# Czech University of Life Sciences Prague

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# Improvement of Soil Sorption Characteristics by Biochar Amendments

**Diploma Thesis**

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## Declaration

I declare that the Diploma Thesis “Improvement of Soil Sorption Characteristics by Biochar Amendments” is my own work and all the sources I cited are listed in the Bibliography.

Černošice, 13.04.2016

Bc. Marek Švec

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Thank you all…

# The Improvement of Soil Sorption Characteristics by Biochar Amendments

## Summary:

The biochar is a re-discovered technology based on pyrolysis of biomass from plant and animal production. It is a carbon rich material with properties and nutrient content depending both on pyrolysis conditions and original biomass. Its major attributes are very large specific surface area, high porosity of different pore size and high cation exchange capacity. Due to its properties, biochar is an effective media for adsorbing and immobilizing soil contaminants, for the case of this study circumscribed to heavy metals. As a soil amendment, biochar alters soil conditions by affecting soil pH, cation exchange capacity, organic matter and nutrient content, water holding capacity, soil biota and other, which might overall enhance soil sorption capacity in relation to soil conditions.

This study evaluates a sorption performance of biochar originating from contaminated biomass obtained from phytoextraction technologies, as pyrolysis is one way of disposing contaminated biomass, and compares it to performance of clean commercially available biochar by amending these biochars into two Fluvisols: Litávka soil, characterized as clay-loamy Fluvisol with significant heavy metal pollution coming from smelter facility, and Choťánky soil, unpolluted sandy-loam Fluvisol coming from agricultural field. For each soil the mixtures with both biochars as well as pure soil and biochar materials (creating sample matrix) were tested in desorption and batch sorption experiments, with Cd, Pb, and Zn metals being in focus of the study. During desorption experiments the release of the three metals from matrix was monitored, and during sorption experiments the sample matrix was loaded with 7 increasing concentrations of Cd, Pb, and Zn in a single element sorption.

The desorption experiment showed no released metals from contaminated biochar. The sorption results show that contaminated biochar is efficient in enhancing soil sorption capacity, especially in sandy-loam Choťánky soil. Moreover, its sorption efficiency is even higher than the one of clean commercial biochar. The examined 1 % (w/w) biochar amendment ratio is however not sufficient for such contaminated soil as Litávka.

**Keywords**: Biochar, Contaminated Biochar Disposal, Sorption, Soil Contamination, Lead, Cadmium, Zinc

# Table of Content

# 1 Introduction

During last few decades, humans have started considering the possible use of biochar, a bio-gas and bio-oil production by-product, as a soil amendment. As agricultural soils are depleting and eroding, nutrients are leaching from bare soils and contaminants are leaking into environment, there has been an effort to develop technologies suitable for mitigating these phenomena that are negatively affecting our soils and environment.

The biochar is a re-discovered technology based on pyrolysis of variety of organic mass, which mainly originates as a waste product from plant and even animal production, and is therefore a cheap source of carbonaceous material. Made by a pyrolysis process, biochar gains properties and behaviour different from an original biomass. It is a carbon rich material with properties and nutrient content depending both on pyrolysis conditions and original biomass. Its major attributes are very large specific surface area, high porosity of different pore size and high cation exchange capacity. As a soil amendment, biochar has proven to alter soil conditions by affecting soil pH, cation exchange capacity, organic matter and nutrient content, water holding capacity, soil biota and other. Due to its properties, biochar is an effective media in adsorbing and immobilizing soil contaminants, both organic components and heavy metals.

Pollution caused by heavy metals is a serious environmental problem occurring globe-wide and increasing significantly with large scale metals utilization after industrial revolution. Although some heavy metals are beneficial or even essential to living organisms in scant amounts, their elevated concentrations are toxic. It is therefore essential to develop techniques which inhibit heavy metals mobility and transportation from soil into plants. Former studies suggest that biochar can be useful tool and soil amendment for limiting risk element mobility and mitigating contamination.

The focus of this study is to determine whether biochar pyrolyzed from contaminated biomass obtained from phytoextraction technologies is suitable for soil application and immobilization of selected heavy metals.

# 2 Literature Review

## 2.1 Soil in Environment

Soil acts as a very unique part of biosphere, a natural buffer and geochemical sink of chemical elements and compounds flow into and from living organisms, atmosphere and hydrosphere. Its productivity is the most significant function for human survival and therefore keeping its ecological and agricultural functions is a task of importance (Kabata-Pendias, 2011).

### 2.1.1 Soil Properties

**Soil and Soil Solution**

Soil consists of solid, liquid (called soil solution) and gaseous phase. However for nutrition and element content, solid and liquid phases are the most important. The interchange of elements between solid and liquid phase is a constantly changing process with chemical and biological activities and is dependent on variety of soil properties: pH, moisture content, colloid characteristics, solid phase components solubility, soil temperature and biological activity. According to Jones (2012), nutrient elements exist in 4 solid forms:

1) water insoluble minerals,
2) slightly water soluble minerals,
3) ions present on soil exchange sites,
4) component of soil organic matter.

Nutrient uptake by plants happens only for ions present in soil solution. Elements adsorbed onto soil particles are not taken by the plant even in case of direct contact. Concentrations of elements present in soil solution and those present in solid state are in equilibrium (Jones, 2012). Therefore sorbing elements onto soil decreases their phytoavailability and overall environmental mobility, which can be utilized when dealing with soil contamination.

**Soil Texture and Structure**

Texture and structure give soil its physical properties. Soil texture represents quantity distribution of sand, silt and clay in soil. These soil separates are distinguished by their physical size diameter (sand 2.0 – 0.02 mm; silt 0.02 – 0.002 mm; clay <0.002 mm). Soil structure is an arrangement of soil separates, how do they form larger particles determining physical properties of soil such as tilth, water infiltration, drainage, and air exchange. This arrangement and stability of soil structure is supported by content of soil organic matter (Jones, 2012).

### Cation Exchange Capacity

Colloidal clay carries a negative charge resulting in ability of soil to sorb and exchange cations – cation exchange capacity (CEC). Amount of this charge is driven by mineral colloid characteristics and content of organic matter. CEC is usually expressed in centimoles per kilogram. Soils with high CEC have some typical characteristics compared to those with low CEC, e.g. high clay content, high organic matter content, high capacity to retain nutrients within profile and high water holding capacity (Adriano, 2001).

Some of the commonly found colloids CEC is mentioned by Jones (2012): Vermiculite 150 cmol/kg, Allophane 100 cmol/kg, Montmorillonite 80 cmol/kg, Illite 30 cmol/kg and Kaolinite 8 cmol/kg (mean values). Relative portion of these colloids determines the CEC of a whole soil. Organic matter content contributes to the soil CEC with the portion called humus, a stable organic matter which has undergone decomposition (mean CEC of 200 cmol/kg).

Under low soil pH, there is typically no or little cation exchange capacity, which increases with higher pH (Lehmann, 2007).

### Soil Organic Matter

Soil organic matter (or humus) refers to humic compounds of soil organic matter which remain in soil after removal of macroorganic and dissolved organic matter. It is a prominent material enhancing soil CEC due to its properties – the humic compounds are amorphous, colloidal, polydispersed, hydrophobic, acidic and high in molecular weight. It may also act as a chelating agent in soil solution. A presence of organic matter alters soil conditions in both physical and chemical ways and improves soil fertility. A portion of organic matter content in soil ranges from 1 % to 5 %, most soils have the content 1 % – 2 %. Soil organic matter has several important functions. Apart of environmental ones (such as soil erosion reduction, aggregate stabilization, tilth improvement, water retention improvement), it is the physicochemical properties that contribute to soil fertility and sorption – CEC increase, pH buffer and also source of essential elements (N, P, S, B). (Adriano, 2001; Jones, 2012).

### Soil pH

Soil pH is a key factor considering fertility and availability of elements (nutrient and other). Measured in soil solution, it refers to a concentration of $H^+$ ions which is in equilibrium with $H^+$ ions adsorbed onto soil colloids – clay and humus. These colloids contribute to soil acidity as they can act as $H^+$ donors. The concentration of $H^+$ adsorbed onto them represents a resistance to change in pH, a soil buffer capacity (Jones, 2012).

## 2.1.2 Soil Sorption

Both soil organic and mineral parts have an influence on present elements. Chemical composition of soil solution is a result of equilibria of solid phase (i.e.: kaolinite, illite and smectite, humus, hydrous oxides of Mn, Fe, and Al) and liquid phase of water with dissolved constituents (i.e.: free or complexed metal ions, dissolved organic carbon and ligands). Interface between these phases is characteristic with vivid reactivity where trace elements participate in various reactions. Processes of both biotic and abiotic nature driving the speciation, fate, mobility, and availability of trace elements are shown in Figure 1. Namely these are ion exchange (adsorption – desorption), solubilisation (precipitation – dissolution), and absorption by living organisms (assimilation – immobilization) (Adriano, 2001).

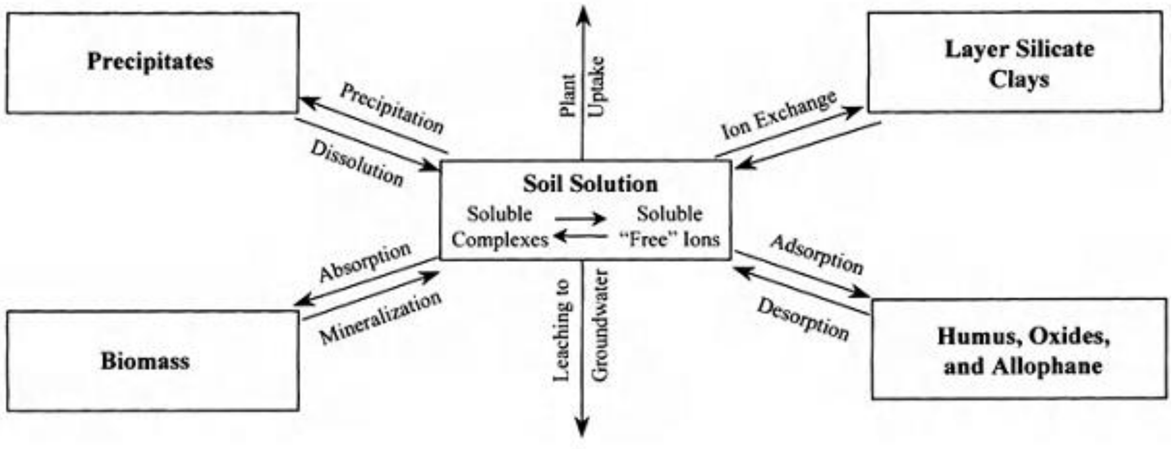


*Figure 1: Schema of key interactive processes in the soil system affecting the partitioning of trace metals between the aqueous and solid phases (from Adriano, 2001)*

Sorption, among the mentioned biogeochemical processes, is considered to be the key mechanism influencing partitioning trace elements between solid and liquid soil phases (Lehmann, 2007). Any removal from solution on a solid particles is called (soil) sorption, an inverse process desorption. Adsorption refers to accumulation of chemicals on liquid and solid interface, absorption stands for accumulation of chemicals within solids or liquids. Incorporation within substances within an expanding solid is then a precipitation. Adsorbing solid phase is called a sorbent, liquid phase contains potential sorptives, and the sorbed substances on or within solids are called sorbates. Soil sorption represents combined effects of ion exchange, specific adsorption, (co)precipitation, and (surface) complexation on the ion transfer from liquid onto solid phase (Thompson and Goyne, 2012). The major sorbents in soil are layer silicate clays, metal-(oxyhydr)oxides, and soil organic matter. In soil cations prevail, therefore cation exchange is emphasized; anions in form of oxyanions are comprised in anion exchange. On the clay and soil solution interface, cations with lower charge may substitute cations of higher charge, gaining an exchange site with one net negative charge which attracts cations from solution. These are bond by weak electrostatic bonds and may be exchanged for another cations from solution, the most abundant cations in soil are bound weakly compared to the most trace cations. These attractions are called nonspecific, are pH independent, on permanent clay charges and cations are sorbed reversibly here. This is also called a physical adsorption and is facilitated by cation exchange (1). Second type of adsorption is called a specific adsorption, chemosorption, or surface complexation (2). Specific adsorption is dependent on pH, cations are sorbed less reversibly and selectively on variable charge surfaces and complexation with organic matter functional groups. During a specific adsorption, some protons are displaced from surface and change in pH occurs. Generally with pH increasing, pH dependent surface charge increases leading to cation exchange increase. Surface charge may also increase with deprotonation of exposed hydroxyl groups in clay layer – in acidic conditions these carboxyl groups can be protonated from soil solution creating positive charge. Increased pH creates higher cation adsorption due to higher negative surface charge density and higher concentration of $–OH^+$ species (Adriano, 2001).

Sorption in soil is ruled by several mechanisms: (1) sorptive concentration in solution, (2) charge of sorptive and sorbent, and (3) solution pH (Adriano, 2001). To describe the sorption affinity of metals for soil solid phase and their fate in soil matrix, two different approaches to modelling exist: an empirical model and a mechanistic (semi-empirical) model. While the mechanistic models, as a model of constant capacity, model of diffusion layer and model of triple layer, are mathematically complex, take in count the electrostatic powers (between ions in solution and charged solid surface), and try to give a basic description of mechanisms involved, the empirical models aims at empiric description of experimental data and do not take in count the electrostatic powers (Dube et al., 2001; Bradl, 2004).

Empirical models utilize simple mathematics relationships between metal concentration in soil liquid phase and solid phase at equilibrium (equal chemical potentials) and constant temperature, called isotherms (Bradl, 2004). Two elemental empirical models are Langmuir and Freundlich adsorption isotherms. The Langmuir isotherm was developed to characterize adsorption of gas onto solids, but has been used to describe adsorption of trace metal ions and concentrations of ions in solutions (Adriano, 2001). While Langmuir model presumes monolayer adsorption and describes well the metal sorption at lower concentrations, the Freundlich isotherm is needed for high metal concentrations. The basic empirical models can be enhanced by involving additional mechanisms, e.g. competition for sorption sites is well described by Langmuir-Freundlich isotherm. An isotherm for multilayer adsorption between gas and solid was developed by Brunauer, Emmett and Teller and is so called BET equation (Bradl, 2004). Competitive Freundlich Adsorption Model and its modified version are examples of models used for extremely heterogenic soil surfaces (Dube et al., 2001).

## 2.2 Trace Elements

Trace elements are a group of naturally occurring elements in environment of great significance on soil fertility although they are present in scarce amount in the soil. While Earth scientists view trace elements as those with concentration in media lower than 0.1 %, biochemists consider trace elements with concentration lower than 0.01 % in an organism. Considerable trace elements are: As, Ag, B, Ba, Be, Cd, Co, Cr, Cu, F, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V and Zn. Depending on particular different use, some of them are referred as trace metals, heavy metals, minor elements or micronutrients. These elements are toxic to living organisms when present in elevated concentrations available to them. They might be required by living organisms in low concentrations, however the group comprises elements with not known functions in living organisms. Because of their environmental toxicity when occurring in abundant amounts, they are also referred to as risk elements (Adriano, 2001).

In case of this study, following trace elements were taken into account: Pb, Cd, and Zn. All three of them can be found in mainly urban areas and are considered most important environmental metals, whose usage increased with growth of primary production, mainly smelting industry. The anthropogenic emissions are 10 – 20 times higher than from weathering of geological materials (Adriano, 2001). Background content is however important, too, as is influenced mainly by geological factors and soil physicochemical properties on particular different sites (Kabata-Pendias, 2011).

Mean values for European top soils as published by Kabata-Pendias (2011) are 0.28 mg/kg for Cd, 32 mg/kg for Pb and 68.1 mg/kg for Zinc. The maximum permissible values in soils of the Czech Republic as given by Czech legislation norm (Decree No.13/1994 Coll) are: 1 mg/kg for Cd, 140 mg/kg for Pb and 200 mg/kg for Zn for normal soils in *aqua regia* extract. These values are however of older date based on data from 1990's and therefore might be considered outdated. A new study by Vácha et al. (2014) promotes updated values that could replace the current legislation – namely 0.5 mg/kg for cadmium, 60 mg/kg for lead and 120 mg/kg for zinc for the normal soils and extraction by *aqua regia*.

### 2.2.1 Soil Contamination

"The soil is nature's purifying agent. The soil as a physical, biological, and chemical filter. The soil as a pollutant sink*"*. These are words used by Adriano (2001) to show the important cleaning roles the soil plays in the environment. Soil undergoes various processes that influence its components including contaminants.

Soil pollution by heavy metals is tracked back to Bronze Age when smelting and ore processing were established. When metals are introduced into soil, their fate depends upon soil physicochemical properties and also on their speciation. Soil pollutants are very persistent and especially pollution by heavy metals seems to be permanent, although present metals are slowly leaching, taken up by plants, eroding and deflating. Residence time of heavy metals is however estimated to last decades and even millennia under temperate climate depending on particular species (Kabata-Pendias, 2011).

Behaviour, mobility and phytoavailability of metal cations in soil depends generally on soil properties and speciation related to chemical forms and time of impaction. Atmospheric forms are oxides, silicates, carbonates, sulphates and sulphides, the forms coming from sludge and waste differ according to origin and treatment, association with organic forms are common in municipal wastes, industrial effluents influence the speciation of factory discharges. Effects on soil properties is influenced by heavy metals chemical reaction with all three soil phases and their residence times. Mobile fraction of metals acts as bivalent cations and is governed by equilibria processes between solid and mobile fractions that are influenced by soil properties, of which pH and redox potential are of most importance. Solubility of heavy metals is thus dependent on soil pH (influenced by presence of soil organic matter) and other factors as cation exchange capacity, carbonates, clay minerals, ferrous and manganese oxides. Permissible rates of trace elements in soils are not same everywhere, they do vary according to local geochemical conditions and also hygienic standards. Initial content, total heavy metal load, dose limitation, plant toxicity and sensitivity and soil characteristics are some of factors needed to be taken into account when assessing acceptable heavy metal rates (Kabata-Pendias, 2011).

Not only trace elements (heavy metals, e.g.: As, Cd, Hg, Pb, Zn) but also organic contaminants (e.g.: PAH, PCB, dioxins) are polluting soils and environment for centuries on a global scale and are thus affecting environmental resources. Over 80 million ha of soil are contaminated worldwide, in European Union over 3 million sites has been reported as potentially soil polluting and from these, 37 % are contaminated by trace elements, 29% by organic pollutants and 33.7 % by mineral oils (EEA 2007a, b; Evangelou et al., 2015).

Immobilization of risk elements in soil renders them less toxic. Focuses on mitigating the risk of groundwater contamination, plant uptake and exposure to living organisms and creates conditions encouraging growth of plants and overall restoration of environment. According to (Evangelou et al., 2015), following amendments have been tested for in situ trace element immobilization: organic matter, zeolites, clay, phosphorus and iron rich materials and manganese oxides. They function on 2 principles, first they help creating insoluble precipitants and hence reduce contaminant solubility, second they increase soil sorption capacity. This increase in binding capacity can be achieved by the adsorbent addition itself or by induced pH changes in soil (Evangelou et al., 2015).

