Marshallplan Report

Heavy metal adsorption on biochar-treated soils

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1. Motivation

When I started my PhD at the University of Natural Resources and Life Sciences (BOKU) in June 2010, I told my supervisor, PD Dr. Franz Zehetner, that I would like to spend some time abroad. After having passed the general qualification for university entrance, I have already spent 12 months in the USA as an AuPair, which I enjoyed a lot. I gained a lot of experiences in foreign culture and the English language, which was later advantageous within the course of my studies and especially for my PhD. One is confronted with English publications; however, even a 12 months stay in an English speaking country cannot really prepare one for the scientific English that is required when working on a PhD. I was able to deal with the challenge; I managed to write my first English publication within the first year; however, I concluded that another stay abroad would not only be beneficial in terms of improving my scientific written English, but also my spoken English, which I considered to be very helpful in terms of upcoming talks in front of an international audience. Hence, in the course of my second year at BOKU, I came up again with the idea of going abroad. I told my supervisor about that; he thought it would be a great idea and opportunity to see how other researchers work at other universities. So we both sat together and discussed how to plan a trip abroad. He came up with Cornell University, which is a partner university of BOKU as well as the idea of applying for a Marshall Plan scholarship that is specifically meant for the scientific exchange between the USA and Austria. Since I liked the stay in the USA, I agreed on that and started planning the trip in July 2011. I contacted Prof. Johannes Lehmann, who leads one of the worldwide acknowledged research groups focusing on Biochar (BC) research. Up until September, it was still unclear how to incorporate work at another university into my PhD thesis, which is titled: "*Effects of Biochar on Carbon sequestration and soil fertility*". We both decided it was best to plan adsorption experiments on BC using heavy metals as this included lab work that was manageable within a limited amount of time but at the same time provided results that are potentially publishable. In addition, the results of the work at Cornell should provide basic information on a planned follow-up project.

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2. The Biochar Project

The Biochar Project with the official title "*Biochar for Carbon Sequestration in Soils: Analysis of production, biological effects in the soil and economics*" started in April 2010. It is a cooperation between BOKU, the Austrian Institute of Technology (AIT), Joanneum Research GmbH, Graz and the Federal Research and Training Centre for Forests, Natural Hazards and Lanscapes (BfW), Vienna, which is financed by the Austrian Research Promotion Agency (FFG, project number: 825438). It is composed of several work packages that are summarized in Figure 1.
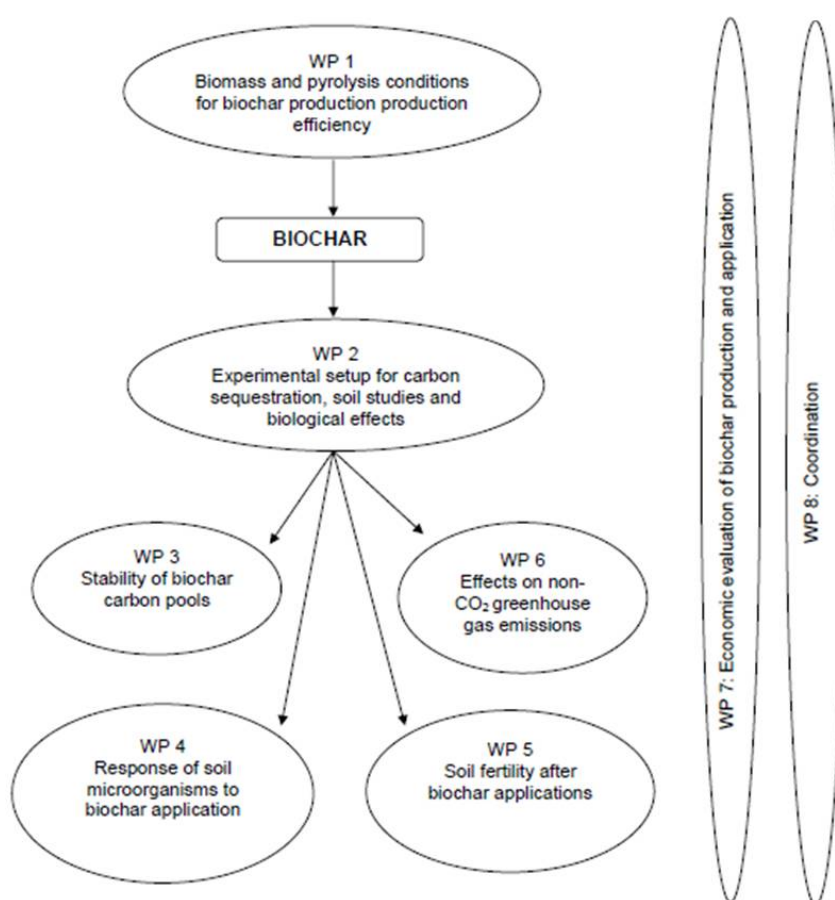

Figure 1 The 8 work packages of the Biochar project.

The work packages include the investigation of BC production and a thorough BC characterization, which was published by Kloss et al. (2012) under the title: "Characterization of Slow Pyrolysis Biochars: Effects of Feedstocks and Pyrolysis

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Temperature on Biochar Properties ". Based on the results, Work Package 2 was set up including the planning of field as well as pot experiments under greenhouse conditions using different BC types. Different work packages subsequently investigated the effects of BC on greenhouse gas emissions, on soil microbial communities and leaching characteristics, which have been carried out in the course of several Master theses. Within the course of the project the question came up how BC application to soil affects heavy metal retention. Coincidentally, a Czech student who was interested in adsorption of different elements to soil asked whether he could work in the BOKU lab for 2 months offered to carry out adsorption experiments with biochar using Cd. Based on the preliminary results, we decided to broaden our knowledge regarding heavy metal adsorption and came to the conclusion that this research question is suitable for a 4 month stay abroad.

3. Scientific background

Before presenting the research questions and results that were obtained at Cornell University, a short overview over the BC issue and adsorption will be given.

