was below detection limit of ICP-OES used to analyze the mobile fractions in surface and deep samples, however only Ni and Pb were above the detection limit. The highest mobile concentration of Ni and Pb was 2.29 mg/kg and 1.11 mg/kg respectively. The low mobile concentration of the metals and metalloids is deduced from the lower total concentration of Cd and other trace elements from the pseudo total digestion analysis performed on the surface and deep samples. The USEPA critical level of Cd in agricultural soils is 0.43 mg/kg (Chavez, 2015) thus the mobilized concentration of Cd (below detection limit of ICP-OES) was found to be below the critical level in the study area.

The concentration of Cd and other trace elements are expected to decrease with depth since the study area was contaminated by industrial activities. Borůvka et al (1996), found that mobility of Cd, Pb and Zn increased through soil depth, however, the result from this study area shows a contrast, Cd and other trace elements values for extraction using $CaCl_2$ were below the detection limit of ICP-OES used for the analysis indicating that Cd in the soil profile are strongly bound to the soil particles and the same trend was observed for other trace elements (Cr, Cu, Zn, Pb and Ni)

5.3 EFFICIENCY OF AMENDMENTS

In order to determine the efficiency of the amendments used (nZVI-BC, BC, wet nZVI-BC, wet BC and control sample), concentration of mobile fractions of Cd and other trace elements from amended samples from Cd14 and Cd6 were determined using 3 extractants (demineralized water, $CaCl_2$ and Acetic acid).

Wet nZVI-BC immobilizes As in the both samples when acetic acid was used as the extractant, and recorded lower values when DEMI was used, mobile fractions were also lower for Cu, Cr, Pb and Zn for wet-nZVI-BC. The amendment was able to bound strongly to trace elements in soil rendering them immobilizable and not available for plant uptake, therefore if the remediation goal is to immobilize the trace elements in a natural condition, the application of wet nZVI – BC in the appropriate condition can be used to prevent further contamination of soils.

Risk metals and metalloids mobilization is determined by the amount of metals present in exchangeable fractions and fractions bound to carbonates (Vanek,2005), metals and metalloids in this fractions can be mobile easily, and are released under natural soil conditions therefore posing more environmental risk to the soil and environment (Kabala & Singh 2001), the result of this study for simple extraction performed on the amended samples using demineralized water (Fig 4.11a and Fig 4.11b) mobilized more risk metals and metalloids that acetic acid and $CaCl_2$

Generally, there are more mobile fraction of Cd and other trace elements in Cd14 samples than Cd6 samples for all the amendments used. This indicates that irrespective of the amendments applied on the soil samples, Cd even in lower total concentration can be easily mobilized and taken up by plants.

However, it is not easy to quantify specific immobilization mechanism and it appears that the combined effect of two or more mechanisms leads to metal stabilization (Cao et al. 2003). Heavy metal immobilization by alkaline amendments is mainly attributed to soil pH rise, which increase negatively charged sites on soil particles and consequently promote cationic metal adsorption (Ok et al. 2007). Moreover, Cd precipitate as Cd(OH)2 is highly probable at pH value above 8 (Lee et al. 2008). Several studies, Hong et al. (2007), Ok et al. (2011) and Ahmad et al. (2012), also used lime-rich materials to reduce the mobility and bioavailability of heavy metals in contaminated soils. Biosolids are known to contain high total concentrations of trace and toxic elements, which exist in more pronounced concentrations in charred product (Bridle and Pritchard 2004; Lu et al., 2013).

The concentration of DOC and DIC in Cd6 was observed to be generally higher than Cd14 soils. It can therefore be concluded that metal and metalloids are retained in soil with higher amount of organic matter, a study carried out by (Xiao, 2015) and (Antoniadis, 2017) agrees that there is high retention of metals and metalloids in soils with high organic carbon content, not only on the amendments applied.

6. CONCLUSION

The most important properties of biochar causing their high sorption capacity are high pH, high O-content, high surface area and the presence of C-O-C functional groups. Therefore, it could be suggested that the most important mechanisms of Cd and Zn removal were electrostatic attraction and complexation with oxygen-containing functional group. Biochar application induced changes in soil chemical properties. For instance, it had significant liming effect. Soil electrical conductivity was higher in analyzed soils after adding the biochar. Likewise, properties nZVI such as high reactivity and large surface area are important in adsorption and degradation of pollutants. The application of both nZVI and BC therefore is modern alternative for remediation of polluted soils. The mobility and distribution of Cd followed no specific pattern in the soil profile and across the field under study. All tested treatments have shown great potential to mobilize Cd in amended soils. Relatively low Cd stabilization combined with low yield and nutrient concentrations response of alkaline amendments make firm conclusion as to the use of nZVI-BC, wet nZVI-BC and BC biochar for remediation of heavy metal contaminated soils. It is noteworthy that, application of nZVI-BC biochar to contaminated soils may bring many benefits such as: reuse of solid waste, pathogen elimination, and stabilize heavy metals and make the soil clean and healthy which will ensure the normal growth of crops. Hence, biochar- nZVI can be potentially an attractive alternative to solve heavy metal pollution problem in urban and peri-urban farming faced by the rapid urbanization and industrialization.

In the case of future research on the same location, more powerful analysis than ICP-OES should be employed as more values are below the detection limit.

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APENDIX

LIST OF FIGURES

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