### 2.2.2 Element Toxicity

Toxicity of trace elements consists of bioavailable intrinsic amounts that have potential to cause adverse effects on living organisms. Their phytoavailable amount in soil solution, which is different from total soil content, is ruled by chemical environment and soil properties such as texture, CEC, organic matter, P content and pH (Tinsley and Darbyshire, 1984; Jones, 2012). The toxicity is increased by their retentive presence in contaminated environment and ecosystems, having relatively long retention time and biological half-life

(Mani and Kumar, 2013). Heavy metals become even more toxic when present in a nutrient poor ecosystems with acidic conditions (Mukhopadhyay and Maiti, 2010). Both heavy metals and organic pollutants can accumulate in plants (among other organisms) to an extend affecting their live functions, such as biochemical and physiological processes, photosynthesis ability, respiration ability and organelles degradation which results into inhibition of growth, stunned development, premature leaf fall, chlorosis, loss of enzymes, reducing yield and even death of plants. Soil microbial processes are particularly sensitive on present chemicals (Mohanty el al., 2011; Mani and Kumar, 2013).

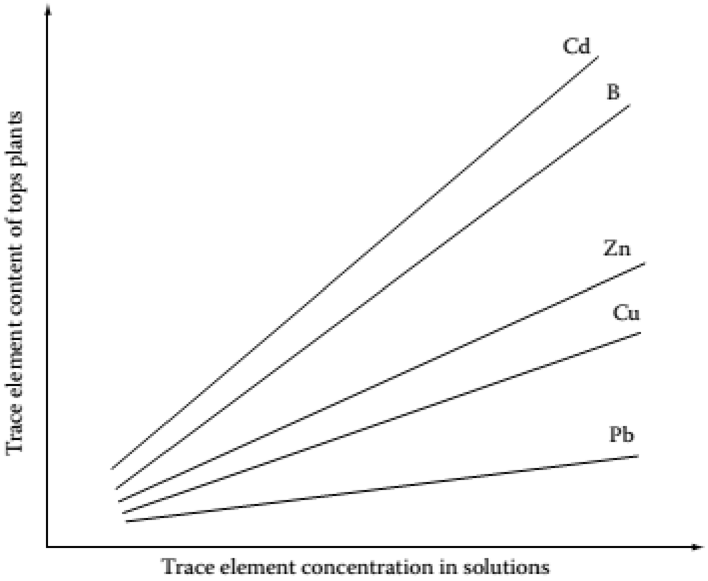


*Figure 2: Trace element uptake by plants according to their concentration in nutrient and soil solution (from Kabata-Pendias, 2011)*

Kabata-Pendias (2011) showed linear response (Figure 2) of trace element absorption by several plant species and concentration in their tissues to concentrations of these elements in nutrient and soil solutions. The phytoavailability of these elements is in correlation with cations present in soil solution (Table 1).

| **Metal species** | **Phytoavailability** |
|---|---|
| • Simple or complex cations in solution phase | Easy |
| • Exchangeable cations in organic and inorganic complexes | Medium |
| • Chelated cations | Slight |
| • Metal compounds precipitated on soil particles | Available after dissolution |
| • Metals bound or fixed inside organic substances | Available after decomposition |

| | |
|---|---|
| • Metals bound or fixed inside mineral particles (primary or secondary soil minerals) | Available after weathering and decomposition |

*Table 1: Relative phytoavailability of metal species in soils (from Kabata-Pendias, 2011)*

### 2.2.3 Cadmium

Cadmium (Cd) is considered one of the most toxic metals with adverse effect on all plants, animals and humans. Comes from natural zinc carbonate and sulphide ores, copper carbonate and sulphide. Its occurrence is connected with lead and zinc ores. Artificially then comes from mining and smelting industry (as parts of various alloys), metal finishing, batteries, plastic industry, fertilizers and sewage sludge. Occurs in form of $Cd^{2+}$ ions, halides, oxides, hydroxides, carbonates and Cd-CN complexes (Adriano, 2001).

Cadmium is a very mobile element whose compounds easily weathers and enters soil solution where it may form complex ions and organic chelates. About 50 % - 90 % of its content in solution is present as immediately plant available $Cd^{2+}$ ion. Cadmium mobility is affected by present soil organic matter, yet the main factor influencing mobility is pH. Cadmium is best mobile in pH range 4.5 – 5.5. At alkaline pH (> 7.5) cadmium is not readily mobile with $CdCO_3$ and $Cd_3(PO_4)_2$ controlling the mobility. In acidic soils, soil organic matter and sesquioxides control cadmium solubility, in alkaline soils, cadmium compounds precipitate. Competitive sorption decreases adsorption of Cd in presence of other metals, such as zinc, lead and copper (Tlustoš et al., 2007; Kabata-Pendias, 2011). At low Cd concentrations in soil, adsorption is the mechanism driving its behaviour (ion exchange), at higher Cd concentrations precipitation prevails (Adriano, 2001).

Symptoms of toxicity in plants include brown margin of leaves, chlorosis, curled leaves, brown stunned roots and reddish veins and petioles (Kabata-Pendias, 2011). Considering human health, cadmium can damage metabolism of calcium, synthesis of vitamin D and collagen, and can also lead to bone degradation, long term oral and nasal exposure can affect kidney functions (Adriano, 2001).

### 2.2.4 Lead

Two categories of lead occur in the environment, primary lead from bedrock minerals and secondary from radiogenic decay of uranium and thorium. Ratio of their isotopes is used to track origin of lead and finding pollution sources (Kabata-Pendias, 2011). Lead naturally occurs mostly as galena (PbS), which is a long-standing subject of mining and smelting. Apart of that it also occurs as pollutant (mainly in top soils) in automobile exhaust (strongly declined), painting industry, steel industry, battery manufacture, plumbing (former use) and sewage sludge. Could be commonly found as Pb metal, oxides, carbonates and metal-oxyanion complexes (Adriano, 2001).

Apart of common $Pb^{2+}$, lead also can rarely appear as $Pb^{4+}$ which however is insoluble. In soil, lead has strong sorption affinity to organic matter, which increases with pH and is also a reason why lead cumulates beneath soil surface. Fixation to clay minerals is strong for lead, too. Mobilization is slow and is influenced by soil acidity and complexes formed with organic matter. Lead is considered the least mobile heavy metal, its concentrations in soil solutions are low, yet the dissolved lead can move through soil horizons to contaminate groundwater. To increase its mobility, i.e. for phytoremediation purposes, lead can be effectively mobilized by chelating agents (Tlustoš et al., 2007). Sorption of lead in soil is an interplay of three mechanisms: (1) specific adsorption generally driven by organic matter and clay, (2) precipitation of partially soluble or stable compounds containing lead, mainly phosphates, and (3) formation of stable complexes with organic matter. Lead has ability to replace K, Ba, Sr and Ca in sorption sites and minerals (Adriano, 2001).

Plant toxicity is exhibited as dark green leaves, wilting of older leaves, stunned foliage and short brown roots (Kabata-Pendias, 2011). Lead exhibits health risk especially for children, permanently damaging nervous system, inhibiting ability to create haemoglobin, and affecting kidney function among other. Pb poisoning caused by long term exposure can lead up to colic, encephalopathy, or even paresis (Adriano, 2001).

### 2.2.5 Zinc

Could be found as ZnS, $ZnSiO_4$, $ZnCO_3$ and mine drainage in nature, artificially occurring could be found in areas of mining and smelting industries, metals finishing, microelectronics, pyro-metallurgical industry and sewage sludge, too. Occurs as Zn metal, oxides, carbonates and $Zn^{2+}$ ions (Adriano, 2001), in soil solution then as free and/or complexed ions: $Zn^{2+}$ (mainly), $ZnCl^+$, $ZnOH^+$, $ZnHCO_3^+$, $ZnO_2^{2-}$, $Zn(OH)_3^-$, $ZnCl_3^-$ and also organic complexes (Kabata-Pendias, 2011).

Zinc concentration in soil prevails in top surface horizons as is sorbed by soil organic matter. Its fixation is relatively low and significantly influenced by soil pH as well as other present metals. Zinc is considered as very mobile element in most soils, however can be bound strongly by clay particles and soil organic matter in neutral and alkaline soils and moreover dissolved organic matter in alkaline pH range of 7 – 7.5 (Wong et al., 2007; Kabata-Pendias, 2011). Two different mechanisms of zinc sorption exist: based on cation exchange sites in acid media and chemosorption influenced by organic ligands in alkaline media. Adsorption of zinc can be reduced at pH < 7 by competing cations which results in high zinc mobility and tendency to leach. At higher pH values the presence of organic compounds and zinc complexation may contribute to the solubility (but not in sandy acid soils where organic matter plays major role in zinc binding). Zinc mobility and plant availability is the highest in acid light mineral soils, fractions connected with Fe and Mn oxides are the most available for plant uptake. Acid leaching is major factor influencing zinc mobility. Zn is well immobilized in Ca and P rich soils, as well as in aerated soils with S content and soils with increased content of Ca-saturated minerals (Adriano, 2001; Kabata-Pendias, 2011).

Zinc is an essential element for plants as it is involved in carbohydrate, nucleic acid and lipid metabolism. Plant deficiency typically results in chlorosis, stunned growth and violet-red points on leaves. Zinc deficiency also affect ion adsorption, which accumulate in higher rates in plant tissues. Toxic effects are necrotic leaf tips, interveinal chlorosis in new leaves, retarded plant growth and injured roots (Kabata-Pendias, 2011).

### 2.2.6 Remediation and Phytoremediation

Dealing with contaminated soils is essential environmental management tool called remediation. Conventional remediation techniques (e.g.: excavation, landfilling and soil washing) are costly and causing several soil and environmental damage – extensive waste disposal, excessive agrochemicals usage, leaching (Mani and Kumar, 2013). Therefore are inacceptable for large scale use.

Phytoremediation is a biotechnological remediation technique which exhibits and utilizes an ability of some green plants and their associated microorganisms to bio-accumulate contaminants for environmental clean-up by their uptake or to mitigate their toxicity (Pilon-Smits, 2009). Among others, Evangelou et al. (2015), who deal with biochar application and phytoremediation combination questions, propose phytoremediation as an appropriate heavy metal remediation technique, which combines cost efficiency with technological accessibility, auspicious effects as keeping ecological quality of soil, causing minimum additional soil disturbance and being aesthetic at the same time. Phytoremediation is however a long-term method (in terms of hundreds of years) and the advantages may become irrelevant due of land use restrictions. The other problem arises on sites with contaminant concentrations so high that are too toxic even for phytoremediation plants (Evangelou et al., 2015).

Phytoextraction, a vital phytoremediation technique for this work, utilizes (hyper)accumulator plants capable of massive uptake of heavy metals from soil and their accumulation in own tissues. Several fast growing tree species has been shown to have a significant phytoextraction abilities: e.g. *Salix*, *Betula* and *Populus* (Gonzales et al., 2008; Nouri et al., 2009; Vollenweider et al., 2011; Mani and Kumar, 2013).

#### 2.2.6.1 Contaminated Biomass Disposal

As phytoextraction process transports heavy metals from soil into plant biomass, a question of contaminated biomass fate arises, as it might be dangerous for environment, e.g. by entering a food chain. Proper management is key here. Composting, compaction and pyrolysis are listed by Sas-Nowosielska et al. (2004) as pre-treatment methods which reduce the original amount of harvested biomass, while four methods are listed by the authors as a final treatment – incineration, direct disposal, ashing and liquid extraction. This work investigates whether pyrolysis product, a biochar, might be used as an amendment for enhancing soil sorption capacity without releasing the extracted pollutants back into environment.

## 2.3 Biochar

As energy demands of society are still increasing and abuse of fossil fuels has induced great emissions of greenhouse gases (GHG) that contribute to a climate change, the urge for finding alternative energy sources has arisen, which would decrease dependency on fossil fuels and also mitigate climate changes. For last decades people have been looking for ways of utilizing renewable energy sources like energy from sun, geothermal energy, wind energy, hydroenergy and also bio-energy (Lehmann, 2007) which also includes the thermochemical decomposition of biomass, pyrolysis, process based on old carbonization techniques.

The discovery of "*terra preta*" stands behind the popularity and abundant use of biochar and charcoal-like materials in soils (Evangelou et al., 2015). *Terra preta* is a unique anthropogenic soil (anthrosol) found in central Amazonia with amazing properties, compared to adjacent infertile soils: it exhibits 3 fold higher content of soil organic matter, nitrogen and phosphorus together with 70 fold increased black carbon content, which gives the soil its black colour. Is also less prone to leaching and contains increased levels of calcium and zinc. The soil was established by pre-Columbian natives between 7000 and 500 years BC, who created it by depositing charcoal, organic wastes, excrements and bones. Created soil allowed them to maintain effective agriculture despite original infertility of the land. The exact knowledge of creation of *terra preta* has been lost, however the rediscovery of this soil exhibited a possible option for sustainable agriculture and solution for mitigating land degradation and climate change (Glaser, 2007).

The concept of biochar concatenates both demand for renewable bio-energy and soil amendment idea from *terra preta* soils.

### 2.3.1 Biochar Definition

Biochar is a carbon rich, porous and sparse material derived from organic matter with no or little presence of oxygen under temperatures in range up to 700 °C in a process called pyrolysis. It is produced for agronomical purposes to be put into the soil, where it improves soil properties (Lehannes and Joseph, 2009).

Charcoal and biochar are technically two equivalents, but from a soil science point of view, there is a need to distinguish all potential charcoal from the specific group of charcoal which is being produced regarding potential benefits and risks they might bring into soil. A concept of the latter is called a biochar, a stable carbon compound that would improve soil quality, while it subtracts atmospheric carbon and sequesters it back into soil (Verheijen et al., 2010).

### 2.3.2 Diminishing Climate Change

Biochar is an exceptional tool for fighting with elevated atmospheric carbon dioxide content in several ways. Green plants used as feedstock biomass assimilate atmospheric carbon dioxide during photosynthesis and are pyrolyzed, producing energy from captured pyrolysis gases and solid residue of biochar, which, if put back into soil, creates a pool of carbon. The portion of carbon retained in biochar depends on feedstock and pyrolysis conditions, however 50 % of carbon recovery is achievable value, mostly due to fact that carbon content in biochar increases compared to original biomass. Carbon in form of biochar is more stable and its oxidation rate is lowered when in soil. Biochar also inhibits emissions of greenhouse gases from soil. Due to deoxygenation, calorific values of chars are higher than original biomass, which contributes to the idea of using chars as an alternative to fossil fuels (Lehmann, 2007).

### 2.3.3 Biochar Origin

Biochar is a heterogeneous material of wide range of properties, coming from its origin – feedstock and production procedure of pyrolysis. As a combination of these, biochar is produced with unique characteristics of its structure, porosity, surface area, form and amount of carbon, its pH, and its cation exchange capacity. These properties characterize biochar and are determining for its further environmental use in soil, its stability, nutrient retention as well as providing microhabitat for microorganisms. The coherence of the described aspects is outlined in Figure 3.

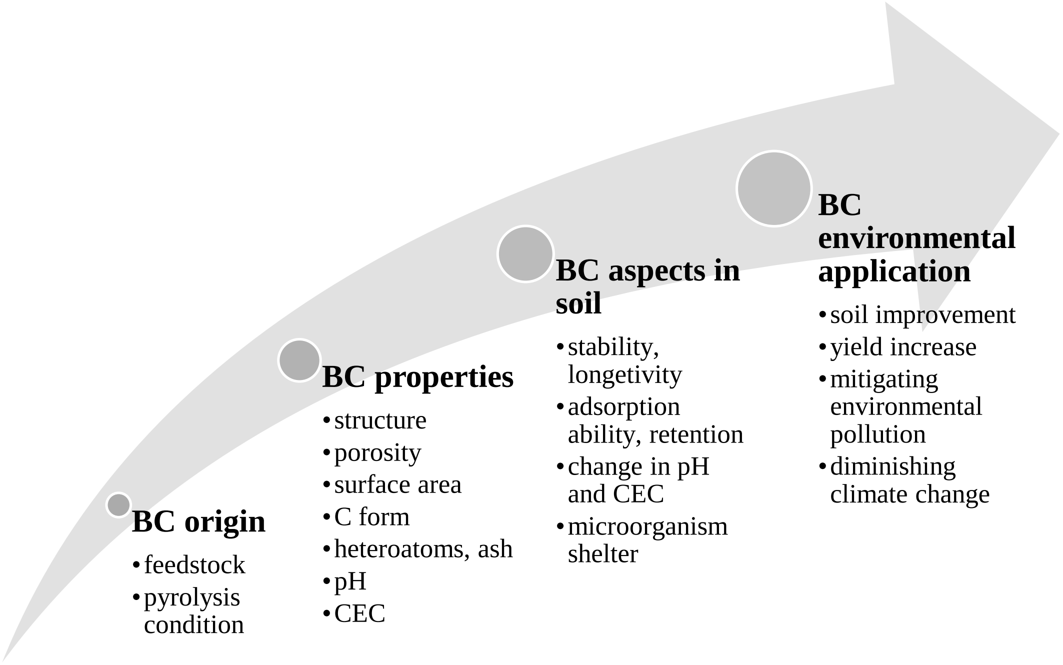


*Figure 3: The utilization of biochar properties (own interpretation)*

#### 2.3.3.1 Feedstock

Feedstock refers to an organic mass, which is used as an input material for biochar production process called pyrolysis. Together with production conditions, feedstock is the determining factor for pyrolysis result, in terms of biochar portion, overall yield or quality. As any organic matter can be used as biochar feedstock, a portion of gas / liquid / biochar yield as well as biochar physicochemical properties varies markedly. Chemical properties and composition of feedstock are determining for the biochar composition, but moreover the biochar undergoes chemical changes (attrition, cracking, microstructure rearrangements) during the pyrolysis (Verheijen et al., 2010).

Variety of materials could be considered as a biochar feedstock. Considering the final biochar value also from economical perspective, the material is intended to be cheap and with no other significant utilization. Typical sources are residues of woods, crops, nutshells and grain husks – carbon rich agricultural by-products. Moreover, some carbonaceous waste materials are also taken into account, such as compost, manure, litter, sewage sludge and municipal waste, which are rich in nutrients by their nature. There is however a risk of pollution, as these materials could also be rich in contaminants and are likely to remain in biochar as ash (Verheijen et al., 2010). According to Tang et al. (2013) the risk is significantly lower compared to treating soil with such materials unprocessed.

| | **Ash** | **Lignin** | **Cellulose** |
|---|---|---|---|
| Wheat straw | 11.2 | 14 | 38 |
| Maize residue | 2.8 – 6.8 | 15 | 39 |
| Switchgrass | 6 | 18 | 32 |
| Wood | 0.27 | 26 – 30 | 38 – 45 |

*Table 2: Different feedstock material composition (Verheijen et al., 2010)*

Lignocellulose materials are abundant biochar feedstock (Amonette and Joseph, 2009). As lignin and cellulose thermal decomposition varies, the proportion of these components in different feedstock determines the pyrolysis result. At given temperature, the lignin loss is less than half of cellulose loss (Demirbas, 2004), suggesting the lignin is more stable compound. Feedstock with high lignin content (wood, husks) provide higher biochar yield with higher stability (Demirbas, 2004; Winsley, 2007). The comparison of characteristics of various lignocellulose feedstock is given in Table 2.

#### 2.3.3.2 Pyrolysis

Pyrolysis has been known since Bronze Age as a production process of charcoal (which was required by metalwork). Industry development and demand for alternative sources of energy in last decades has emphasized pyrolysis for production of bio-oil as a liquid portion of pyrolysis result. The current view is however focused also on produced charcoal not as a residue, but as a valuable product (Zámostný and Kurc, 2011).