3.1 The Biochar Issue

BC is a carbon (C) -rich product formed during the thermal decomposition of biomass under anoxic or low-oxic conditions and at temperatures below 700°C. The process, which leads to BC, is called pyrolysis (Lehmann and Joseph, 2009; Sohi et al., 2009; Roberts et al., 2010). The term BC refers to the intentional generation of charcoal for soil amendment and C sequestration in the soil, whereas conventional charcoal, which is als produced during pyrolysis, is rather used for heating purposes (Lehmann and Joseph, 2009). Main purposes of BC application to soil are compiled in

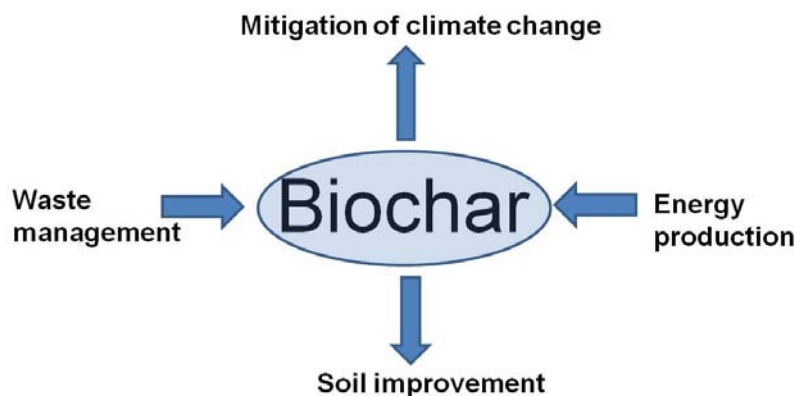*Heavy metal adsorption on biochar-treated soils*

Figure 2 Motivation of Biochar application to soil (Lehmann and Joseph, 2009; modified)

The Amazonian Terra Preta soils served as a role model, where charcoal derived from cooking purposes were incorporated in the soil and showed a significantly better soil quality compared to the surrounding unfertile soils (Glaser et al., 2001; Glaser et al., 2007). Pyrolysis is carried out in closed furnaces where oxygen flow is limited to a minimum by flushing the container with a noble gas such as Argon (Ar) to prevent the biomass from combusting (Kloss et al., 2012). In addition, highest treatment temperature and furnace residence time can be controlled. Depending on those factors as well as the chosen feedstock, BC properties may greatly vary (Brown, 2009; Collison et al., 2009; Sohi et al., 2009), which in turn influences the effect of BC once applied to the soil.

BCs have some unique properties that, besides C sequestration, may positively influence soil nutrient status and plant yield, such as a rise in soil pH. The loss of carbon during pyrolysis in addition to dehydroxylation processes create voids within the the material, which leads to an increase in specific surface area (SSA) and porosity. Both properties increase with rising pyrolysis temperatures and may be masked by condensating volatiles or tars that clog the pores at lower pyrolysis temperatures (Bagreev et al., 2001; Lua et al., 2004; Zabaniotou et al., 2008). Based on the pore formation and increase in SSA, cation exchange capacity (CEC) of BCs may increase, which is important for water-, nutrient holding capacity but also for contaminant retention (Chan and Xu, 2009). An interesting fact is that BC may be oxidized once applied to the soil; thus CEC may further increase with time.

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3.2   Sorption

Sorption is one of the most important processes in the soil and occurs at the interface of the gaseous, liquid and solid phase (Sposito 1989). Sorption is defined as the attachment (adsorption) or detachment (desorption) of dissolved or gaseous ions or molecules at surfaces of solid phases. In detail, the sorption process is dependent on the type of sorbate (substance that is bound to a surface). Charged ions may be bound to a surface by electrostatic forces. The type of binding is rather weak and the kinetics are rather quick as opposed to the coordinative binding of ions or molecules to the sorbent (solid phase that binds a substance), where the kinetics are very slow and the binding is strong. The latter is also called specific adsorption or chemisorptions and describes an inner-sphere surface complexation (Sposito 1989). In addition, metals may precipitate at the surfaces of a sorbent and build a new solid phase (Scheffer and Schachtschabel, 2010).

As the soil is characterized by different components such as clay minerals, oxides and soil organic matter (SOM) that all play a role in the sorption process, the adsorption of substances to the those sorbents varies according to their relative abundance. A high abundance of clay minerals predominantly causes cation adsorption, which is due to the permanent negative charge of clay minerals caused by isomorphic substitution. Oxides and SOM, however, have a variable charge that is influenced by pH. The point of zero charge for Oxides is in the alkaline range, which means that Oxides in slightly acidic or neutral soils are responsible for anion adsorption. Carboxyl and OH groups on SOM particles are mainly responsible for adsorption (Scheffer and Schachtschabel, 2010).

As Vienna is surrounded by a significant amount of vineyards, I chose Cu as one sorbate, which is often used as a fungizide but is detrimental to the environment. In addition. In addition, I chose Cd as a second heavy metal, which is specifically toxic to humans. In addition, adsorption of Cu and Cd in BC treated soils may be different as Cu is prone to form complexes with SOM, whereas Cu may precipitate at the sorbents' surface.

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3.3 Adsorption isotherms

The output of the adsorption experiments will be adsorption isotherms. They describe the relation between the concentration of an ion or compound in the solid phase to that in the liquid phase (soil solution) at equilibrium. In this case, the results of the Cu and Cd concentration at equilibrium were plotted against the calculated amount of Cu/ Cd adsorbed to the soil and soil-BC mixtures, respectively. Three common isotherms were used:

Henry isotherm (linear):

$\theta = K_H \, c_{sol}$ $\quad\quad\quad$ K_H – Henry const.

Langmuir isotherm (no plateau formation→ no saturation):

$\Theta = K_L c_{sol}/1 + K_L c_{sol}$ $\quad\quad$ c_{sol}- concentration of solution; K_L – Langmuir const

Freundlich isotherm (plateau formation→ saturation):

$\theta = K_F c_{sol}^{\alpha}$ $\quad\quad\quad$ K_F – Freundlich const., α – exponent

4. Research questions

Knowing the above-described BC properties as well as the mechanisms of sorption, which depend on the types of sorbents, I found it interesting to consider following: Apart from clay minerals, adsorption of substances to sorbents is pH dependent. This refers to oxides and SOM. The oxide content of a soil cannot be influenced by BC application; however, BC contributes to a certain extent to SOM and interacts with it, which potentially may increase the sorption potential. Depending on the pyrolysis temperature, BC may have a considerable SSA and CEC, which is responsible for adsorption. In addition, BC application to soil indirectly contributes to sorption mechanisms, which is caused by a partly significant pH increase as a higher pH induces a dissociation of a proton of COOH and OH functional groups and therefore increases the abundance of negatively charged functional groups (Sposito 1989).