The word pyrolysis comes from Greek words “pyro”, which stands for fire, and “lysis”, which stands for decomposition. It is a process of chemical decomposition of organic mass at temperatures from 300 °C to 1000 °C under no oxygen conditions. Practically, it is not always possible to create oxygen free conditions and at least a subtle amount of oxygen is present during the process, causing minor oxidation. Considering the oxygen conditions, the pyrolysis process is distinguish from another thermal decomposition of organic matter, combustion, where the oxidation is dominant process due to abundance of oxygen and results in creation of carbon dioxide. In pyrolysis, predominant portion of carbon remains in the feedstock. Naturally occurs during wildfires and lava eruptions, but the process has been widely used by industry for creation of coke, charcoal, methanol, petrol and other products. Regardless of their artificial or natural origin, the solid compounds are generally referred to as (pyrogenic) black carbon (Verheijen et al., 2010).

**Selected terms of associated carbonaceous pyrogenic materials** (Verheijen et al., 2010):

| | |
|---|---|
| • Black carbon | group of carbon residues from firing or heating, |
| • Charcoal | pyrolyzed (charred) organic matter, |
| • Char | synonym for charcoal, |
| • Biochar | charcoal for soil and agricultural application, |
| • Activated carbon | charcoal which surface properties has been modified by activation for better reactive surface. |

Figure 4 gives an overview of forms of black carbon are naturally occurring with respect to their properties, including natural charcoal produced by wildfires. The biochar materials overlap with pyrogenic black carbon, however its composition and properties may differ according to feedstock and production conditions, which in case of biochar pyrolysis are controllable (Verheijen et al., 2010).

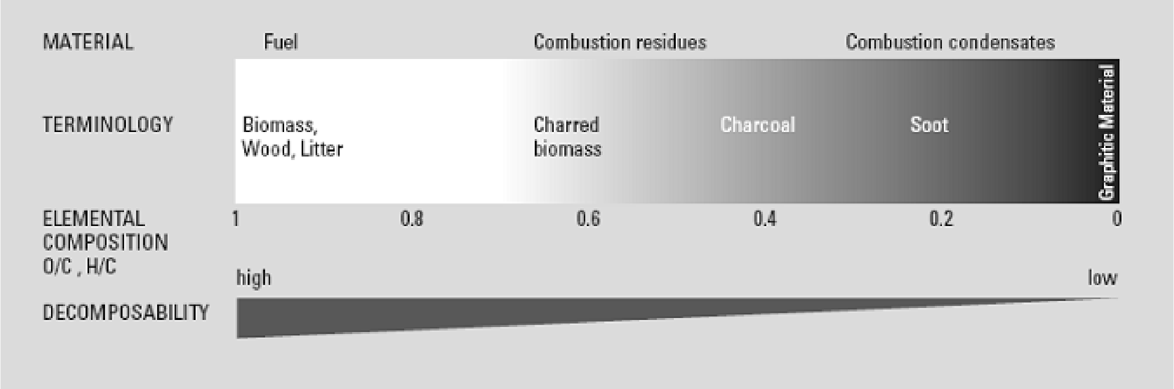


*Figure 4: Forms of pyrogenic black carbon (from Verheijen et al., 2010)*

Apart of feedstock used, a pyrolysis process depends on its running conditions, which determine the result (Lehmann, 2007). Generally, three different components are produced: gas, liquid and solid residue, but depending on the conditions, both quality and quantity of products differ. Liquid portion, called bio-oil, is a mixture of water and various oxygenated organic derivatives, such as acids, alcohols, phenols, ethers, esters, sugars and nitric acid derivatives. Pyrolysis gas, syngas, is a blend of volatilized tars and other condensable organic compounds – gaseous C1-C3 hydrocarbons, hydrogen, carbon oxide and carbon dioxide and oxides of nitrogen. Coke or char is a solid residue consisting of unreacted mass particles, chars and ashes. The result of pyrolysis process depend on several major elements: (1) temperature, (2) heating rate, (3) reactor type and settings, (4) nitrogen flow rate, and (5) residence time of vapour and solids (Verheijen et al., 2010; Zámostný and Kurc, 2011; Shabangu et al., 2014).

Two basic type of pyrolysis are distinguished – fast and slow pyrolysis. Fast one consists of rapid heating of small particles of feedstock and produces 60 – 75 % of liquid and about 12 % solid products. Slow pyrolysis, also called conventional, uses slower heating of coarse material with residence time 5 – 30 minutes and producing up to 35 % of solids. Special case of pyrolysis under extreme temperature (> 800 °C) is called gasification, yielding about 85 % of syngas and only 15 % solid residues (Maschio et al., 1992; Verheijen et al., 2010; Shabangu et al., 2014). Differences in pyrolysis results according to its type are shown below in Figure 5.

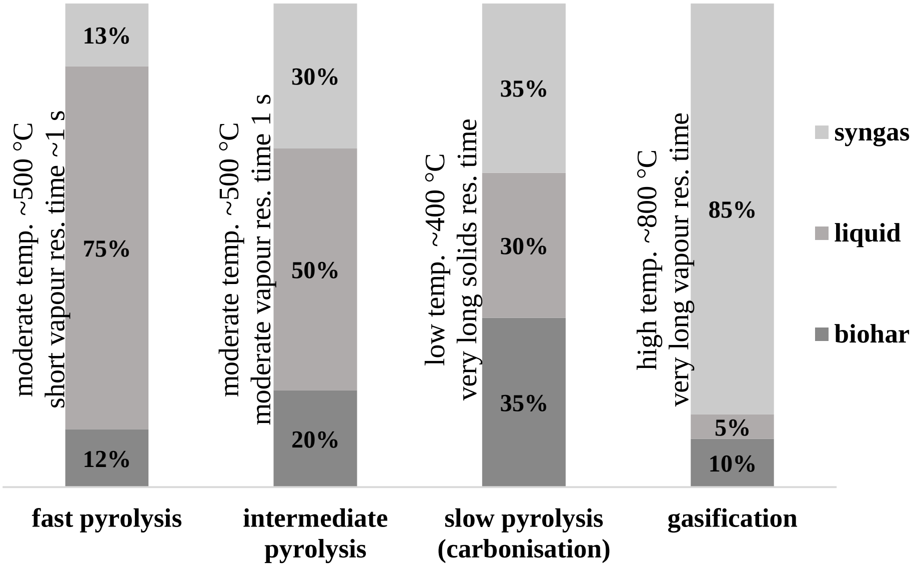


*Figure 5: Post-pyrolysis residues proportion according to different types of pyrolysis with different operation temperatures and residence times (adapted from Verheijen et al., 2010)*

Temperature and residence time are considered the main factors affecting the 3 portions of pyrolysis result. However, all of the above mentioned aspects contribute to the final biochar, its yield, as well as its physicochemical properties as surface area and micropore surface. The pore area and structure depend mainly on removed carbon during decomposition. Feedstock and carbon removal flow induced cracking is responsible for creating large macro-crack, which contribute to biochar complexity (Lehmann and Joseph, 2009).

Optimum production temperature taking into account sufficient biochar yield while obtaining biochar properties suitable for amending soils has been suggested by Lehmann (2007) to lie in range from 450 to 550 °C, as shown in Figure 7. Temperatures below 400 °C generally produce biochar of low pH, low CEC and small surface area.

### 2.3.4 Biochar Structure

#### 2.3.4.1 Surface Area, Porosity

The original structure of biomass feedstock material has major influence on the final biochar structure. During the pyrolysis the feedstock undergoes alterations by thermal conversions, volatiles are lost and the original skeleton of minerals and carbon determines the structure. Organic structures degrade at temperatures above 120 °C, namely hemicellulose at 200 – 260 °C, cellulose at 240 – 350 °C and lignin at 280 – 500 °C, therefore their portion determines the structure modification during processing. Inorganic content, ashes, has also influence on result. The loss of volatiles, condensation of some of them, ash content fusion or sintering and carbon removal by oxidation during the heating are responsible for creating biochar structure and porosity. Moreover, feedstock properties and different decomposition at biochar surface and inside are responsible for creations of cracks. Biochar structure is essentially amorphous with incorporated crystalline structures of conjugated aromatic compounds. The amorphous part consist of aromatic-aliphatic compounds with residual volatiles and inorganic ashes. Various heteroatoms (e.g. oxygen) are located on edges of ordered carbon sheets and form functional groups (Downie et al., 2009).

During the pyrolysis, some pores may be filled and blocked with condensed volatiles such as tars, which volatize and leave the pores at higher temperatures, and other decomposition products as well as mineral ashes (Downie et al., 2009).

Biochar high surface area is a function of its porosity and pore distribution, mainly micropores (diameter < 2 nm) contribute to the total surface area. The surface area rises with increasing production temperature. Brown et al. (2006) found that biochars produced at 450 °C had surface area smaller 10 $m^2g^{-1}$, while biochars produced at 600 – 750 °C had their area circa 400 $m^2g^{-1}$. Mesopores (diameter 2 – 50 nm) are important to liquid-solid adsorption processes. Macropores (diameter > 50 nm) are important as micro- and mesopores feeders, but also for their high pore volumes they bring utility to soil from perspective of aeration, hydrology and microbe shelter (Downie et al., 2009). Overall porosity and pore-forming processes increase in range 400 – 600 °C and is attributed to activation caused by dehydroxylation releasing water molecules (Amonette and Joseph, 2009). Figure 6 shows differences of porosity of coconut biochars created under different temperatures as well as result of milling the biochar into powder, picture is obtained by FESEM (field emission scanning electron microscopy) micrograph (Anyika et al., 2014).

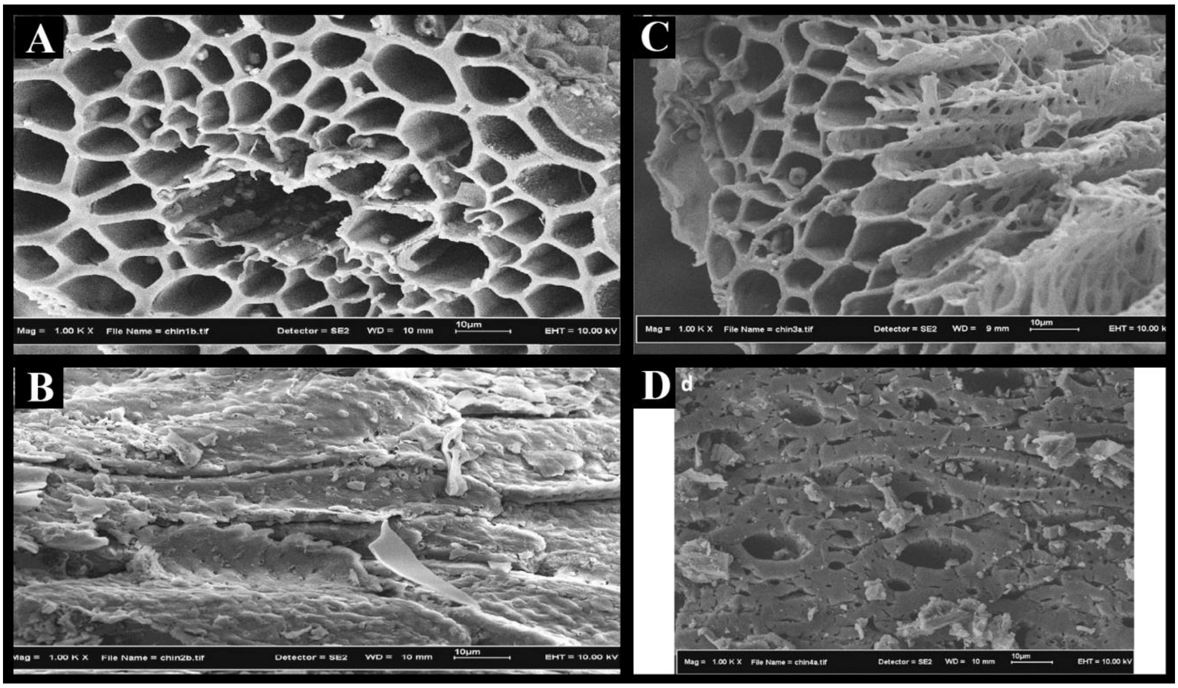


*Figure 6: Field Emission Scanning Electron Microscopy (FESEM) micrograph of Coconut shell granular biochar derived at temperatures: A) 350 °C; B) 450 °C; C) 650 °C and D) powdered biochar derived at 650 °C, showing their different pore structure (collage adapted from Anyika et al., 2014)*

#### 2.3.4.2 Biochar Surface Chemistry

Biochar surface chemistry is influenced by biochar heterogeneous composition, containing carbon of both graphene crystalline structure and random aromatic structures, volatile matter (tars), mineral ashes and moisture. Relative proportion of biochar content determine its behaviour and stability, which determine its fate and application suitability (Amonette and Joseph, 2009). Wood-based biochars are typically more resistant and coarse, while biochar from crop residues and manures are typically less stable and contain more nutrients, which contributes to their degradability. Heteroatoms such as oxygen, hydrogen, nitrogen, sulphur and phosphorus are incorporated within aromatic rings as various functional groups (e.g. hydroxyl, amino, ketone, ester, nitro, aldehyde and carboxyl) and are major contributors to biochar reactivity, they are either electron donors nor electron acceptors which can exist relatively close to another and thus give the biochar both acidic and basic properties (Verheijen et al., 2010).

Ratios between biochar elemental components serve as indicators of its properties. O/C and H/C ratios are used to measure degree of aromaticity (thus stability), they decrease with higher production temperature, as is indicated in Figure 4. C/N ratio is used among organic substrates to indicate ability to release or mineralise inorganic nitrogen in soil. (Amonette and Joseph, 2009).

### The pH

Lehmann (2007) claims the biochar pH can range from 4 up to 12. The pH changes with feedstock, production temperature, extent of oxidation and aging (Lehmann et al., 2011). Production temperature correlates positively with biochar pH, high production temperature indicates higher pH as is shown in Figure 7. The change of pH over time is implicated by feedstock properties affecting biochar behaviour. A decrease in pH is caused by oxidation of carbon to carboxylic acids, an increase in pH is caused by breaking up of alkaline minerals (Cheng et al., 2006; Anyika et al., 2014). Moreover Farrell et al. (2013) reported direct correlation between biochar pH and its content of carbonates.

### Surface Charge

Surface charge of biochar is a result of its various acidic and basic functional groups which were mentioned above. The biochar surface chemistry influences its surface charge which results in its cation and anion exchange capacity, shortly CEC and AEC, respectively. These indicate the ability to retain and exchange ions, how well are nutrients bound and how unlikely they are to leach. Newly produced biochars have positive surface charge indicating its high AEC, which diminish over time by binding phosphates and nitrates from soils (Cheng et al., 2008, Anyika et al., 2014). Negative surface charge corresponds with biochar CEC. Original biochar CEC is relatively low, but increases with time due to oxidation processes on surface which create oxygenated functional groups giving the biochar negative surface charge. Negative surface charge replaces positive surface charge and gives biochar high CEC, which is a major key to its nutrient retention. (Lehmann, 2007; Lehmann and Joseph, 2009). Positive affinity between production temperature and biochar CEC (i.e. higher production temperature implies higher CEC) was suggested by Lehmann (2007) and was later confirmed by Anyika et al., 2014 as a fact of shorter oxidation period of biochars coming from higher temperatures. CEC values vary from negligible to 40 cmol $g^{-1}$ (Verheijen et al., 2010).

Figure 7 summarizes the findings about how biochar physicochemical properties are dependent on pyrolysis temperature. The higher the temperature is, the higher the biochar surface area, pH and CEC are, and oppositely the lower the biochar yield is, due to carbon loss.

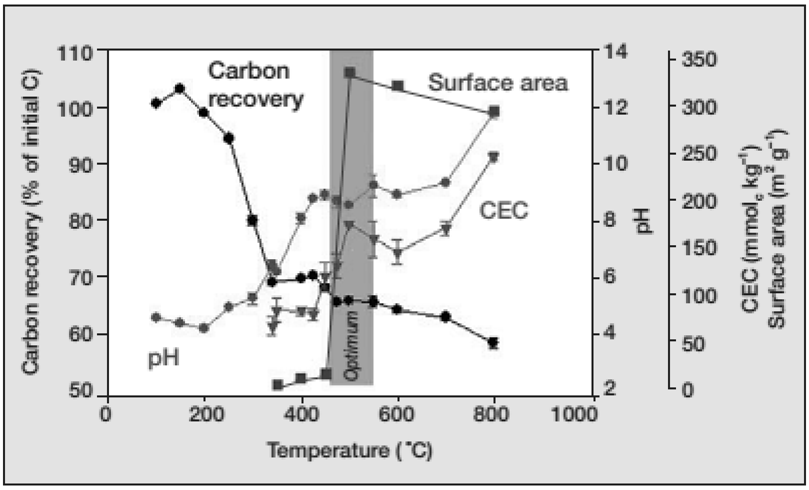


*Figure 7: The dependence of biochar pH, CEC, surface area and carbon yield on production temperature (from Lehmann, 2007)*

#### 2.3.4.3 Activated Carbon

Although biochar production conditions (mainly temperature) alter its structure, industry has developed procedures how to enhance the surface and sorption capacity even more, through a process called activation, physical or chemical, which alter structure and introduce more functional groups (Tang et al., 2013). Physical activation utilizes flow of carbon dioxide, air or their mixture to release the volatiles and enhance crystalline carbon formation. Chemical activation introduces compounds such as phosphoric acid, hydrochloric acid, sulphuric acid, zinc salts or alkali metal hydroxides to the biochar precursors (Downie et al., 2009). For example Azargohar and Dalai (2006) examined biochar precursor activated with potassium hydroxide. They concluded all temperature, nitrogen flow rate, activation agent / biochar ratio and original chemical and structural properties to influence the activation. Their activated carbon had in mean 50 fold higher internal surface area, mainly due to micropores and also exhibited higher aromatization. Xue et al. (2012) examined a hydrothermally produced biochar activated by $H_2O_2$ application, suggesting the $H_2O_2$ modified hydrochar could be cheap, affordable and sustainable sorbent. Special case of carbon activation was done by Zhang et al. (2013) who used $\gamma$-$Fe_2O_3$ colloids and nanoparticles embedded in biochar to treat arsenic rich water. Biochar showed strong affinity towards arsenic sorption and at the end of experiment could be separated from solution simply by using a magnet.

## 2.4 Biochar Amendments to Soil

When biochar is applied into soil, its properties affect environment which is applied into. Biochar CEC, pH, surface area and retention ability highly impacts the original soil properties that typically results into soil enrichment and improvement (that is however a purpose of biochar). Although each biochar and soil are unique and each biochar application has to be properly examined as Verheijen et al. (2010) state and there are some cases of biochar negative impact onto soil (e.g. decreasing crop yield by increasing already too high initial pH), biochar may improve soil by altering soil structure, pH and CEC, returning organic carbon to soil, retaining nutrients and water. Therefore the biochar has effect on soil processes like nutrient leaching, pollution, presence of soil biota and emissions of greenhouse gases from soil. Moreover, as biochar undergoes degradation, its properties such as CEC, pH, surface area and retention ability changes over time after application. Surface area and pore volume may change by clogging of pores by minerals and organic matter or by mineralization of this volatiles matter. This all can change the biochar sorption ability (Lehmann, 2007; Lehmann et al., 2011). Biochar long-term behaviour investigation is however needed, as Verheijen et al. (2010) claim, the only knowledge we have about any long-lasting charcoal is the one of t*erra preta* soils, that were created using vegetation biomass, whereas a modern biochar can be produced from literally any organic matter and its fate is not yet explored.

Due to biochar ability to sequester carbon and retain nutrients, the changes in soil induced by biochar amendments do favour plant growth and crop yield, mostly in poorly fertile soils (Uzoma et al., 2011) and also increase plant resistance to diseases (Elad et al., 2010). Biochar not only retains nutrients, but also a variety of contaminants and its application can be therefore used for mitigating environmental pollution. Moreover, biochar nature and production contribute to diminish climate change by both sorbing emissions and altering carbon and nitrogen cycles (Tang et al., 2013).

### 2.4.1 Biochar Stability

Biochar as a whole is resistant to microbial, chemical and physical decomposition, it is able to resist both oxidation to carbon dioxide or reduction to methane (Lehmann, 2007). Biochar has proven to be stable under variety of conditions in laboratory (Bird and Gröcke, 1997) and environment, e.g. in mentioned Amazonian *terra preta* soils. However, carbon in biochar exists in 2 forms: persistent aromatic structures and more volatile aliphatic and oxidized carbon structures. Even though majority of biochar carbon is present in aromatic structures, which oxidise and degrade slowly, finally all carbon degrades to $CO_2$. The half-life of pyrolytic carbon was estimated from 100 to 5000 years according to conditions (Preston and Schmidt, 2006). The portion of carbon forms in biochar depends on original feedstock properties, charring conditions and process of formation (direct charring vs. volatile organic particles condensation). Various fractions of biochar tend to degrade at different rate, also depending of char exposure and environmental condition. Biochar exists in a form of particulates and a decay process has to start on their surface, so the oxidation is limited to only the outer areas of these particulates, even for hundreds of years. (Lehmann, 2007; Zimmerman, 2010).

Hamer et al. (2004) stated that biochar C/N ratio (content of carbon versus content of nitrogen) correlates with its stability. Lower N content then means higher ratio and indicates higher longevity due to lower nitrogen degradation and sequestering. C/N ratio is dependent on feedstock chemical structure and pyrolysis temperature, high production temperatures corresponds with low aliphatic and high aromatic carbon content (Hilscher and Knicker, 2011; Anyika et al., 2014). Also, the H/C and O/C ratios are indicators of biochar stability as they point out the portion of less stable carbon.

Although its longevity coming from stable aromatic structure, losses of biochar from the environment occur as an erosion and biochar is observed to sediment at sites close to erosion source or in oceans (Stallard, 1998; Masiello, 2004).

### 2.4.2 Nutrient Retention

Biochar amendment to soil has been shown to significantly improve sorption affinity towards soluble nutrients as ammonium, nitrates, phosphates and other ionic compounds and reduce their leaching into environment (Lehmann, 2007; Tang et al., 2013). Nutrients present in soil are available to plants by adsorbing to minerals or soil organic matter. While soil mineral content is usually unlikely to change, the content of organic matter is manageable. Organic content positively influences the soil ability to retain cations (cation exchange capacity). Biochar is due to large surface and surface charge even more efficient in adsorbing cations and moreover is even able to adsorb anions of phosphates and nitrates. The cation exchange capacity of biochar is direct affinity to pH, as more negative bonds are capable of binding cations. The point of pH, where cation exchange capacity is zero (point of zero net charge) is dependent on biochar production temperature, increases with the temperature. However, Anyika et al., 2014 claim that higher production temperatures results in higher hydrophobicity of biochar and thus the nutrient retention of such biochars is negligible. The temperature of production also positively influences char's pH and surface area, and has negative impact on biochar yield, as is shown in Figure 7 (Lehmann, 2007). Combining all the findings together, Lehmann (2007) suggested optimum production temperature for biochar between 450 and 550 °C.

Biochar retention ability lowers the amount of nutrients leaching into groundwater and eroding into surface waters. Moreover by this nutrient retention the total amount of fertilizers needed to grow biomass is lowered (Verheijen et al., 2010).

### 2.4.3 Pollution Treatment

For the biochar and contaminant interactions, all the participating aspects are important: (1) physical and chemical properties of biochar, (2) soil and environment properties, and (3) physical and chemical properties of contaminants (Evangelou et al., 2015).

Pollutants present in soil can transfer to crops and soil organisms or leach into water and cause toxic effects. Due to pore structure, aromatic and aliphatic structures, recalcitrance and retention capability biochars have shown ability to improve soil sorption and mitigate leaching of pollutants, organic and inorganic. Numerous researchers and studies have examined biochar of different origin for its environmental potential of immobilization and even degradation of pollutants in soil – especially heavy metals, dioxins, PAHs and pesticides (Lehmann and Joseph, 2009; Tang et al., 2013).

#### 2.4.3.1 Organic Pollutants and Pesticides

Biochar is an exceptional tool for remediation of organic pollutants. Main mechanisms involved in sorption processes are adsorption and partition. Surface adsorption is based on adhesion interactions between pollutant and biochar surface, partition of pollutant molecules takes place in biochar micropores, sorption overall depends on biochar surface area and pore size distribution. For biochars made at lower temperatures (less carbonized) the partition process prevails, while for high temperature biochars (more carbonized) the prevailing process is surface adsorption. The electron interactions and porefilling mechanisms also contribute to binding of organic pollutants (Qiu et al., 2009; Wen et al., 2009, Tang et al., 2013).

Biochars can effectively bound PAHs and moreover stimulate microorganism soil activity that causes PAH degradation. Biochar can rapidly sorb PAH and then slowly release it for microbial degradation, which leads to lasting bioremediation process with degradation and adsorption happening at one time (Anyika et al., 2014).

Similarly as with other organic pollutants, biochars are also efficient in sorbing pesticides that are applied on soils to control pests. Biochar can lower the risk of pesticide transfer from place of application into environment and human food-chain, by both lowering the exposure to humans and also decreased bioavailability and uptake by plants, where the pesticides could accumulate as residues. At the same time, this lowers the pesticide efficiency (Tang et al., 2013).

#### 2.4.3.2 Heavy Metals

Numerous studies confirmed variety of biochars to be able to remove heavy metals from soils and water solutions. Retention and immobilization by biochar in soil provide a tool which releases the pollutants in significantly slower rates and minimizes the environmental pollution risk (Tang et al., 2013). Remediation by biochar lowers the amounts of heavy metals available to plants as well as those leaking into environment.

Precipitation, electrostatic and non-electrostatic interactions are the main mechanisms of how biochar enhances heavy metal remediation (Jiang et al., 2012a). Biochar introduces large surface with negative charge resulting in high CEC which provide electrostatic attraction with positively charged metal ions and increase adsorption capacity of soil. However it is the aspects of surface functional groups, such as volatile matter content, point of zero charge ($pH_{pzc}$), O:C and N:C ratios, over the surface area, fixed carbon and ash content, that play major role in trace element binding (Evangelou et al., 2015). As biochar usually has more alkaline pH than soil which is applied into, the shift in soil pH to more alkaline induced by introduction of biochar may result in precipitation and mobility decrease of cationic metals due to reduced competition between $H^+$ and metal ions for exchange sites on both biochar and soil matrix. This mobility decrease might not be so apparent in neutral or alkali pH soils. Various functional groups on biochar surface play role in non-electrostatic interactions between biochar and heavy metals. Functional groups such as carboxylic, hydroxyl and alcohol form complexes with metals. The mentioned mechanisms operate concurrently when considering biochar enhanced sorption (Beesley et al., 2010; Jiang et al., 2012a; Lu et al., 2012).

Lu et al. (2012) described possible sorption mechanisms of TE on biochar in soil, using Pb as a representative (Figure 8). As proposed by the authors, these consist of:

1) exchange of metal with $Ca^{2+}$, $Mg^{2+}$ and other cations on biochar surface, attributing to co-precipitation and innersphere complexation with complexed humic organic matter and mineral oxides,
2) surface complexation of metal with different functional groups and innersphere complexation with free hydroxyl of mineral oxides and other surface precipitation,
3) other inner sphere complexation with free hydroxyl of mineral oxides, physical adsorption and surface precipitation (Lu et al., 2012; Evangelou et al., 2015).

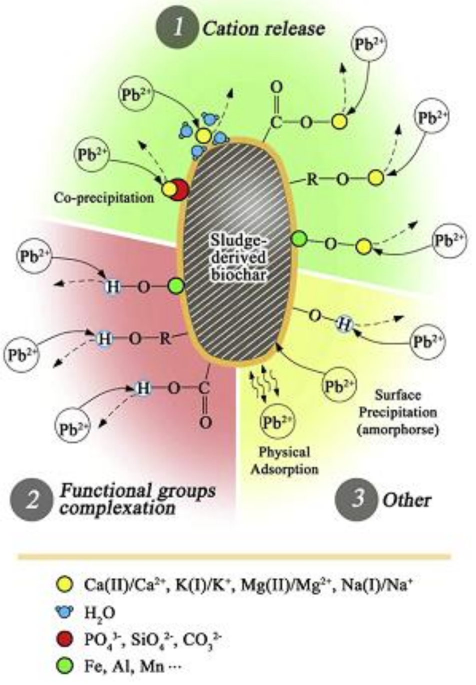


*Figure 8: Conceptual illustration of Pb adsorption mechanism on sludge-derived biochar (SDBC), including: (1) metal exchange with Ca and Mg, attributing to co-precipitation and innersphere complexation with complexed humic matter and mineral oxides of SDBC; (2) surface complexation with free carboxyl and hydroxyl functional groups, and innersphere complexation with the free hydroxyl of mineral oxides and other surface precipitation; (3) others, innersphere complexation with the free hydroxyl of mineral oxides and other surface precipitation (from Lu et al., 2012)*

In case of Pb sorption on biochar, Lu et al. (2012) exhibited over pH range 2 – 5 that majority of Pb was removed by irreversible precipitation and combination into larger compounds on mineral surface and sorbed Pb was difficult to be released. Similarly Jiang et al. (2012a) stated that non-electrostatic mechanisms creating complexes between Pb and functional groups prevail over electrostatic mechanisms. These finding refine former report by Qiu et al (2008) who stated that adsorption of lead (generally heavy metals) by biochar occurs through the electrostatic interactions between positive metal and deprotonated negative functional groups of carbon, where a rise in pH induced dissociation of acidic groups (loss of $H^+$), thus increasing adsorption, and who also stated that metal adsorption is reduced by screening role of dissociated salts neutralizing the charge of carbon.

Xu et al. (2012) addressed increased sorption capacity of manure derived biochar to presence of mineral components (e.g., $PO_4^{3-}$, $CO_3^{2-}$) which serve as additional sorption sites.

### 2.4.4 Water Retention

Biochar large porosity, allowing it to retain water and air, is compensated by hydrophobicity of organic particles which have a strong adsorption affinity to biochar surface. Biochar introduction into soil therefore brings both these processes together (Anyika et al., 2014). A study by Kinney et al. (2012) states that both retention and hydrophobicity properties depend on feedstock and production temperature. Hydrophobicity is, according to them, minimal in low production temperature biochars (400 – 600 °C) and correlates with presence of alkyl functional groups derived from low temperature biochar aliphatic groups. A negative correlation between water binding capacity and hydrophobic organic matter binding capacity is also proposed by Verheijen et al. (2010).

Ojeda et al (2015) examined biochar ability to affect water functions in soil. Their major finding was that biochar amendment affects mainly soil nutrient flux. Water retention in their sandy-loam soil was not altered, unlike previous study by Sun and Lu (2014) who reported improvement in water retention on clayey soil. They also reported that the biochar hydrophobicity decreased over 1 year time.

### 2.4.5 Biochar Toxicity

Biochar itself might be toxic depending on its properties guided by production conditions. Producing biochar from feedstock contaminated with chlorinated organic compounds may result in creating biochar with content of dioxins, furans, polychlorinated biphenyls and poly-aromatic hydrocarbons. Introducing such biochars into soil and water systems exhibit a threat for surrounding environment. Moreover, biochar is likely to contain majority of mineral material from its feedstock, including heavy metals, as they are less volatile and increase their concentrations during pyrolysis. Biochar may then act as a point source of these elements (Evangelou et al., 2015).

The PAH content in biochar was observed with conclusion that PAH content varies with biomass used and production temperature, the least PAH content together with their highest immobilisation was determined at high production temperatures (Tang et al., 2013). Biochar is however efficient in PAH degradation and immobilization while providing substrate for microorganism as was examined by Anyika et al. (2014).

A threshold for possible pollutant content in biochar not exhibiting a threat for soil application has been developed and set by International Biochar Initiation (IBI biochar standards, 2014).

#### 2.4.5.1 Biochar from Phytoremediation Biomass

Stals et al. (2010a) pyrolyzed contaminated biomass from phytoremediation and examined the transport of contaminants from biomass into the bio-oil. From three species they tested, *Salix fragilis* was proposed as the ideal feedstock to be pyrolyzed for its good phytoremediation ability, high bio-oil yield and minimum heavy metal transition from biomass to oil at pyrolysis temperatures of 350 and 450 °C. This supports their other finding (Stals et al., 2010b), where they concluded that examined Cd, Cu, Pb and Zn content is present in bio-oils almost negligible, whereas most of the heavy metals content accumulate in the solid residue. This only changed at production temperature 550 °C, where both biochar yield and heavy metal retention in biochar was low. They also suggested that flash pyrolysis can be valuable instrument in dealing with deposition problems of phytoremediation contaminated biomass as flash pyrolysis high temperatures and short residence time yields highest liquid product. Stals et al. (2010a) furthermore warns against these contaminated biochars combustion emissions.

### 2.4.6 Benefits and Risks

Soil properties change with biochar addition. Char properties changes with feedstock and pyrolysis conditions and therefore characterisation of each biochar has to be made before it is used in each particular case, because biochar amendment into soil is irreversible, once applied and incorporated, the biochar cannot be removed (Verheijen et al., 2010; Manya, 2012).

The major findings of biochar application and soil and environmental use were summarized and reviewed by Verheijen et al. (2010) and are listed bellow in Table 3. Some of the findings were modified concerning later literature.

**Positive findings**

- Naturally occurring pyrogenic black carbon improves soils (biochar analogues are present in soils over the world)
- Increased crop yield has been reported esp. from tropical areas
- Liming effect due to biochars' neutral and basic pH, improvement of acidic soils
- High sorption ability towards both organic and inorganic contaminants improves overall soil sorption capacity and retention, thus reduce mobility of these contaminants
- Influence on soil biota, including stimulation of microbiota and earth worms (not valid for high application rates)
- Increase in mycorrhizal activity

**Negative findings**

- Biochar erosion (both wind and water) is likely to occur when applied on soil surface and not incorporated into soil
- Risk of contamination introduced by contaminated biochar, this however could be controlled by feedstock and pyrolysis control
- Crop residue removal from site, which would otherwise be incorporated into soil
- Health and fire risk connected with production, transport, storage and application

**Findings of unknown effect and possible questions**

- Limited range of known charcoal amendments effect and lack of empirical evidence, because naturally occurring pyrogenic black carbon amendments come from thin group of feedstock and formation conditions
- Carbon negativity of wide biochar application despite being discussed, it is still of unknown range
- Nitrogen cycle influence, while dependent on water regime and hypothesised a positive affinity with support of soil microbiota, needs investigation
- Environmental mobility is not widely investigated, e.g. loss, transport through soil profile and into water

- Risk assessment on contaminant availability for particular biochar and soil properties – this area is currently undergoing extensive research
- Pore and porosity impact on soil properties
- Possible soil compaction during application
- Water retention is both influenced by porosity and hydrophobicity
- Accelerated degradation of biochar by use of agro-technical means
- Soil CEC effect from a long term perspective
- Albedo of soil is altered by biochar application, which might lead to alternation of soil temperature regime

*Table 3: The list of major findings connected with biochar application and usage (adapted from Verheijen et al., 2010)*

# 3 Hypothesis and Objectives of Work

**Hypothesis of Thesis:**

Biochar will improve soil sorption characteristics and thus reduce a leak of contaminants into an environment.

Biochar derived from contaminated biomass from phytoextraction will perform similar efficiency as commercially available biochar made of clean biomass.

**Objective and Aim of Thesis:**

The main aim will focus on an evaluation of soil sorption ability after biochar application. For this purpose two types of biochar and two soils will be chosen. Properties of biochar derived from contaminated biomass will be compared with properties of commercially available clean biochar. The next target will focus on changes of sorption ability of two types of Fluvisol after biochars application. The first Fluvisol will be extremely contaminated with heavy metals while the second will be obtained from uncontaminated area. Application of the dose of 1 % (w/w) of contaminated and clean biochar into contaminated and uncontaminated Fluvisols will be evaluated.

# 4 Materials and Methods

The basic idea of the experiment was to test the sorption performance of contaminated biochar and commercially available uncontaminated biochar when these are amended into both soil polluted by heavy metals and agricultural soil clean of pollution. Mixtures of both biochars with both soils as well as pure soils and pure biochars were tested in desorption experiment for heavy metal release in background electrolyte. All the sample types (sample matrix) were loaded with 7 different concentrations of solutions of heavy metal (Cd, Pb, Zn) nitrate salts in batch sorption experiment to evaluate performance of various biochar amendment.

## 4.1 Soil Samples

Fluvisols from two sites were used for the experiment. The first soil sample came from locality Trhové Dušníky (**Litávka)** at Příbram city (GPS 49°43'07.0"N 14°00'47.0"E). This area in vicinity of Litávka stream is contaminated by heavy metal depositions from former local Pb smelter. The second sample comes from an agricultural field by village **Choťánky** (GPS 50°09'13.6"N 15°06'10.1"E). This soil is used for growing agricultural plants and thus considered unpolluted. Samples from both sites were collected from arable layer (0 – 30 cm depth), were air dried, sieved through a 2 mm sieve and homogenized.

### 4.1.1 Analytical Methods

Risk element content was determined by decomposition of mixture of 0.5 g soil and 8 ml $HNO_3$, 5 ml HCl, and 2 ml HF in a closed microwave heating system using device Ethos 1 (MLS GmbH, Germany). The element contents were determined by ICP-OES (Agilent 720, Agilent Technologies Inc., Santa Clara, USA). Cation Exchange capacity was determined according to Gillman (1979) by saturating the soil complex with $Ba^{2+}$ in repeating extraction with $BaCl_2$ solution. Then a solution of $MgSO_4$ was added into saturated soil. Baryum was precipitated as $BaSO_4$, and $Mg^{2+}$ ions were bind onto free soil sorption sites. Magnesium in solution was determined by ICP-OES and cation content in $BaCl_2$ extract was determined and CEC calculated.

An initial pH value of each sample matrix (soils, biochars, and mixtures) was measured by adding 50 ml of 0.01 M $CaCl_2$ to 10 g of prepared sample (soil and/or biochar)

(20 % w/v ratio), having the mixture shaken for 2 hours (ISO 10390, 2011) and then allowing to settle for another 1 hour before measurement.