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The actual pH change after BC application is dependent on the original pH of the soil (Kloss et al., 2012).

Based on this knowledge I developed a working plan in compliance with Prof. Lehmann using our existing pot experiment. The work carried out at Cornell can be divided into two parts and followed following research questions:

Part 1)

- *How does soil application of different BC types affect heavy metal adsorption (Cu, Cd)?*
- *How does soil application of BC pyrolyzed at different temperatures affect heavy metal adsorption)*
- *How does sorption capacity of BC treated soils change over time (BC aging)?*

Part 2)

- *How do biochar differences caused by different pyrolysis temperatures (e.g. functional groups and pore system) affect macroscopic heavy metal sorption?*

Experimental set up of the pot experiment

Following the above-mentioned research questions I decided to use selected soil-BC mixtures from our pot experiment. The pot experiment started in November 2010 and was designed using three different agricultural soils from Austria with varying properties. Basic Soil properties of the used soils are displayed in Table 1. The Planosol showed the lowest pH and CEC; hence the Planosol was representatively chosen as the most suitable soil for the adsorption experiments.

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Table 1 Basic soil parameters of the soils used in the pot experiment

Parameter	Chernozem	Cambisol	Planosol
geology	loess	tertiary	granite
texture	silt loam	clay loam	loamy sand
pH ($CaCl_2$)	7.4 ± 0.1	6.6 ± 0.1	5.4 ± 0.0
EC / $\mu S\ cm^{-1}$	173.6 ± 5.2	103.9 ± 0.1	41.2 ± 12.3
CEC / $mmol_c kg^{-1}$	208.6 ± 4	209.4 ± 2	75.1 ± 0
C/N ratio	11.9 ± 1	13.8 ± 1	14.9 ± 2
carbonate / w.-%	15.81 ± 0.1	0.48 ± 0.0	0.31 ± 0.0
C_{org} / w.-%	1.5 ± 0.02	2.36 ± 0.03	1.64 ± 0.04

In addition, BCs of three different feedstocks (Straw (*Triticum aestivum*, WS), mixed woodchips (WC) and vineyard prunings (*Vitis vinifera,* VP)) were slowly pyrolyzed in a rotary furnace at 525°C and under Ar atmosphere. In addition, VP was also pyrolyzed at 400°C to investigate the influence of pyrolysis temperature on soil, plant yield and sorption potential. BC application rate was 1 and 3 w.-%, respectively. In addition, control soils without BC were used. The pots that were used had a dimension of 40 cm height and a diameter of 23.5 cm and were additionally equipped with an outlet to collect leachate water. The pot experiment currently set up at the AIT in Tulln is shown in Figure 3.

Figure 3 Experimental setup of the pot experiment at the AIT, Tulln

Three crops were grown on the pots starting end of November 2010:

- Mustard (*Sinapis alba L.* cv. Serval)
- Barley (*Hordeum vulgare* vc. Xanadu)

- Clover (*Trifolium pratense* cv. Reichersberger Neu)

All pots received a N standard fertilization of 40 kg ha^{-1} for mustard and 100 kg N ha^{-1} for barley. Clover was not fertilized. Soil sampling was carried out immediately after preparing the soil-BC mixtures (November 23rd, 2010) as well as after barley harvest (July 8th, 2011).

5. Adsorption experiments at Cornell
5.1 Materials

I chose 9 selected treatments to follow the research questions (Part 1) as described above. One pot replicate of each treatment was excavated. The soil-BC mixtures were air-dried and sieved to 2 mm. The soil treatments (t=1; soil was in the pots for 14 months) are the following:

- Planosol (control, no BC)
- Planosol + 3 w.-% wheat straw BC (WS)
- Planosol + 1 w.-% woodchips (WC)
- Planosol + 3 w.-% woodchips (WC)
- Planosol + 3 w.-% vineyard pruning (VP400)
- Planosol + 3 w.-% vineyard pruning (VP525)

In order to follow the research question concerning BC aging in the soil, initial soil-BC mixtures (t=0; were not in the pots) were additionally used:

- Planosol t=0 (control, no BC)
- Planosol + 3 w.-% WS (t=0)
- Planosol + 3 w.-% WC (t=0)

In order to follow the research questions of Part 2), selected BC were used. Those BCs underwent an extensive characterization by (Kloss et al., 2012). In detail, the BCs were:

- Spruce, pyrolyzed at 400°C (S400)
- Spruce, pyrolyzed at 525°C (S525)

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The soils were shipped to Prof. Lehmann in April 2012.

5.2 Methods

Part 1)

For the adsorption experiments, I chose 8 concentration steps for Cd: 0, 0.5, 2, 10, 25, 50, 100 and 200 mgL^{-1}. As naturally higher Cu concentration must be anticipated in soils, the 0.5 mgL^{-1} for Cu was left out and replaced by 400 mgL^{-1}. CdCl^2 and CuCl^2 were chosen for the preparation of the Cd/ Cu stock and working solutions. First, stock solutions needed to be prepared, which were later diluted to the concentration steps mentioned above. The preparation of those solutions will be explained for CdCl^2 and are equivalent for CuCl^2. All solutions were prepared with 0.01 M CaCl^2 as a background electrolyte.

M(CdCl$_2$*2 1/2 H$_2$O)   228.34 g/ mol

M(Cd)   112.41 g/mol

➔ **49.23 %** Cd present in the salt

1 g CdCl$_2$ contains 0.492 g Cd

Using the rule of three the amount of CdCl2 needed to obtain a 1000mgL^{-1} solution was calculated.

➔ **2.031 g** of CdCl$_2$ needed to be weighed in and filled up with 1000 mL 0.01 M CaCl$_2$ to get a 1000 mgL^{-1} stock solution . (M(CuCl$_2$*2 H$_2$O) = 170.49 g/mol, **2.683 g** of the CuCl$_2$ was weighed in to get a 1000 mgL^{-1} stock solution)

In the second step, it was calculated how much working solution of each concentration step was needed as well as how much stock solution was needed to prepare it.