### 4.1.2 Soil Characteristics

| | | Soil | |
|---|---|---|---|
| **Element** | **Unit** | **Litávka** | **Choťánky** |
| Ca | mg/kg | 2110 | 914 |
| Cd | | 40.6 | 0.10 |
| Cu | | 67.4 | 3.33 |
| K | | 6030 | 1035 |
| Mg | | 3126 | 557 |
| P | | 553 | 301 |
| Pb | | 3706 | 11.6 |
| Zn | | 5623 | 22.0 |
| $pH_{CaCl2}$ | | 5.93 | 5.91 |
| CEC | mmol/kg | 103 | 33 |

*Table 4: Overview of Litávka and Choťánky soil characteristics (element total content).*

Table 4 displays elemental composition (total content expressed in mg/kg as average with standard deviations), and pH and CEC of both soils. The Litávka soil is characterized as clay-loamy Fluvisol, the Choťánky soil as sandy-loam Fluvisol. The content of all measured elements is several fold higher in Litávka soil, noteworthy is the content of Cd, Pb, and Zn, which are in focus of this study. Cation exchange capacity is 3 fold higher in favour of Litávka soil.

## 4.2 Biochar Samples

Two biochars of different composition were tested in the experiment to determine their sorption performance. Biochars were crushed in a mill into a powder to enhance their surface area.

### 4.2.1 Analytical Methods

Surface area measurements were performed using ASAP 2050 (Micrometrics Instrument Corporation, USA) surface area analyser using nitrogen adsorption isotherms at 77 K. Specific surface areas (SSA) were detected by layered adsorption BET model (Brunauer et al., 1938). The content of C was detected by using the Flash EA 1112 in CHNS/O configuration (Thermo Fisher Scientific, USA). Ash content was determined by incineration at 550±10 °C until achieving constant weight, according to CSN EN 15403 (2011). Risk element content was determined by neutron activation analysis k0-INAA (Kubešová and Kučera, 2010). Cation exchange capacity and initial pH values were measured analogically to soils as described in soil analytical methods section.

### 4.2.2 Biochar Characteristics

| | | **Biochar** | |
|---|---|---|---|
| **Element** | **Unit** | **Contaminated** | **Clean** |
| K | g/kg | 16.1 | 0.5 |
| Ca | | 28 | 2.9 |
| Mg | | not detected | 2.2 |
| Fe | | 2.8 | 4.1 |
| Cd | mg/kg | 27 | <0.1 |
| Pb | | 282* | bdl** |
| Zn | | 950 | 8.3 |
| C (total) | (% w/w) | 64 | 93 |
| ash | (% w/w) | 13 | 12 |
| CEC | mmol/kg | 176.4 | 94.5 |
| $pH_{CaCl2}$ | | 7.3 | 10.1 |
| $SSA_{(BET)}$ | $m^2/g$ | 176 | 486 |

* determined by x-ray fluorescence
** bellow detection limit

*Table 5: Overview of contaminated and clean biochar characteristics.*

The biochars are characterized in Table 5. The first biochar (**contaminated**) was obtained by pyrolysis of contaminated willow biomass grown at experimental phytoremediation short-rotation coppice plantations at old smelter facility of Příbram locality, medium contaminated with heavy metals (49° 42′ 24″ N, 13° 58′ 32″ E). The material was pyrolyzed in a muffle furnace with inert atmosphere of nitrogen with flow 1 $m^3/h$ under atmospheric pressure, residence time 30 minutes and final temperature 500 °C. The second (**clean**) is uncontaminated commercially available biochar, produced from coconut shells and activated by water steam (purchased from Erspol., Ltd., Czech Republic). The ash content of both biochars is similar, whereas they differ in other characteristics: contaminated biochar has twice higher CEC, 1/3 lower surface area, and neutral pH compared to alkaline clean biochar. The clean biochar contains 93 % of Carbon, whereas the contaminated biochar is rich in other elements, including presumed high heavy metal content.

## 4.3 Experiment Design (Sample Matrix)

In order to clarify desorption and sorption behaviour of examined soils amended with biochars, mixtures of soils with biochars were prepared, biochars were added to soils in 1 % w/w ratio. As an experiment control, pure soils and biochars were tested, too. 8 total sample types were present in sample matrix: (1) pure soil from Litávka locality (L), (2) pure soil from Choťánky locality (Ch), (3) pure contaminated biochar (Bk), (4) pure clean commercial biochar (Bc), (5) mixture of Litávka soil and contaminated biochar (LBk), (6) mixture of Litávka soil and clean commercial biochar (LBc), (7) mixture of Choťánky soil and contaminated biochar (ChBk), and (8) mixture of Choťánky soil and clean commercial biochar (ChBc), as depicted in Table 6.

|  |  |  |
|---|---|---|
| Soil | Choťánky | Ch |
|  | Litávka | L |
| Biochar | Contaminated | Bk |
|  | Clean | Bc |
| **Treatment:** | **Soil** + | **Biochar** |
| L | Litávka | - |
| Ch | Choťánky | - |
| LBc | Litávka | Clean |
| ChBc | Choťánky | Clean |
| LBk | Litávka | Contaminated |
| ChBk | Choťánky | Contaminated |
| Bc | - | Clean |
| Bk | - | Contaminated |

*Table 6: Experiment design showing the designation of samples prepared from soils and biochars.*

## 4.4 Batch Sorption Experiment

Adsorption experiments were conducted using batch equilibration technique and utilizing single element sorption. For metal adsorption experiments the biochar and soil samples were loaded with solutions of heavy metal salts in 0.01 M $KNO_3$ background electrolyte (Trakal et al., 2011). Namely $Cd(NO_3)_2$ $3H_2O$ (Sigma–Aldrich), $Pb(NO_3)_2$, and $Zn(NO_3)_2$ $6H_2O$ (Lachner) for Cd(II), Pb(II) and Zn(II) solutions, respectively. Stock solutions of nitrate salts were prepared in 7 concentrations. Concentration series for Cd was: 0.02 mM, 0.04 mM, 0.1 mM, 0.2 mM, 0.4 mM, 2 mM, and 4 mM. For both Pb and Zn the series were: 0.05 mM, 0.1 mM, 0.25 mM, 0.5 mM, 1mM, 5 mM, and 10 mM (Trakal et al., 2012).

Using 50 ml tubes, the volume of 20 ml of single metal solution was added to 1.0 g of each sample matrix. Mixtures were shaken for equilibrium on reciprocating shaker for 24 hours (Uchimiya et al., 2011a, b), centrifuged (solutions turbid after the centrifugation were on top of that filtered), and finally measured by ICP-OES (Agilent 720, Agilent Technologies Inc., Santa Clara, USA). The pH values were measured after equilibrium was achieved. The experiments were performed as triplicates and contained blind samples.

## 4.5 Batch Desorption Experiment

A desorption experiment was set up to determine concentration of heavy metals desorbed from the samples into solution. Volume of 20 ml of 0.01 M $KNO_3$ was added to 1.0 g of each sample from sample matrix in 50 ml tubes (Trakal et al., 2011). The suspensions were shaken for 24 h on a reciprocating shaker for equilibrium (Uchimiya et al., 2011a, b), then centrifuged and finally the supernatants were measured for heavy metal concentration by ICP-OES (Agilent 720, Agilent Technologies Inc., Santa Clara, USA). As in the sorption experiment, the pH values were measured after equilibrium was achieved. The experiments were performed as triplicates and contained blind samples.

## 4.6 Calculations and Models

The sorbed metal concentrations (uptake) was calculated using (Eq. 1):

$$c_{sorb} = \left(c_0 - c_{eq} - c_{desorb}\right)\frac{V}{m} \tag{1}$$

Where $c_{sorb}$ (mg kg$^{-1}$) is the sorbed concentration, $c_0$, $c_{eq}$, and $c_{desorb}$ (mg kg$^{-1}$) are the initial, equilibrium, and desorbed concentrations of metal in solution (mg L$^{-1}$), respectively, $V$ is the volume (L), and $m$ is the amount of dried biosorbent (g).

The obtained $c_{sorb}$ and $c_{eq}$ data were plotted into Freundlich (Eq. 2) and Langmuir (Eq. 3) model equations and used for Freundlich and Langmuir isotherm construction.

$$c_{sorb} = K_f {c_{eq}}^n \tag{2}$$

$$c_{sorb} = \frac{S_{max}K_L C_{eq}}{1+K_L C_{eq}} \tag{3}$$

Where $c_{sorb}$ is the uptake (mg kg$^{-1}$), and $c_{eq}$ is the equilibrium liquid-phase concentration of metal (mg L$^{-1}$), $n$ represents empirical coefficient, $K_f$ represents Freundlich sorption coefficient, $K_L$ represents Langmuir sorption coefficient (characterizing bonding energy associated with an equilibrium constant), and $S_{max}$ (mg kg$^{-1}$) represents the maximum sorption capacity determined by the number of reactive surface sorption sites in an ideal monolayer system (Trakal et al. 2011, Břendová et al., 2015).

Data were processed in MS Excel 2013 and for Langmuir and Freundlich data modelling the CHBJSSSAJ 71 spreadsheets ver. 1.6 were used (Bolster & Hornberger, 2007).

# 5 Results

## 5.1 Evaluation of pH

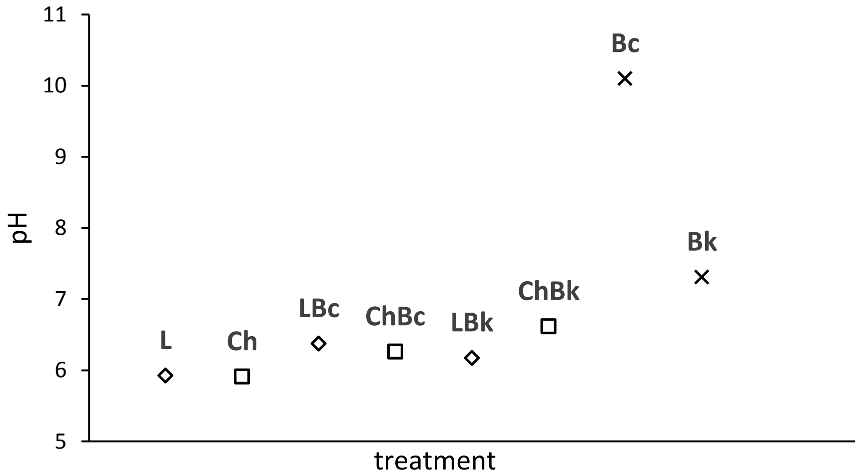


*Figure 9: Original pH values (measured in $CaCl_2$) of sample matrix.*

Figure 9 shows pH values (measured in $CaCl_2$ solution) of soils, biochars, and mixtures before the loading with heavy metals solutions. Both soils (L, Ch) have similar acidic pH (5.93 and 5.91), which slightly increases with biochar amendment (LBc: 6.4, LBk: 6.2; ChBc: 6.3, and most markedly ChBk: 6.6). Clean biochar (Bc) is extremely alkaline (pH 10.1) compared to contaminated biochar with neutral pH (7.31).

The pH values during the sorption experiment were measured in order to evaluate the shift in pH considering the (1) increasing amount of heavy metal in solution, and (2) impact of biochar amendment into the soil.

### 5.1.1 Cadmium

Figure 10 shows development of pH with changing concentration of Cd solution, grouped by soil type. From left: (a) Litávka soil (L), Litávka soil + clean biochar (LBc), and Litávka soil + contaminated biochar (LBk); (b) Choťánky soil (Ch), Choťánky soil + clean biochar (ChBc), and Choťánky soil + contaminated biochar (ChBk); and (c) clean biochar (Bc), and contaminated biochar (Bk) (the same pattern of graphs and treatments grouped is used for all three tested heavy metals). Loaded with Cd solutions, both soils and mixtures with biochar have similar pH pattern over increasing Cd concentration. In Litávka soil the amendment of clean biochar causes slight decrement of pH, while the amendment of contaminated biochar causes slight pH increment. Overall in Litávka soil and its mixtures the pH increases with increasing Cd concentration up to c = 0.2 mM for maximal pH (L max 6.14 at c = 0.1 mM; LBc max 6.08 at c = 0.1 mM; LBk max 6.14 at c = 0.2 mM). For higher Cd concentrations the pH decreases, close to original values at maximum concentration.

Pure biochars loaded with Cd solutions show stable pH (7.8 – 7.9) up to c = 2 mM, where pH of clean biochar begins to increase, and pH of contaminated biochar begins to decrease (Bc = 8.6, Bk = 7.4 at c = 4 mM).

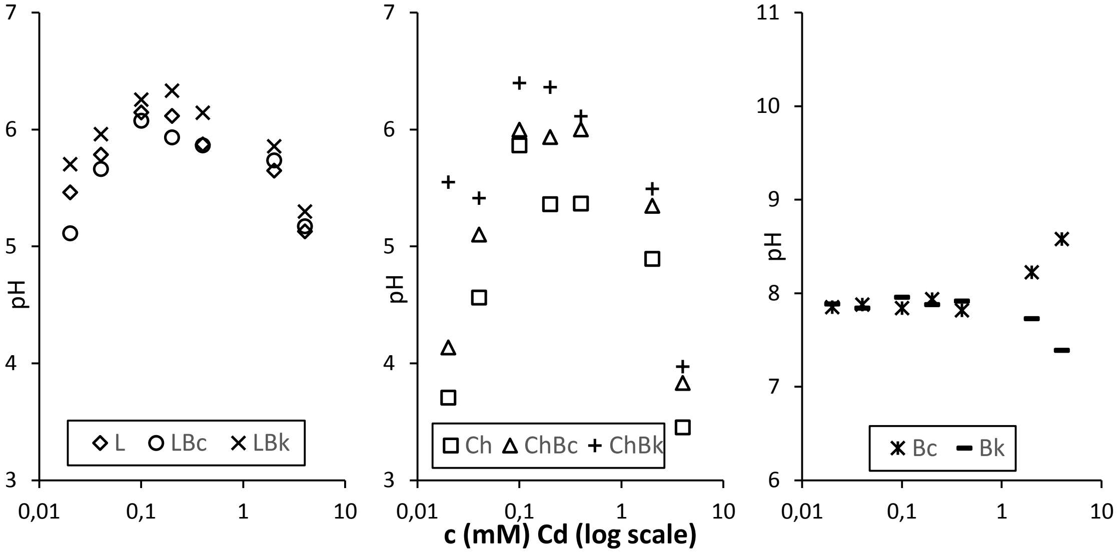


*Figure 10: Development of pH in Cd solutions according to soil and biochar type.*

### 5.1.2 Lead

Figure 11 displays the development of pH of the solutions during Pb sorption. All treatments show decreasing pH values with higher concentrations of Pb solution. Both Litávka and Choťánky soils exhibit similar behaviour over concentration line, pH 6.2 – 6.5 at c = 0.05 mM, and end at pH 4.1 – 4.5 for c = 10 mM. Values of Choťánky soil and mixtures decreases more rapidly over the first half of concentration line, compared to Litávka soil and mixtures.

Contaminated biochar amendment into soil exhibits the highest pH values in both soils (on average 0.2 points at Litávka soil and 0.5 points in Choťánky soil, compared to untreated soil).

Pure clean biochar pH is negligibly decreasing around 10.4 with rising concentration up to c = 1 mM, then decreases rapidly, up to 7.3 at final c = 10 mM. Contaminated biochar pH slightly decreasing around 7.9 up to c = 1 mM, then decreases to pH = 7 at c = 10 mM.

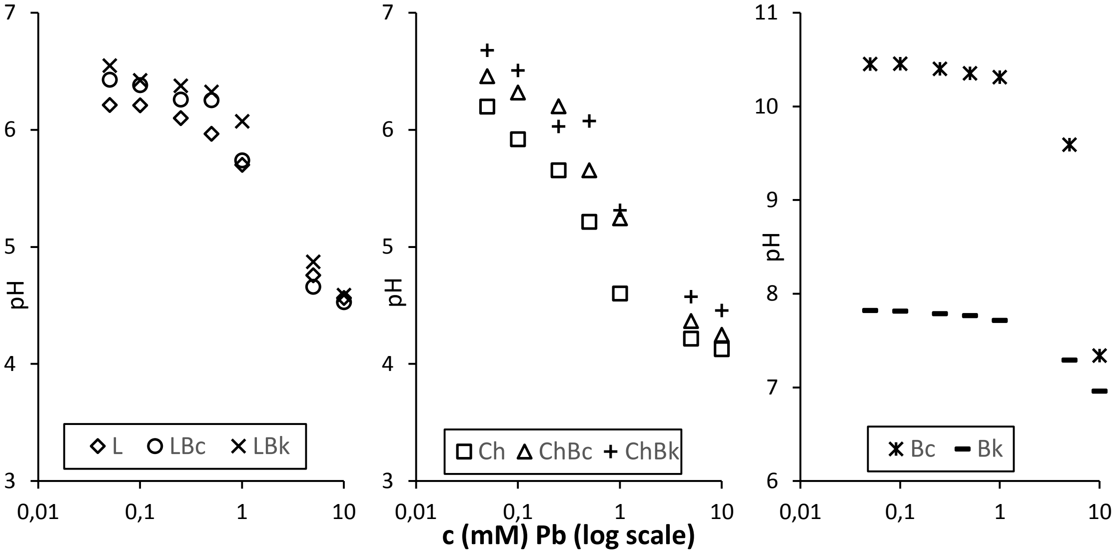


*Figure 11: Development of pH in Pb solutions according to soil and biochar type.*

### 5.1.3 Zinc

Figure 12 displays the pH values of sample matrix being loaded with Zn solutions. The pH of Litávka soil and its mixtures decreases steadily from 6.3 to 5.6 over concentration line. No significant effect on pH is reached by biochar addition overall. At c = 0.5 mM and lower, the application of clean biochar causes a minor pH decrease (in orders of 0.1 – 0.3 points).

Choťánky soil and mixtures shows similar process, but with more apparent pH decrease with increasing solution concentration. Biochar amendment enhances pH by 0.1 – 0.2 units for clean biochar, and 0.2 – 0.3 biochar for contaminated biochar.

Testing pure biochars, the pH of clean biochar gradually decreases from 10.5 to 9.9 (at c = 1mM), then drops significantly at c = 5 mM and 10 mM (pH 9.0 and 7.1). Contaminated biochar pH slightly decreases 7.8 – 7.7 up to c = 1mM, and drops at c = 5 mM (pH 7.3) and c = 10 mM (pH 6.9).

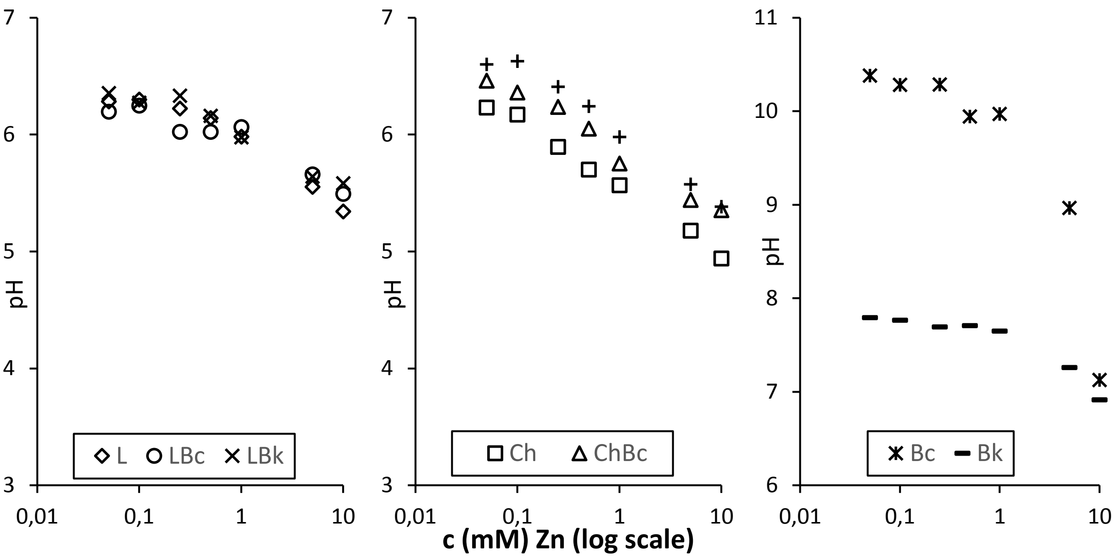
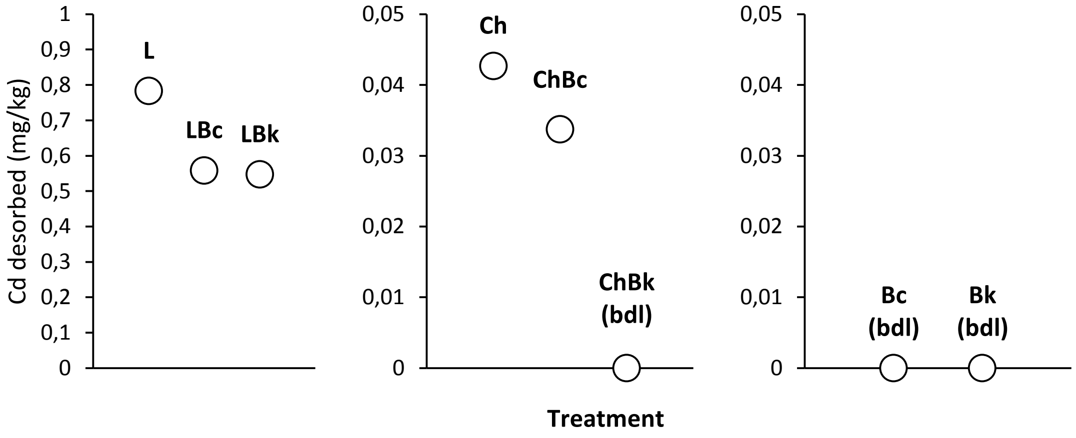


*Figure 12: Development of pH in Zn solutions according to soil and biochar type.*

In cases of Cd, Pb, and Zn overall, the contaminated biochar amendment causes the rise of pH, to a greater extend compared to clean biochar. This behaviour occurs despite having lower pH then the clean biochar and occurs in cases of testing the sorption of Pb, Zn, and higher concentrations of Cd.

## 5.2 Desorption Experiment



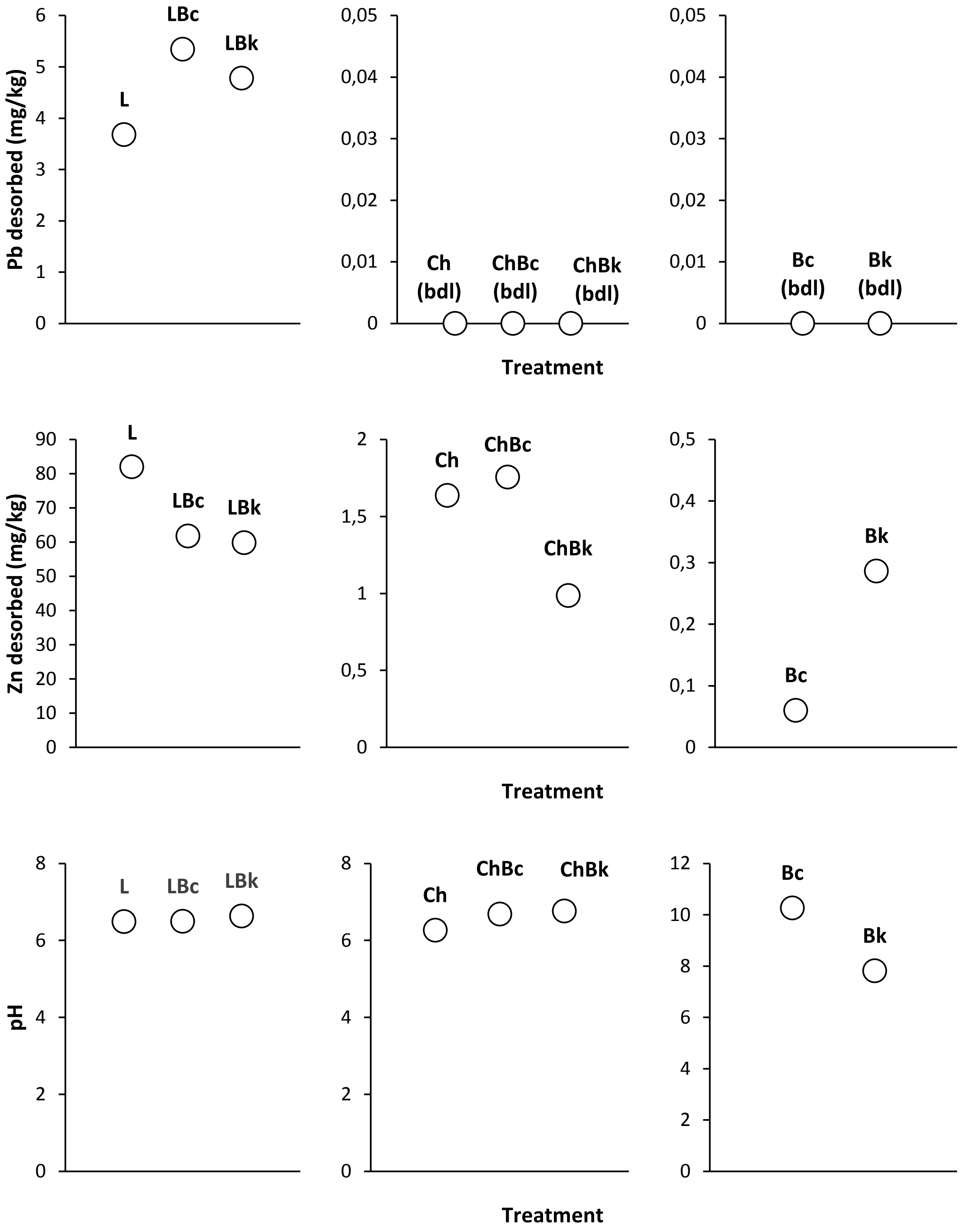


*Figure 13: Desorption of heavy metals from sample matrix and pH overview of desorbed solutions.*
*(*bdl = bellow detection limits)*

Desorption experiment (Figure 13) reports significant values only in Litávka soil and its mixtures, due to high original heavy metal content in the soil. Desorption from Litávka soil: Cd desorbed 0.78 mg/kg from total 40.6 mg/kg; Pb desorbed 3.68 mg/kg from total 3706 mg/kg; and Zn desorbed 82 mg/kg from total 5623 mg/kg. Biochar application reduces desorption in case of Cd and Zn (25 % difference compared to untreated soil), but enhances desorption of Pb (50 % for LBc and 30% for LBk).

Choťánky soil is clean of pollution, therefore it and its mixtures show no significant desorbed metal concentrations (for Cd all treatments show <0.1 mg/kg; for Pb no measurable amounts; and for Zn: Ch shows 1.6 mg/kg desorption, ChBc 1.7 mg/kg, and ChBk 1.0 mg/kg).

Cd and Pb overall desorbed in low rates, while desorbed amounts of Zn reached several fold higher values.

No significant difference was shown between biochars performance as soil amendment, despite the contaminated biochar heavy metal original content.

Moreover, desorption from both pure biochars displayed no release of Cd and Pb, and only a negligible amount of Zn (0.06 mg/kg for Bc and 0.3 mg/kg for Bk).

The pH values observed during desorption experiment show coherent data with no significant difference between original and biochar amended soils (L: 6.5, LBc: 6.5; LBk: 6.6; Ch: 6.3, ChBc: 6.7; ChBk: 6.8). The pH of pure biochars shows extremely alkaline value 10.3 for Bc and neutral value 7.8 for Bk (corresponds with $CaCl_2$ measurement).

## 5.3 Sorption Experiment

The sorption behaviour of pure and biochar amended soils as well of pure biochars was tested in a single metal sorption, the data were grouped by soil and biochar type in separate graphs. Graphs plot sorbed concentrations of metal (c sorbed) in relation to equilibrium concentration of solution (c eq). The pH graphs were constructed over the same c (eq) range to visualize the effect of pH onto the sorption.

### 5.3.1 Cadmium Sorption

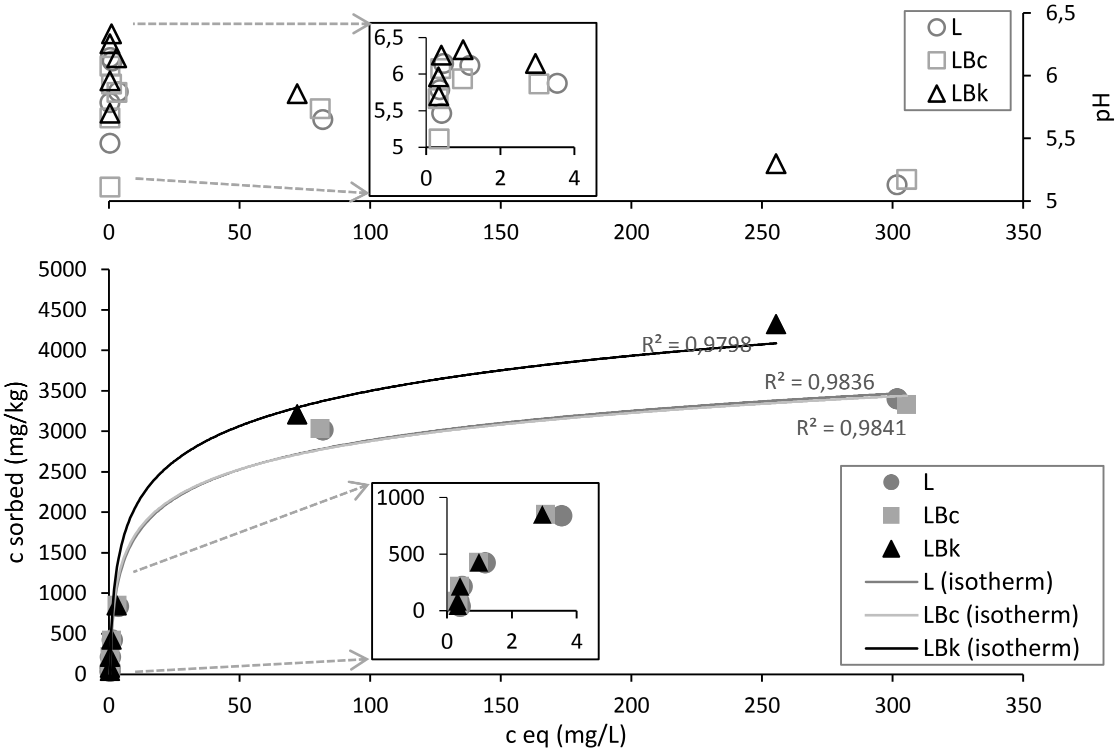


*Figure 14: Sorption of Cd onto Litávka soil (L) and its biochars mixtures (LBc, LBk)*

Figure 14 displays the sorption of Cd onto Litávka soil and biochars. Constructed isotherms characterize well the observed data. Sorbed amounts followed order LBk > LBc > L with maximum sorbed amounts 4320 mg/kg, 3400 mg/kg, and 3330 mg/kg, respectively. Pure soil and its mixture with clean biochar exhibit similar trend, contaminated biochar amendment enhances sorption while keeping the highest pH of the three treatments.

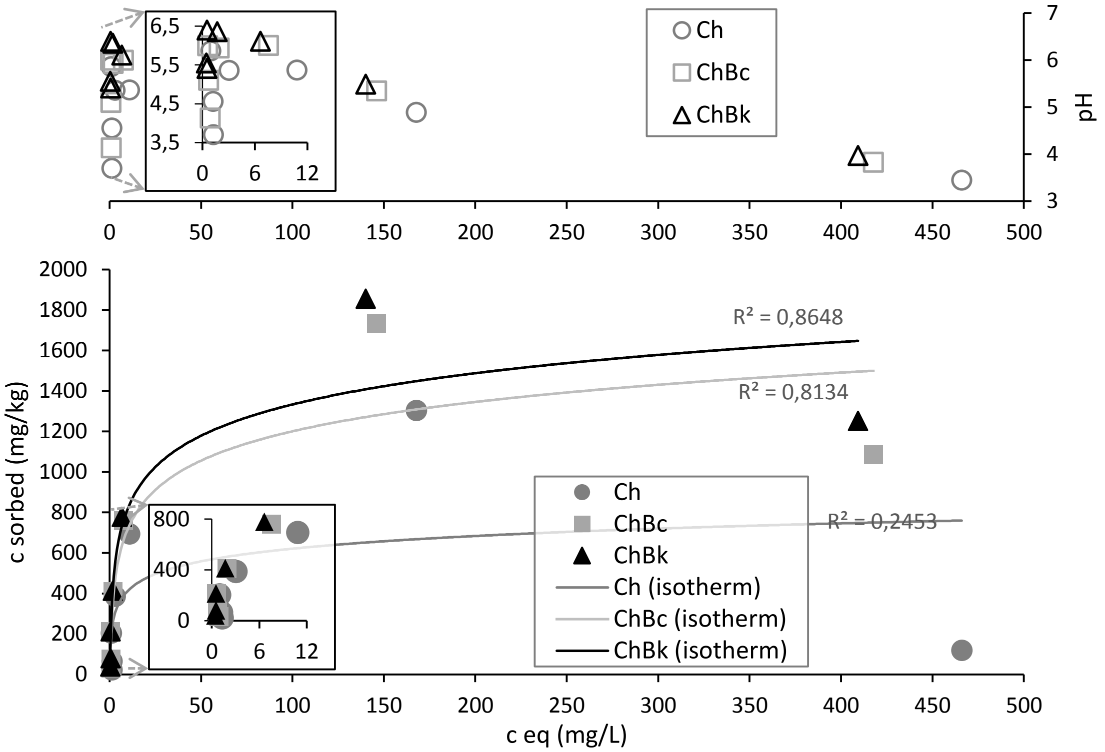


*Figure 15: Sorption of Cd onto Choťánky soil (Ch) and its biochars mixtures (ChBc, ChBk)*

Figure 15 displays sorption isotherms of Cd onto Choťánky soil and mixtures. Biochar application increases pH, which leads to increased sorption compared to untreated soil. Contaminated biochar exhibits the highest sorption, the sorption followed order: ChBk > ChBc > Ch. Maximum sorption is achieved at c = 2 mM (Ch: 1300 mg/kg, ChBc: 1760 mg/kg, and ChBk: 1830 mg/kg); at c = 10 mM a major drop in sorption of all three treatments occurs (Ch: 120 mg/kg, ChBc: 1080 mg/kg, ChBk: 1250 mg/kg), accompanied by significant pH decrement. The sorption of pure soil drops 10 fold at max c = 10 mM.

Clean biochar shows (Figure 16) great sorption capacity leaving negligible Cd amounts in solution (max 0.1 mg/L) while pH shifts over one unit. Due to rapid increase in c (sorb), no sorption isotherm can be constructed. Contaminated biochar has similar sorption capacity, leaving higher, but still minimum equilibrium Cd c(eq) in solution (max 12 mg/L).

Both pure biochars perform several fold higher Cd sorption compared to their performance in soil.

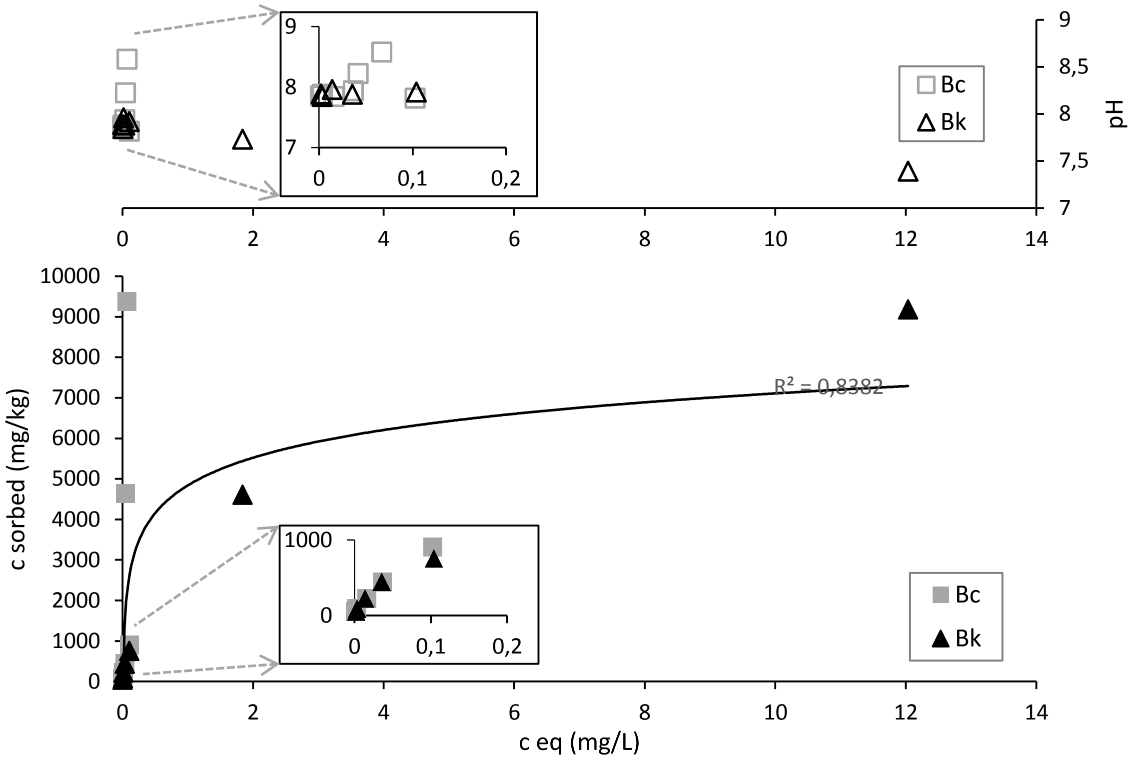


*Figure 16: Sorption of Cd on clean (Bc)and contaminated (Bk) biochar*

### 5.3.2 Lead Sorption

Figure 17 displays sorption of Pb onto Litávka soil and mixtures with biochars. Obtained data fit well into constructed isotherms. Both biochar amendments perform similar sorption capacity trend, but both amendments display decreased sorption capacity compared to the untreated soil (L: 14720 mg/kg, Bc and Bk: 16480 mg/kg at maximum c = 10 mM). Sorbed and equilibrium concentrations (more metal released) at higher Pb load correspond with decrease of pH (by 1 – 2 units).