Calculation working solution: replicates   3

                                        Treatments   9

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<u>mL   40</u>

V (mL) working solution/ concentration step: 1080

At this, the measurement of Blanks (working solutions without soil) needed to be considered as well. As a preparation of this volume is not easily possible, I decided to prepare working solutions of **1000 mL** and then another 500 mL flask when the other one was used.

$$c_1 \cdot V_1 = c_2 \cdot V_2$$

with: c_1 = 1000 mgL^{-1} Cd

             c_2= 0.5 mgL^{-1} Cd   (as lowest concentration step)

             V_2= 1000 mL

$$V_1 = \frac{c_2 \cdot V_2}{c_1}$$

➔ 0.5 mL of the stock solution needed to be filled up with 0.01 M CaCl$_2$ in order to get a 0.5 mgL-1 working solution.

The calculation of the other concentration steps followed the same equation. The concentration steps for Cd as well as the Volume of stock solution needed are displayed in Table 2.

Table 2 Volume of stock solution needed for the preparation of working solutions for Cd. The calculation steps for Cu is equivalent.The respective amount of stock solution was filled up with 1000 mL 0.01 M CaCl$_2$.

concentration step (c2)	(c_1) Stocksolution (mL)
0.5	0.5
2	2
10	10
25	25
50	50
100	100
200	200

387.5

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In case less stock solution was needed (e.g. for follow-up measurements), c_1 was halved and filled up with 500 mL 0.01 M $CaCl_2$. In addition, Table 2 shows that only 387.5 mL of the stock solution was needed. Hence, instead of a 1000 mL volumetric flask, I could have also used a 500 mL flask. However, based on those calculation I would only be able to perform adsorption experiments for 8 treatments instead of 9 and the Blanks. Considering potential mistakes or follow-up measurements I still prepared the stock solution using the 1000 mL volumetric flask. All flasks were acid washed in a 10 % HCl bath prior to the preparations of the solutions. Volumetric flasks containing Cd working solutions are shown in Figure 4.

Figure 4 Cd working solutions

After preparing the needed solutions, 4 g of soil was weighed into acid-washed centrifuge tubes and treated with 40 mL of the respective working solution and shaken for 24 h on a horizontal shaker and filtrated. The first part of the filtrate was discarded. The filtration process is shown in Figure 5.

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Figure 5 Filtration of samples after 24 h adsorption

One composite sample from the three replicates of each treatment was prepared. Subsequently, the pH was measured in the solution. The rest of the filtrate was stabilized using a drop of HNO_3.

Cd/ Cu concentration was measured using an Atomic Absorption Spectrometer (AAS; Buck Scientific Atomic Absorption Spectrometer Model 210 VGP). The technique of an AAS is based on the excitation of an atom using light. Each element is excited at a specific wavelength, which is emitted by a cathode lamp. The wavelength of Cd is 228.9 nm, of Cu 324.7 nm. The sample is sprayed into an acetylene flame; the absorbed light intensity is directly related to the Cd/ Cu concentration in the filtrate. The output variable is given as an absorbance value. The AAS is displayed in Figure 6.

Figure 6 Atomic absorption spectrometer

Before measuring the Cd/ Cu concentrations, standards needed to be prepared ranging from 0- 2 ppm. As the adsorption experiment was used with $CaCl_2$ as background electrolyte, the standards also needed to be made with 0.01 $CaCl_2$. Using the standards, a calibration curve can then be fitted according to which the absorbance value of each sample can later be transferred to ppm. The calibration curve was generated by plotting the absorbance against ppm and fitting the quadratic equation:

$$f = y0 + ax + x^2$$

The R² determines the quality of the model and ranges between -1 and 1. The closer R² is to -1 or 1, the higher is the quality.

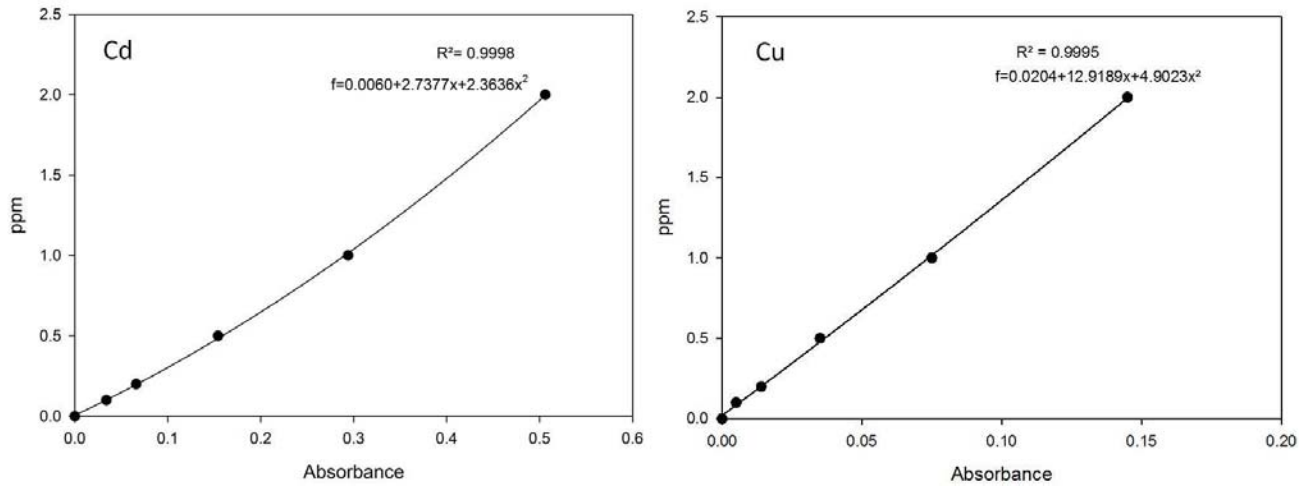The calibration curves for Cd and Cu are displayed in Figure 7.

Figure 7 Calibration curves for Cd and Cu

Using the quadratic equations shown in Figure 7, the measured absorbances could be transferred to ppm.