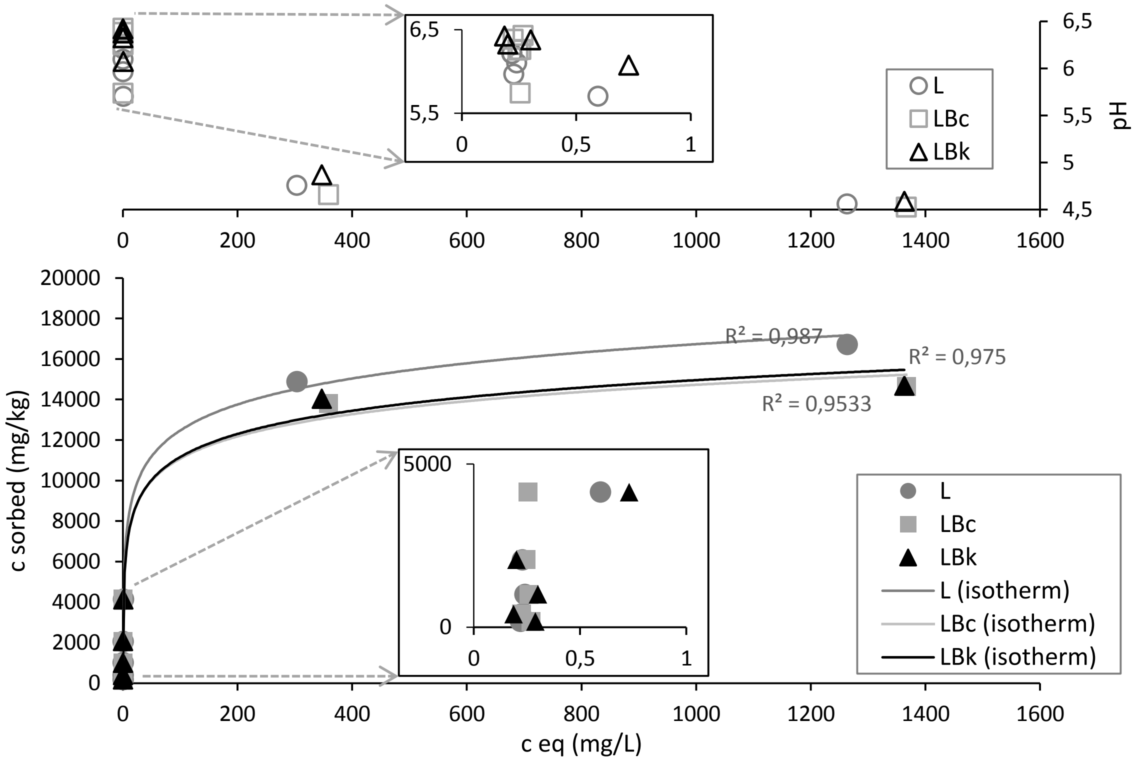


*Figure 17: Sorption of Pb onto Litávka soil (L) and its biochars mixtures (LBc, LBk)*

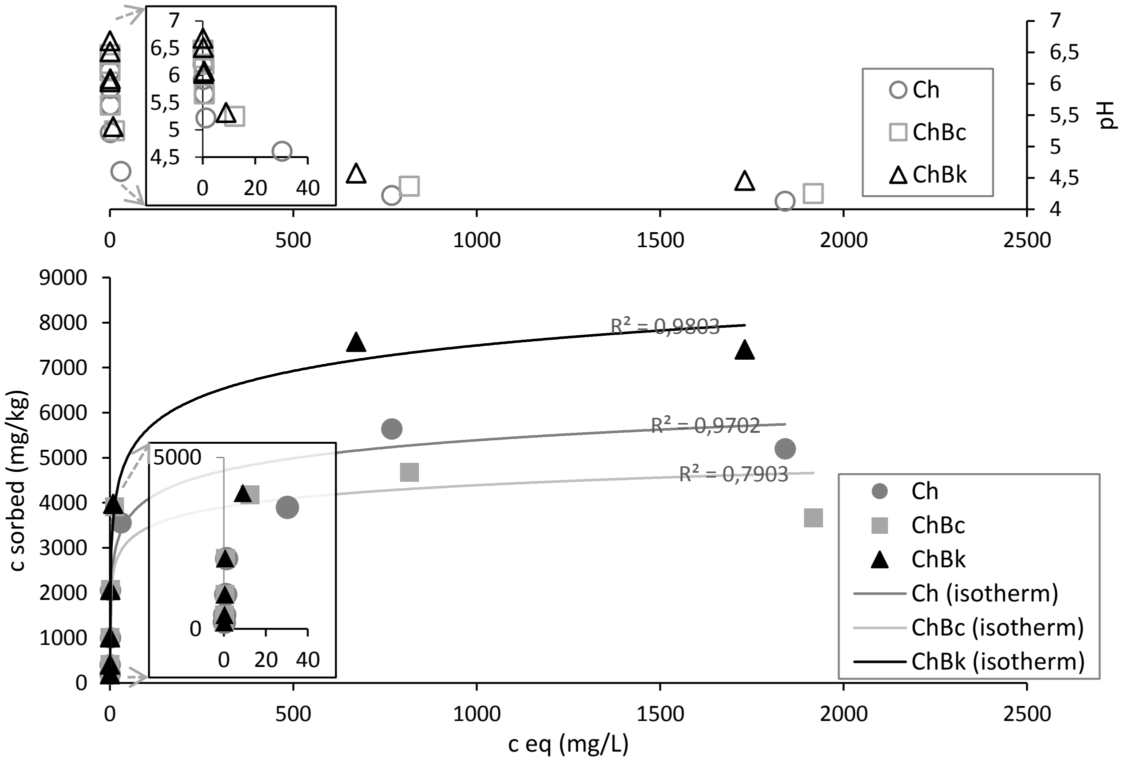


*Figure 18: Sorption of Pb onto Choťánky soil (Ch) and its biochars mixtures (ChBc, ChBk)*

The sorption isotherms of Choťánky soil and its biochar mixtures (Figure 18) show trend ChBk > Ch > ChBc. From all pH dependent values. Max sorption capacity in all biochars is obtained at load c = 5 mM (ChBk: 7570 mg/kg, Ch: 5640 mg/kg, and ChBc: 4680 mg/kg). A slight decrease in sorption occurs at c = 10 mM.

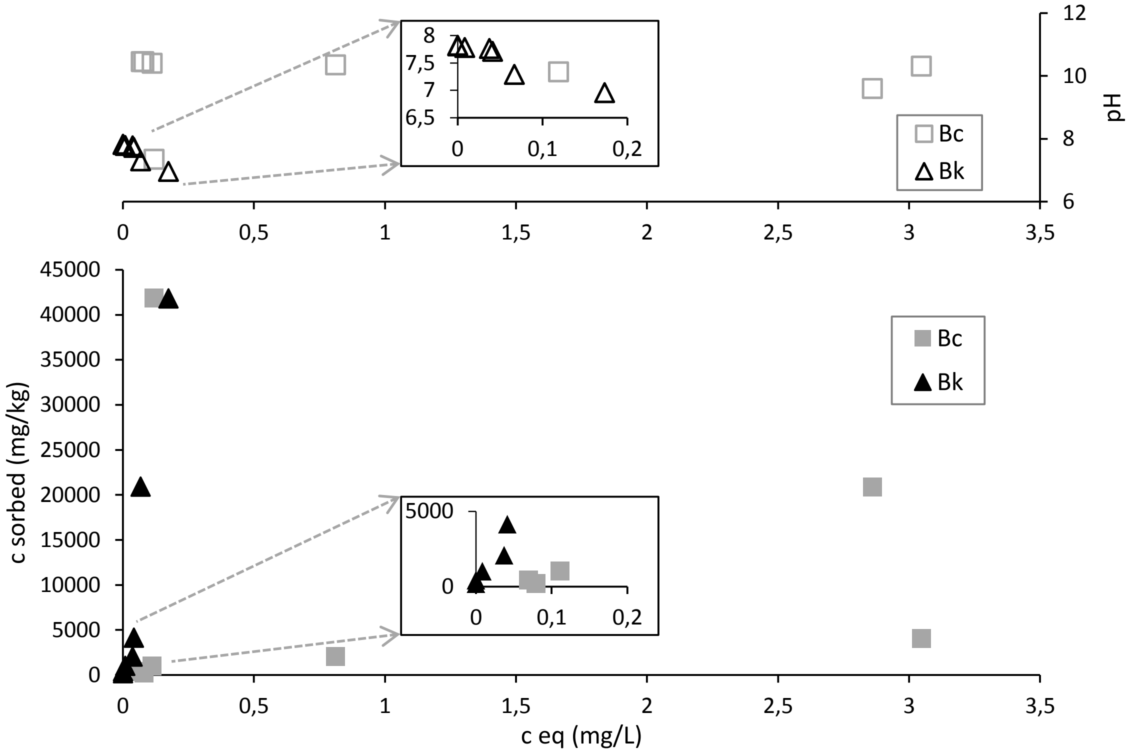


*Figure 19: Sorption of Pb onto clean (Bc) and contaminated (Bk) biochar*

Pure biochars (Figure 19) show no uniform behaviour or trend in sorption capacity with changing Pb load in solution. No isotherms can be constructed over obtained data. Contaminated biochar sorption capacity rises rapidly with increasing solution concentration, while clear biochar shows no trend with changing solution concentration. Obtained data show that released and sorbed Pb amounts correspond with changes in pH values.

### 5.3.3 Zinc Sorption

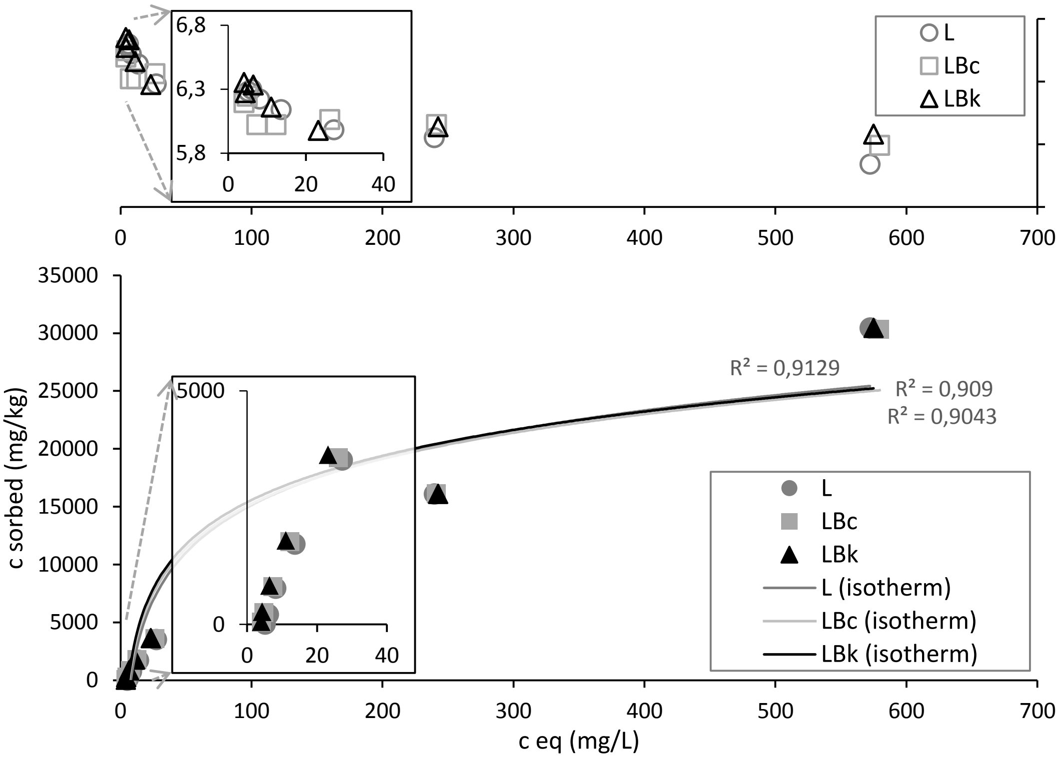


*Figure 20: Sorption of Zn onto Litávka soil (L) and its biochars mixtures (LBc, LBk)*

Sorption isotherms over Litávka soil and its mixtures (Figure 20) with biochars show negligible effect of biochar amendment. All pH and sorbed concentrations show similar process, pH decreases gradually over one unit in all treatments over increasing Zn concentration in solution. Increment in sorption corresponds well with slight decrement of pH, with maximum sorbed amounts exceeding 30000 mg/kg for all treatments.

Choťánky soil and mixtures with biochars in Figure 21 show contaminated biochar amendment sorption performance exceeding the performance of clean biochar amendment and pure soil (maximum sorbed c: ChBk: 35900 mg/kg, ChBc: 29300 mg/kg, and Ch: 29700 mg/kg). The gradually decreasing pH values correspond with gradually increasing sorption on all three treatments.

Figure 22 shows sorption of Zn onto pure biochars. Both biochars exhibit great sorption capacity (Bc sorbed 40000 mg/kg while leaving 18 mg/L in solution, Bk sorbed 38700 mg/kg while leaving 157 mg/L in solution). Clean biochar data show a rapid pH drop with increasing Zn solution concentration. Biochar sorption data are not uniform at the beginning of concentration line, not reliable enough to construct isotherm. Contaminated biochar performs better sorption at lower Zn solution concentrations compared to clean biochar, but at solution concentration 5mM and 10mM leaves 8 fold higher Zn concentrations in equilibrium solution.

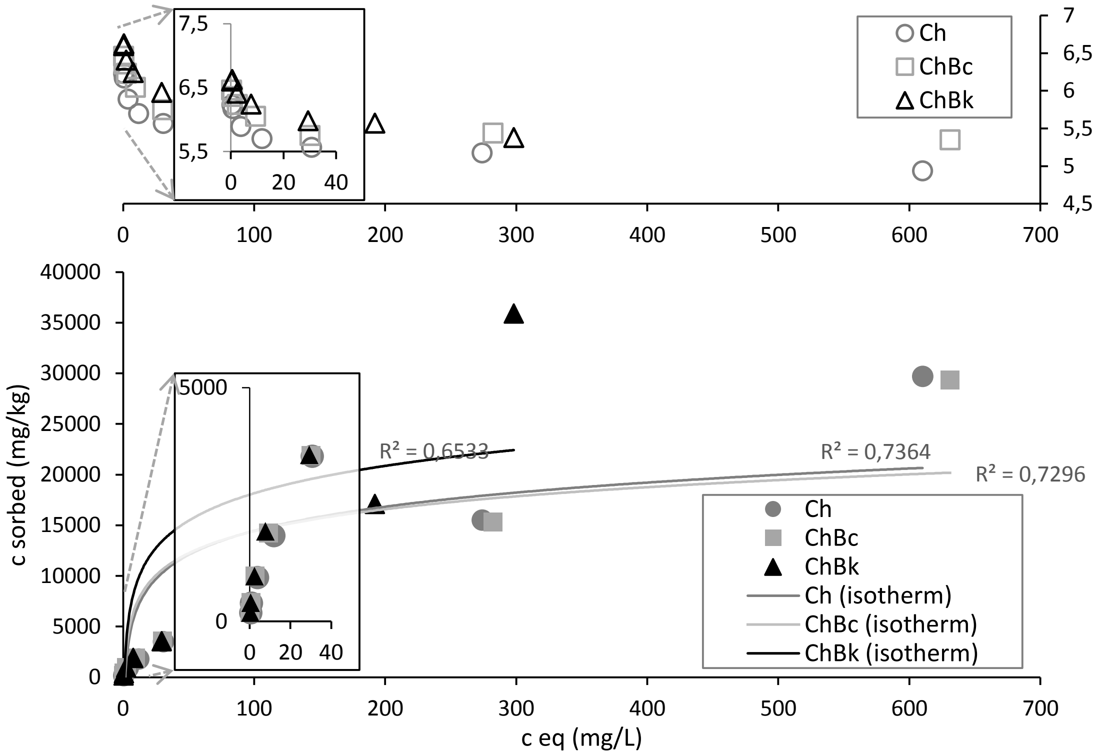


*Figure 21: Sorption of Zn onto Choťánky soil (Ch) and its biochars mixtures (ChBc, ChBk)*

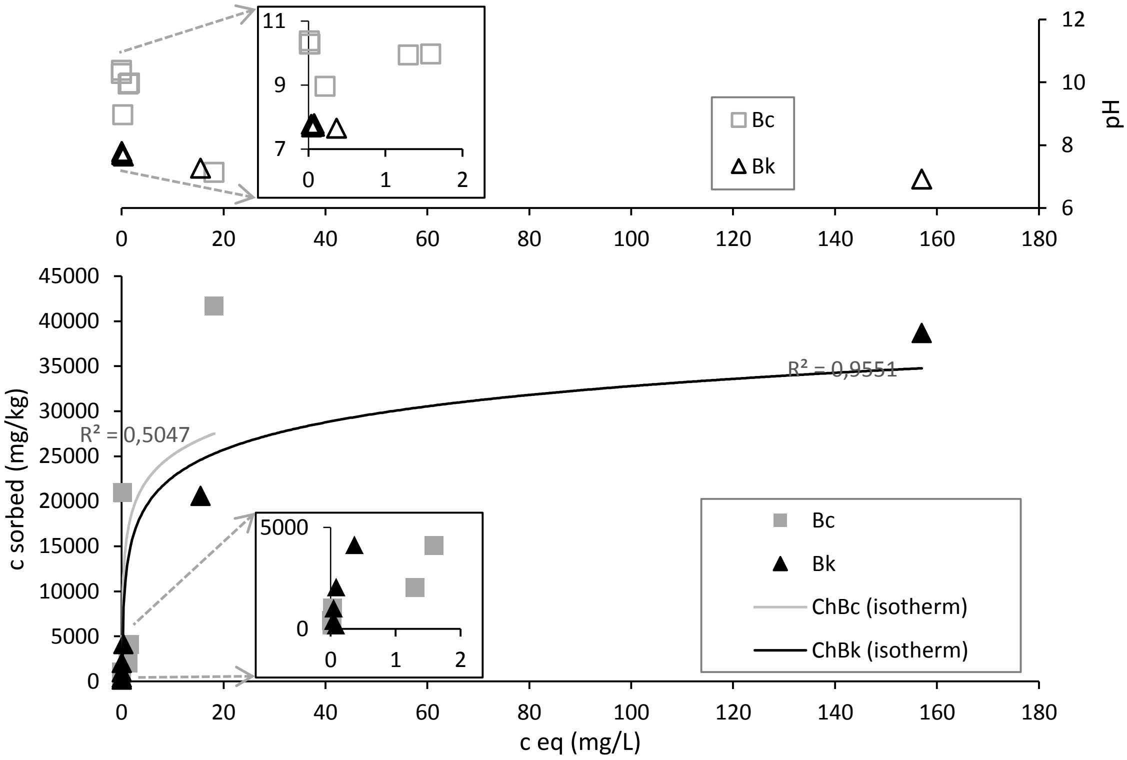


*Figure 22: Sorption of Zn onto clean (Bc) and contaminated (Bk) biochar*

The efficiency of sorption of Cd, Pb, and Zn on each soil and its biochar amendments, as well as on pure biochars is depicted in Table 7. In Litávka soil, the best sorption efficiency for Cd is achieved with amendment of biochars, however the values do not vary significantly with exception of load 4 mM; for Pb the best values are obtained in untreated soil, though the values of treatments are again close with exception of 5 mM and 10 mM; and for Zn the contaminated biochar rates the best sorption efficiency overall. In Choťánky soil, the contaminated biochar demonstrates the best sorption efficiency for all metals (with the only exception for 0.1 mM Pb, with minimum difference 0.2 %). Sorption efficiency for both pure biochars rates extremely high up to 100 %, with only significant drop in sorption located at maximum Zn load for Bk (92.5 % value).