The amount of adsorbed Cd/ Cu was calculated by substracting the concentration of the Cd/ Cu in the solution from the concentration of Cd/ Cu in the Blanks. Subsequently, the unit ppm (mgL^{-1}) needed to be transferred to mg kg^{-1}. This was carried out by referring the results in mgL^{-1} to the weight of the soil as well as the volume of the working solution:

$$\Delta c\left[mg\ kg^{-1}\ soil\ \right]=\frac{\Delta c\left[mg\ L^{-1}\right]\cdot V_{Extraction}}{m_{Extraction}}$$

$$\Delta c\left[mg\ kg^{-1}\ soil\ \right]=\frac{\Delta c\left[mg\ L^{-1}\right]\cdot 40mL}{4g\cdot}$$

Part 2)

The aim of part two was to go deeper into adsorption mechanisms using adsorption experiments on pure BC (VP400 and VP525). Prior to carrying out the experiment, the BC was ground with a Thomas Wiley Mill (Model ED-5) to < 2mm and pre-treated in three different ways. The pre-treatments and the reasons for them are explained in Figure 8.
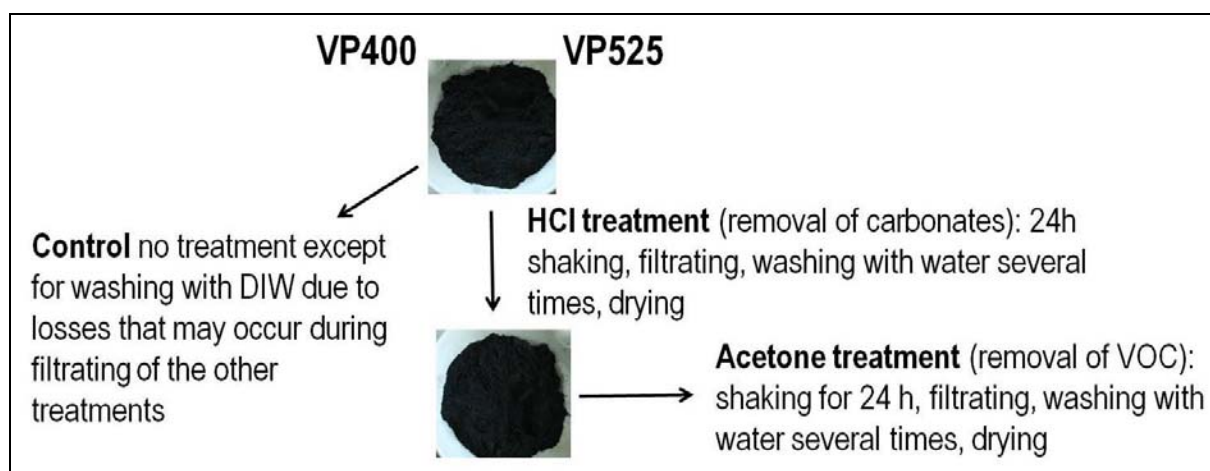
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Figure 8 scheme of the BC pre-treatments (DIW: Deionized water; VOC: volatile organic compounds).

As pH plays an important role for adsorption and was anticipated to change with the different pre-treatments, pH was adjusted to 5 after pre-treating using HCl and KCl, respectively. PH adjustment was carried out for a bulk sample using a pH meter as shown in Figure 9. At this, the required acid or base was added drop-wise and let adjust for several hours until it reached pH 5.

Figure 9 pH adjustment of biochars

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After each treatment step, the bulk BC was filtered through a funnel analogous to the Part 1), washed with deionized water to remove the HCl and Acetone, respectively. The BC was removed from the filter and put in an oven heated to 60°C. After drying the pre-treated BC, the BC was weighed into centrifuge tubes and the adsorption procedure was carried out as described above. However, the weight was 0.3 g and the applied Volume 30 mL.

5.3 Results

The following chapter shows some selected results of the adsorption isotherms for Cd and Cu. As the central conclusions are not much influenced by the different isotherms, this report only shows the Langmuir isotherms. The Langmuir equation proclaims that a plateau forms with increasing heavy metal concentration, which can be expected for a soil. A basic BC characterization is shown in Table 3.

Table 3 Basic characterization of the BC used in the pot experiment. Different letters indicate significant differences at $p < 0.05$ (Tukey's test).

biochar	pyrolysis temperature	ash content (w.-%)	pH (CaCl$_2$)	EC (mS cm^{-1})	CEC (mmol$_c$ kg^{-1})	C/N ratio	BET -N$_2$ SA (m^{2}g^{-1})
straw	525°C	28.10	9.7 ±0.0 c	5.2 ± 0.1 d	148.5 ± 0.8 d	63.8 ± 1.6 c	12.26 ± 1 c
woodchips	525°C	15.20	8.9 ±0.1 b	1.6 ± 0.0 c	93.0 ± 1.9 b	58.2 ± 0.7 b	26.41 ± 1 d
vineyard pruning	400°C	4.30	8.3 ± 0.0 a	1.5 ± 0.0 b	123.5 ± 1.3 c	52.0 ± 2.4 a	1.69 ± 0 a
vineyard pruning	525°C	7.70	8.8 ± 0.1 b	1.1 ± 0.0 a	78.8 ± 1.4 a	58.0 ± 1.9 b	4.85 ± 0 b

The BCs show different amounts of ash with straw obtaining the highest ash content. BCs are very alkaline and show pH in the range of 8.3 and 9.7.

Part 1)

Effects of different biochars on Cd and Cu adsorption in a Planosol

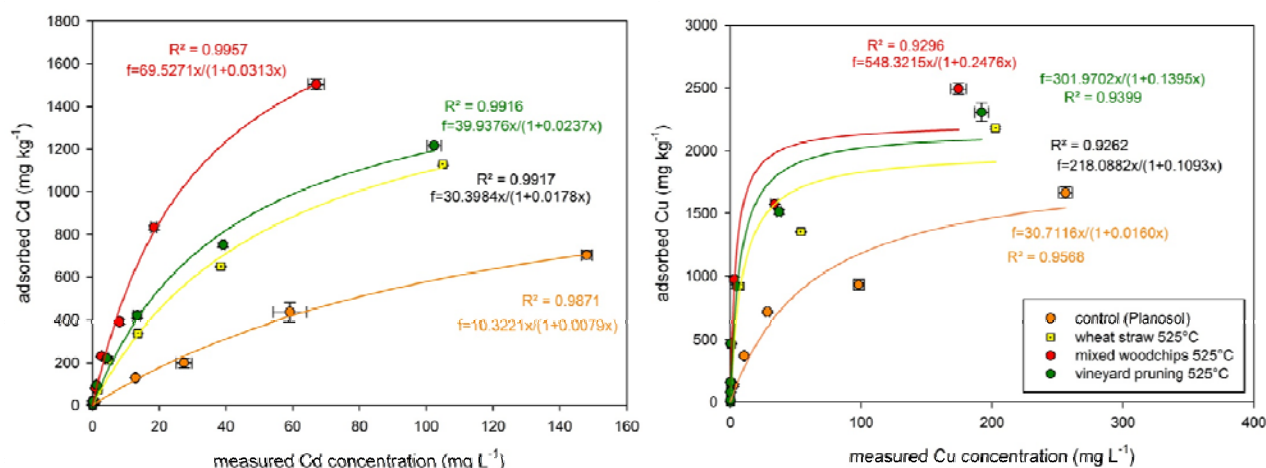The Langmuir adsorption isotherms for Cd (left) and Cu (right) are shown in Figure 10.

Figure 10 Langmuir adsorption isotherm for Cd (left) and Cu (right) for the different biochar treatments (3 w.-% BC application rate).

Figure 10 shows that the different biochar types all considerably increased adsorption both for Cd and Cu. WC showed the highest increase, whereas the least increase was found for WS.

Effects of pyrolysis temperature on Cd and Cu adsorption in a Planosol

The effect of different pyrolysis temperatures on Cd (left) and Cu (right) adsorption is displayed in Figure 11.
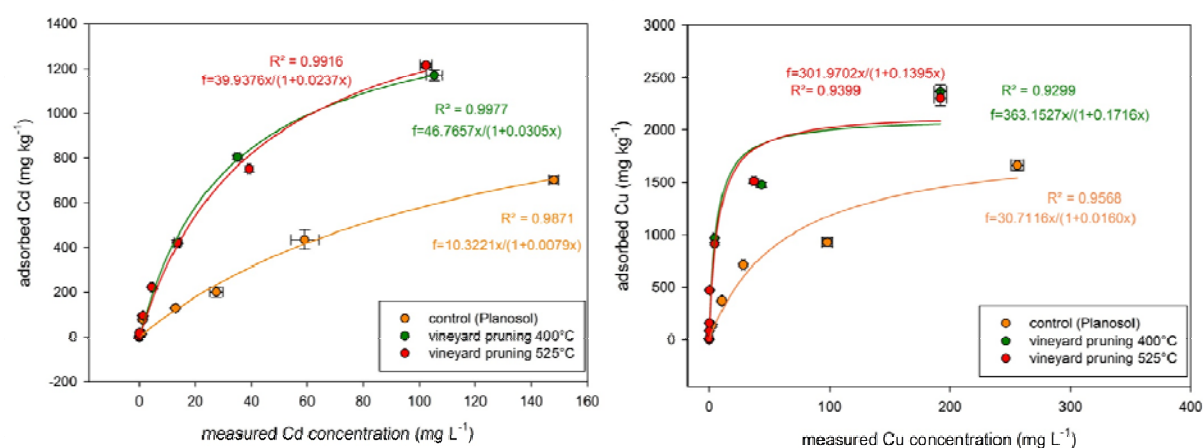

Figure 11 Effect of pyrolysis temperature on Cd (left) and Cu (right) adsorption in a Planosol (Langmuir isotherm; vineyard pruning BC; 3 w.-% BC application rate).

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Figure 11 shows that both pyrolysis temperatures considerably increased the adsorption of Cd and Cu. However, adsorption isotherms of VP400 and VP525 are very alike unlike expected.

Effects of biochar aging in the soil on Cd and Cu adsorption

The effect of BC aging in the soil was investigated for WS and WC. As explained above, the time difference between t=0 and t=1 was 14 months. Figure 12 shows the effect of WS aging on Cd (left) and Cu (right).
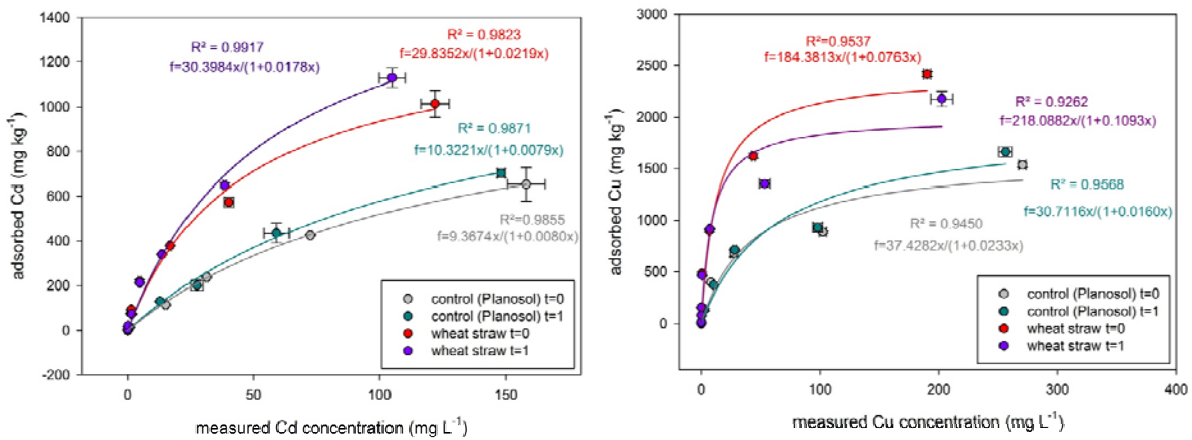

Figure 12 Effects of biochar (WS) aging in the soil on Cd (left) and Cu (right) adsorption (Langmuir adsorption isotherm; 3 w.-% application rate). Time difference between t=0 and t=1 was 14 months.

Figure 12 shows that adsorption of Cd adsorption considerably increased after 14 months, which may be due to BC aging. However, Cu adsorption in the WS treated soil decreased.