| **Metal Solution** | **Treatment** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **L** | **LBc** | **LBk** | **Ch** | **ChBc** | **ChBk** | **Bc** | **Bk** |
| Cd 0.02 mM | 81.4% | 84.5% | **85.1%** | 47.8% | 64.2% | **82.1%** | 100% | 99.9% |
| Cd 0.04 mM | 91.1% | **92.2%** | 92.2% | 73.5% | 84.8% | **88.9%** | 99.9% | 99.9% |
| Cd 0.1 mM | 95.5% | **96.3%** | 96.2% | 91.5% | 94.7% | **95.5%** | 99.9% | 99.9% |
| Cd 0.2 mM | 94.6% | **95.5%** | 95.5% | 86.5% | 91.4% | **92.5%** | 99.8% | 99.8% |
| Cd 0.4 mM | 92.2% | 93.3% | **93.5%** | 76.3% | 83.5% | **85.5%** | 99.8% | 99.8% |
| Cd 2 mM | 64.9% | 65.3% | **69.1%** | 28.0% | 37.3% | **39.9%** | 100% | 99.2% |
| Cd 4 mM | 36.1% | 35.3% | **45.9%** | 1.3% | 11.5% | **13.3%** | 100% | 97.5% |
| Pb 0.05 mM | **95.9%** | 94.5% | 94.6% | 98.3% | 98.4% | **98.5%** | 99.2% | 100% |
| Pb 0.1 mM | **98.1%** | 97.6% | 97.9% | 98.6% | **98.7%** | 98.5% | 99.7% | 100% |
| Pb 0.25 mM | **99.2%** | 99.0% | 98.9% | 98.7% | 98.9% | **99.1%** | 99.8% | 100% |
| Pb 0.5 mM | **99.6%** | 99.5% | 99.6% | 98.8% | 99.3% | **99.4%** | 99.2% | 100% |
| Pb 1 mM | 99.6% | **99.7%** | 99.5% | 85.5% | 94.1% | **95.7%** | 98.5% | 100% |
| Pb 5 mM | **71.1%** | 65.8% | 66.9% | 26.9% | 22.3% | **36.1%** | 99.7% | 100% |
| Pb 10 mM | **39.8%** | 34.9% | 35.1% | 12.4% | 8.7% | **17.6%** | 100% | 100% |
| Zn 0.05 mM | 6.0% | 27.2% | **27.8%** | 95.3% | 96.8% | **97.0%** | 99.8% | 99.1% |
| Zn 0.1 mM | 51.2% | 61.8% | **64.6%** | 96.0% | 96.8% | **97.5%** | 99.9% | 99.8% |
| Zn 0.25 mM | 76.1% | 79.6% | **81.6%** | 92.6% | 95.0% | **95.4%** | 100% | 99.9% |
| Zn 0.5 mM | 83.0% | 85.2% | **86.5%** | 88.6% | 91.0% | **92.6%** | 98.8% | 99.9% |
| Zn 1 mM | 85.0% | 85.9% | **87.5%** | 85.2% | 85.5% | **85.9%** | 99.2% | 99.8% |
| Zn 5 mM | **76.8%** | 76.7% | 76.6% | 73.9% | 73.1% | **81.7%** | 100% | 98.5% |
| Zn 10 mM | **72.6%** | 72.3% | 72.5% | 70.9% | 69.9% | **85.8%** | 99.1% | 92.5% |

*Table 7: Sorption efficiency of soils treatments according to soil and biochar type, grouped by tested heavy metal load.* ***Bold*** *are the maximum efficiency values for particular soil treatment at each metal concentration.*

## 5.4 Langmuir and Freundlich Sorption Models

| | | efficiency | Langmuir parameters | | efficiency | Freundlich parameters | |
|---|---|---|---|---|---|---|---|
| **Element** | **Treatment** | **E** | **$K_L$** | **$S_{max}$** | **E** | **$K_F$** | **n** |
| **Cd** | L | 0.998 | 0.092 | 3479.2 | 0.938 | 23.51 | 0.351 |
| | Ch** | 0.970 | 0.095 | 1387.0 | 0.905 | 10.30 | 0.368 |
| | LBc | 0.998 | 0.114 | 3399.5 | 0.932 | 23.42 | 0.336 |
| | ChBc | 0.882 | 0.161 | 1436.3 | 0.702 | 9.58 | 0.247 |
| | LBk | 0.986 | 0.061 | 4347.0 | 0.976 | 29.29 | 0.393 |
| | ChBk | 0.917 | 0.174 | 1578.9 | 0.757 | 10.68 | 0.249 |
| | Bc | n.a.* | n.a.* | n.a.* | n.a.* | n.a.* | n.a.* |
| | Bk | 0.997 | 0.402 | 11063.0 | 0.991 | 224.84 | 0.445 |
| **Pb** | L | 0.983 | 0.424 | 15900.7 | 0.922 | 1829.59 | 0.316 |
| | Ch | 0.941 | 0.388 | 4999.8 | 0.894 | 1426.59 | 0.189 |
| | LBc | 0.955 | 0.494 | 14265.9 | 0.906 | 1867.41 | 0.295 |
| | ChBc | 0.943 | 0.787 | 4222.9 | 0.678 | 1578.96 | 0.140 |
| | LBk | 0.982 | 0.404 | 14441.4 | 0.905 | 1813.13 | 0.298 |
| | ChBk | 0.963 | 0.188 | 7403.3 | 0.914 | 1759.06 | 0.206 |
| | Bc | n.a.* | n.a.* | n.a.* | n.a.* | n.a.* | n.a.* |
| | Bk | n.a.* | n.a.* | n.a.* | n.a.* | n.a.* | n.a.* |
| **Zn** | L | n.a.* | n.a.* | n.a.* | 0.998 | 244.88 | 0.760 |
| | Ch | 0.995 | 0.001 | 94576.0 | 0.999 | 233.41 | 0.755 |
| | LBc | n.a.* | n.a.* | n.a.* | 0.998 | 276.66 | 0.739 |
| | ChBc | 0.993 | 0.001 | 90762.9 | 0.998 | 253.20 | 0.735 |
| | LBk | n.a.* | n.a.* | n.a.* | 0.998 | 287.83 | 0.734 |
| | ChBk | 0.888 | 0.007 | 40592.2 | 0.989 | 5.07 | 1.554 |
| | Bc | 0.707 | 0.102 | 60267.4 | 0.735 | 6269.10 | 0.647 |
| | Bk | 0.989 | 0.063 | 42531.2 | 0.956 | 3780.58 | 0.462 |

* not available results

** modelled without the last concentration

*Table 8: Evaluation of Langmuir and Freundlich models.*

Sorption data were modelled by both Langmuir and Freundlich equations (Table 8) to evaluate isotherm type. For Cd and Pb the Langmuir model fits better. Zn sorption isotherms were better characterized by empirical Freundlich model. Models were however not able to calculate values for both clean and contaminated biochars for Pb, and contaminated biochar for Cd.

# 6 Discussion

## 6.1 The pH Shift Induced by Biochar Amendment

The rise of pH values is observed when soils are amended with both contaminated and clean biochars. Lucchini et al. (2014) attributes this effect to increment of ash fraction together with dissolution of hydroxides and carbonates from biochar.

In cases of testing sorption of Pb, Zn and higher concentrations of Cd, the contaminated biochar amendment into both tested soils increases pH values to a greater extend compared to clean biochar, despite having significantly lower pH itself. This suggests that the shift in pH is caused by changes in chemical properties of soil, e.g. CEC change which is significantly higher in Bk compared to Bc, or by its high basic K content which is released after metal sorption.

The observed decrease of pH occurring with utilizing higher metal concentrations load can be attributed to hydrolysis effect and release of $H^+$ protons from functional groups facilitating sorption at soil surface (Mouta et al., 2008).

## 6.2 Desorption Experiment

Despite the Pb and Zn original content in Litávka soil (3706 and 5623 mg/kg, respectively), the desorbed amounts of Zn is more than 10 fold higher compared to Pb, due to strong fixation of Pb onto the soil matrix (Kabata-Pendias, 2011).

The facts that (1) desorption from both biochar amendments into Litávka soil shows similar results, and (2) no metals are released from pure contaminated biochar, indicate that heavy metals are bound strongly in the contaminated biochar, as was previously found by Beesley et al. (2010). The authors compared improvement in soil sorption by compost and biochar amendment over time, finding out biochar is a suitable solution for reducing leachable Cd and Zn content.

Biochar application into contaminated Litávka soil results in increased desorption of Pb - LBc to a greater extend then LBk. This is in contrast with typical behaviour when precipitation occurs while introducing biochar into soil (e.g. Břendová et al., 2015), and might be caused by system-specific changes in soil chemical balance leading into changes in Pb speciation, or a change in charge caused by different isoelectric point (Qui et al., 2008).

These issues are however not part of this thesis and would need further investigation in future. In case of Cd and Zn, both biochar (Bc and Bk) amendments worked successfully in decreasing metal desorption, which is in agreement with former finding of Trakal et al., 2011.

The degree to which the biochar amendments decrease the desorption is in agreement with Beesley et al. (2010) for Cd and to a lesser extend also for Zn, where authors report more rapid desorption decrease. Trakal et al. (2011) also report similar results in desorption changes induced by biochar amendment.

## 6.3 Sorption Experiment

The sorption followed order Pb > Cd > Zn in Litávka soil treatments and Zn > Pb > Cd in Choťánky soil treatments. This finding is partially in agreement with Trakal et al. (2011), who reported Cd to be the least sorbed metal, however reported Pb to be sorbed better than Zn. Findings of this study differ, in Litávka soil due to high initial Zn content in soil and weak fixation of Zn (as mentioned below in Zn sortion section), and in Choťánky soil the difference might be caused by Zn immobilization in acidic soil by humic acids from soil organic material as proposed by Clemente and Bernal (2006).

### Cd Sorption

The decrease in pH at higher c(eq) of Cd in Litávka soil is followed by higher equilibrium and sorbed concentrations. Beesley and Marmiroli (2010) reported that raising the pH by biochar amendment reduces Cd mobility in soil, which assists Cd retention in biochar (with respect to high Cd concentrations in soil).

The isotherms for Cd in pure Choťánky soil are modelled without last concentration (c = 10 mM) value showing significant 10 fold decrement in sorption (resulting in almost negligible sorption onto pure soil), which might indicate connection with both low CEC of soil and also acidic pH of solution mobilizing the heavy metal and preventing sorption. Sorption in Choťánky soil treatments is markedly increased by biochar amendments resulting in higher sorption.

### Pb Sorption

The sorption of Pb at lower metal concentrations (up to 1 mM) occurs under higher pH compared to sorption at metal concentrations 5 mM and 10 mM. The sorption at concentrations up to 1 mM is characterized with high efficiency for all treatments of both soils, only leaving trace concentrations of Pb (<1 mg/L) in solution for Litávka soil and minor concentrations (<40 mg/L) for Choťánky soil. The difference in equilibrium concentrations might be attributed to the difference of CEC in favour of Litávka soil. Lu et al. (2012) found that Pb sorption on biochar in moderately acidic conditions is increasing with rising pH due to hydrolyzed $Pb^{2+}$ which is more likely to be sorbed than free $Pb^{2+}$. The main mechanism driving sorption described by them is precipitation, connected with a release of $Ca^{2+}$ and $Mg^{2+}$, thus the sorbed Pb can be considered stable.

In case of Pb sorption in Litávka soil, untreated soil performs better than when amended with biochars, indicating the biochar amendment is not sufficient for such contaminated soil. In Choťánky soil, contaminated biochar amendment enhances sorption, in contrast to clean biochar which even decreases sorption at higher c(eq). This finding is in contrast to former study by Trakal et al. (2011) that reported sorption enhanced by biochar amendment caused by organic matter increment.

Comparing Pb sorption onto Litávka and Choťánky matrixes, Litávka is able to sorb twice higher amounts of metal compared to Choťánky, and Choťánky treatments leave significant amounts of metal in solution.

### Zn Sorption

Clemente and Bernal (2006) claim that in acid soil the Zn is immobilized by humic acids from organic material. Zn shows the highest sorbed values of the tested metals. Trakal et al. (2011) however showed during multi-element sorption experiment, that Zn is sorbed in lower rates than other metals such as Cu and Pb.

Biochar amendment into contaminated Litávka soil show no difference in sorption. This might be due to already high original Zn content in soil, and its predominant fixation onto Mn and Fe hydroxides and clay minerals in soil (Trakal et al., 2011). The exception is 0.05 mM Zn concentration load where sorption onto pure Litávka soil is weak and increases significantly by biochar amendment and might be attributed to weak fixation of Zn in presence of other cations in solution (Trakal et al., 2012) and increased organic matter from biochar (Clemente and Bernal, 2006). The difference in sorption efficiency is however remarkable for contaminated biochar in Choťánky soil.

### Langmuir and Freundlich Models

For description of Cd and Pb sorption, Langmuir model is more suitable, indicating the sorption is monolayer, whereas for Zn the Freundlich model fits more. Trakal et al. (2011) reported similar results, finding Langmuir model suitable for Cd and Pb, but not for Zn.

The maximum sorption capacity followed order: LBk > L > LBc > ChBk > ChBc > Ch for Cd, and L > LBk > LBc > ChBk > Ch > ChBc for Pb. Models were not able to calculate most values for both clean and contaminated biochar pointing to some unaccountable behaviour of pure biochars, occurring also during the sorption experiment, that suggests the biochar affects soil properties rather facilitates sorption on itself.

### Sorption Overview

| | Litávka soil | Choťánky soil | note |
|---|---|---|---|
| **Cd** | Bk | Bk | L $c_{(sorb)}$ > Ch $c_{(sorb)}$ [2.4 fold] |
| **Pb** | soil | Bk | L $c_{(sorb)}$ > Ch $c_{(sorb)}$ [2.5 fold] |
| **Zn** | all comparable | Bk | comparable $c_{(sorb)}$ in both soils |

*Table 9: Overview of sorption showing the most efficient sorbents for each soil*

Table 9 summarizes the sorption efficiency table from results section and overviews the sorption experiment showing the most efficient treatment for each metal and soil type. In majority of cases the contaminated biochar Bk show the best performance, however in Litávka soil the results varied: for Pb the untreated soil has the best sorption capacity, and for Zn all treatments show comparable results. For Cd and Pb the Litávka soil and its biochar mixtures showed approx. 2 fold higher sorption capacity compared to Choťánky soil treatments. For Zn the results were again comparable.

In most cases the soil itself was able to adsorb significant amounts of metals comparable with biochar amendment, mainly the uncontaminated clean biochar (the contaminated biochar showed overall better sorption capacity). This is in agreement with Jiang et al. (2012b) who claims that soil can decrease active and bioavailable heavy metals by itself through adsorption and precipitation mechanisms. However, this is not true for performance of Choťánky soil with low CEC, where biochar amendment improved sorption significantly. Concluded, it can be claimed that the examined biochar amendment 1 % (w/w) is not sufficient for sorbing high concentrations of metal loads, as Trakal et al. (2011) asserted, too. Studies from some other authors (e.g. Uchimiya et al., 2010; Uchimiya et al., 2011a, b; Břendová et al., 2015) use biochar rates ranging from 5 % to 20 %.

The overall great results of contaminated biochar amendment are in agreement with former research of Trakal et al. (2011) and might point to the fact, that amendment of such biochar enhance soil sorption capacity. Sorption results of pure contaminated biochar show that metals bind strongly onto biochar. It should be noted, concerning the biochar amendment sorption performance that Uchimiya et al. (2010) concluded biochar amendment immobilizes metals added into solution rather than original leachable soil content.

# 7 Conclusion

Contaminated biochar has proven to be an effective soil amendment in means of enhancing heavy metal sorption capacity especially in moderately acidic sandy-loam Choťánky soil with low CEC. The contaminated biochar was characterized by neutral pH, low carbon content, high content of other elements and high CEC. Its application as amendment enhanced sorption in most cases studied and its sorption efficiency displayed even better results than the one of commercial uncontaminated biochar. The sorption capacity of clean biochar is affected by its alkaline pH, high carbon content, and low CEC, which assists precipitation instead of sorption. Moreover, the desorption experiment showed that biochar prepared from contaminated biomass does not release heavy metals incorporated in it from original willow feedstock, thus represents no threat by potentially releasing heavy metals from its structure, and could be considered as a promising soil amendment tool for enhancing sorption for specific soil conditions.

For moderately acidic clay-loamy Litávka soil contaminated with high original heavy metal content and high CEC, only the amendment of contaminated biochar for Cd sorption increased the sorption. For Pb and Zn sorption, the pure soil sorbed significant amounts of metals by itself. In case of Pb sorption, the biochars even decreased sorption efficiency of soil, and for Zn all three treatments performed similarly with no significant difference.

The amounts of metals sorbed in order Pb > Cd > Zn in Litávka soil treatments and Zn > Pb > Cd in Choťánky soil treatments. For Cd and Pb sorption, Litávka soil treatments displayed higher sorption compared to Choťánky soil (2.4 fold for Cd, 2.5 fold for Pb) at high metal load concentrations (2 and 4 mM for Cd; 5 and 10 mM for Pb). At lower Cd and Pb concentrations the treatments of both soils displayed similar sorption efficiency. Zn sorption at 5 and 10 mM concentration loads showed comparable results in both soil treatments, while at lower Zn concentrations the sorbed amounts were 1.4 fold higher in Choťánky soil treatments.

It should be noted that 1 % (w/w) biochar ratio amendment was not sufficient for such contaminated soil as Litávka from smelter facility, and was suitable only for binding lower concentrations of metal loads.

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# 9 List of Abbreviations

| | |
|---|---|
| AEC | anion exchange capacity |
| Bc | clean biochar |
| bdl | bellow detection limits |
| BET equation | Brunauer, Emmett and Teller equation |
| Bk | contaminated biochar |
| $c_{(0)}$ | initial metal concentration in solution |
| $c_{(desorb)}$ | desorbed metal concentration |
| $c_{(eq)}$ | equilibrium metal concentration in solution |
| $c_{(sorb)}$ | sorbed metal concentration |
| CEC | cation exchange capacity |
| E | efficiency of Langmuir and Freundlich models |
| FESEM | field emission scanning electron microscopy |
| GHG | greenhouse gases |
| Ch | Choťánky soil |
| ChBc | mixture of Choťánky soil and clean biochar |
| ChBk | mixture of Choťánky soil and contaminated biochar |
| ICP-OES | inductively coupled plasma optical emission spectrometry |
| $K_f$ | Freundlich sorption coefficient |
| $K_l$ | Langmuir sorption coefficient |
| L | Litávka soil |
| LBc | mixture of Litávka soil and clean biochar |
| LBk | mixture of Litávka soil and contaminated biochar |
| n | Freundlich empirical coefficient |
| PAH | polycyclic aromatic hydrocarbons |
| PCB | polychlorinated biphenyl |
| SDBC | sludge derived biochar |
| $S_{max}$ | maximum sorption capacity |
| SSA | specific surface area |
| TE | trace element(s) |
| w/v | weight to volume ratio |
| w/w | weight to weight ratio |