Figure 13 shows the effect of WC aging in the soil on Cd and Cu adsorption.
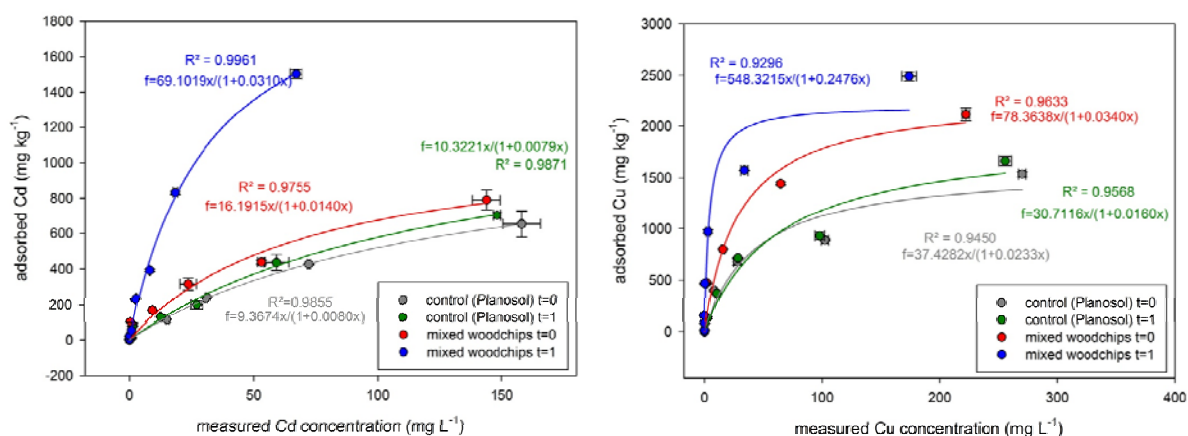
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Figure 13 Effects of biochar (WC) aging in the soil on Cd (left) and Cu (right) adsorption (Langmuir adsorption isotherm; 3 w.-% application rate). Time difference between t=0 and t=1 was 14 months.

At the beginning of the pot experiment, Cd adsorption was close to the adsorption in the control soil. However, especially Cd adsorption was considerably influenced by BC aging in the soil. Interestingly, adsorption also slightly increased in the control soil.

Part 2)

The aim of Part 2) was to detect adsorption mechanisms by pre-treating and pH-adjusting of the selected BC (S400 and S525). Figure 14 shows the final pH in the filtrate after 24 h adsorption.
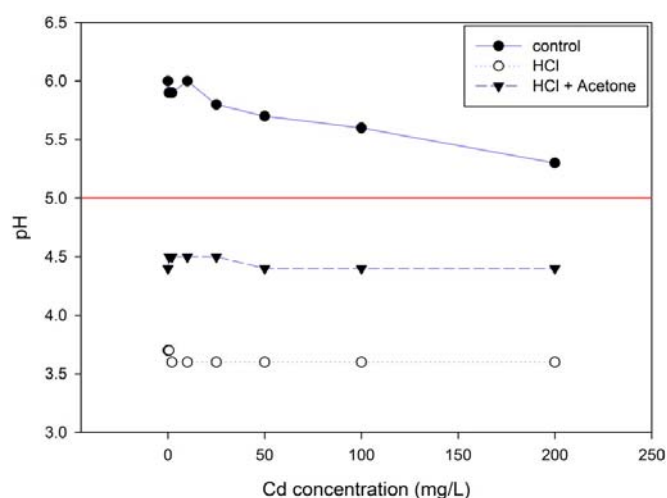

Figure 14 pH of spruce biochars (400°C) after pre-treating the biochars.

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The red line shows the pH to which the BCs needed to be adjusted. However, the control BC was above 5 and the BCs that were pretreated with HCl are still below 5. Hence, despite the pH adjustment, which was followed using a pH meter, pH of all treatments are too different to rule out the influence of pH for heavy metal adsorption. The interpretation of the following results is therefore problematic. The obtained data are not suitable for publication; however, in the course of this report the results will still be presented. The pre-treatment could unfortunately not be repeated. Pre-treating and filtrating several times before carrying out the adsorption led to higher sample losses than anticipated. BC loss after each treatment amounted to 40-50 %. In addition, the adsorption experiment was limited to Cd because of the limited BC availability. Figure 15 displays the adsorption isotherms for the pre-treated BC (S400 and S525).
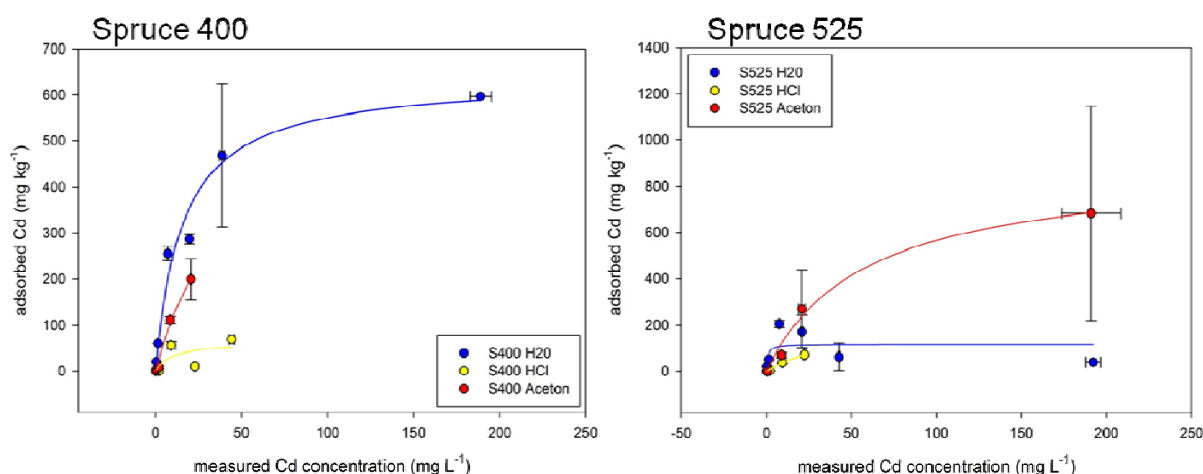

Figure 15 Adsorption isotherms (Langmuir) for pure biochars after pre-treatment

Figure 15 shows that the Langmuir isotherms considerably vary according to the pre-treatments. However, as mentioned above, pH adjustment failed so that a pH effect cannot be excluded. In addition, standard deviations are very high, which shows that carrying out adsorption experiments with pure BC are not possible when they are carried out analogous to soil.

5.4 Discussion

Soil-Biochar mixtures

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All BC types showed considerably higher adsorption isotherms in the Planosol (Figure 10). Primarily, this may be caused by the high alkalinity of the different BCs. However, differences in adsorption were found for the different feedstocks. Despite the highest pH (Table 3) WS showed the lowest increase in adsorption potential. This shows that other mechanisms than a mere pH effect caused the higher adsorption for Cd and Cu. An explanation would be the high ash content of WS. In addition, WS had by far the highest salt content, which may have interacted with Cd and Cu ions, respectively. The highest increase in adsorption was found for WC, which hast the second highest pH. In addition, WC is characterized by the comparatively highest SSA in the range of 26.41 m² g^{-1}, which is also responsible for adsorption. It can be concluded that WS treated soil increased adsorption potential for Cd and Cu due to a mere pH effect, whereas woody biomass with higher SSA cause a pH effect in the soil and, additionally, may directly adsorb Cd and Cu ions on the BC itself due to higher SSA.

Differences in the adsorption isotherms concerning different pyrolysis temperatures of the same feedstock were expected with higher pyrolysis temperatures causing a higher adsorption of Cd and Cu. This is, because volatilization and the formation of the high SSA only evolve starting at between 400°C and 500°C pyrolysis temperatures. In addition, lower pyrolysis temperatures may cause volatiles to more easily condensate and clog the pores, thus reducing the SSA. However, Figure 11 shows that adsorption of VP400 was not very different from the adsorption of VP525. Consequently, when considering applying BC to a soil in order to remove heavy metals, pyrolysis temperature plays only a minor role. It is more important to choose the right feedstock to increase adsorption of heavy metals.

An interesting observation was found for the investigation of BC aging in the soil. WS and WC treated soils were collected at an interval of 14 months as described above. According to literature, biotic and abiotic oxidation of BC may occur with time (Cheng et al., 2006), which may lead to an increase in surface functional groups responsible for CEC and adsorption potential. Indeed, within the scope of the pot experiment, we found an increase in CEC within 7 months for some of the BC treated soils (data not shown). In accordance with those results, we found a considerable increase in

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adsorption isotherms both for WS and WC treated soil (Figure 12 and Figure 13). Analogous to Figure 10, WC leads to higher adsorption compared to WS and also shows a much more intense aging effect than WS. However, Figure 12 shows that adsorption for Cu actually decreased with aging. Cu is prone to complexation with SOM; one can assume that within the 14 months, SOM decomposition may occur, which may decrease the complexation potential and therefore reduce adsorption. However, Figure 12 also shows that adsorption in the control increases with time, which indicates that no significant SOM decomposition has occurred. However, it can be assumed that adsorption potential increases with time once BC is applied to the soil, which is an important feature for soil remediation.

Pure Biochars

As mentioned before, pH adjustment failed (Figure 14) and impaired a definite interpretation of the adsorption isotherms. Aim of the BC pre-treatment was to remove carbonates from the BC surface using HCl as well as removing volatiles from the BC by subsequently washing some of the HCl treated BC with Acetone. This would be of particular interest for BC pyrolyzed at lower temperatures. As a control, a subsample of BC was washed with water. Indeed, Figure 15 shows that BC (both pyrolysis temperatures) that was only washed with water showed the highest adsorption isotherm. In addition, S400 shows that S400 pretreated with HCl and Acetone showed a higher adsorption isotherm than S400 only treated with HCl. This may indicate that Acetone successfully removed any condensates that clogged the pores and therefore increased adsorption capacity. However, once more it must be considered that the adsorption isotherms may be less influenced by the pre-treatments but by a pH effect. Further research and optimization of the pre-treatment is needed to fully understand adsorption mechanisms.

6. Conclusion and further research

The results of the adsorption experiments showed that BC application to soil may be a useful tool for heavy metal removal in soils. At this, the choice of feedstock is more important than pyrolysis temperature. In addition, BC applied to soil undergoes interactions with the soil as well as oxidation, which further increases adsorption

capacity. However, further research is needed in terms of finding out about adsorption mechanisms in detail.

7. Impressions and experiences at Cornell

The 4 months stay at Cornell proved to be very useful not only in terms of the results but also in terms of networking with other scientists working in BC research. I was able to connect with them and exchange about methods and results and discussing them. I learned that a change in the working ambience may be very fruitful since talking and discussing about one's research field with different people offers different points of views. By this, new ideas about future research come up. The structure of the lab work was different from what I experienced at BOKU. Each student/ worker in the lab has for instance his/ her own space, where they can work and also store their utensils. The people at Cornell were very open to me when I came. They were very well prepared and knew that I was coming. I had my own desk in an office but had to bring a laptop. All the chemicals I needed were provided by the institute so I had no additional expenses. Merely some C/N measurements were charged at the beginning; however, Prof. Lehmann then offered to cover the expenses. The working climate at Cornell was very nice and comfortable, although the building where I worked was not very inviting. The building where I stayed (Bradfield Hall; Figure 16) was a 12 story building that had no windows. Hence, it was a very awkward feeling at the beginning, because I was not used to working in an office without any windows. The artificial light was depressing at the beginning.

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Figure 16 Bradfield Hall at Cornell Campus

Although my supervisor was originally from Germany we spoke English all the time because it was easier for both of us. I was very happy to meet other PhD students whose' background was also Biochar. We exchanged specifically about the problems and challenges that occurred in the lab. Once a week, Prof. Lehmann organized a so called lab meeting. During the lab meeting, one of the group members presented their newest results or talked about their challenges. It was very helpful to have a lab meeting, because you had a lot of people around that could give you advice in a very short time. I presented twice; my first presentation was about the research I had done at BOKU so far to give them an idea about what I am doing. The second presentation was held at the end of my stay when I had most of the results that I was able to obtain.

Within the following months, my working group at BOKU wants to deepen the connections with Cornell by writing a publication about the obtained results. As some of the results are not yet publishable as mentioned above, some of the experiments need to be repeated at BOKU as some of the samples ran out due to massive sample losses. In addition, the obtained results as well as the contacts I have made during my stay may prove to be useful for future projects that may follow up when I am done with my PhD.

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Ithaca, the town where I lived, is kind of a unique place in the States. A lot of so called alternative people live there. I experienced that even in the States there are movements that are focusing on ecological farming and other eco-products that were favorably purchased by most of the citizens. I personally met a lot of people who are against intensive mass animal farming and are therefore vegetarians. Even the cantine near Bradfield Hall specialized on supporting the local farms by selling beef from local farmers. A lot of people in Austria and Germany are skeptical about the States because of Fast Food. In fact, I lived there healthier than I ever did before. Every Saturday, the famous Farmer's Market was held at the Cayuga Lake. Farmers from close by sold their dairy products and meat; in addition, a lot of breeders sold their plants next to wood artists (Figure 17).

Figure 17 Farmers Market at Cayuga Lake, Ithaca

Socializing was hard at the beginning; in addition I had some private problems that initially made my stay a hard time. However, I was able to connect with some great people that included me in their peer groups. Ithaca is a very small town that does not have a lot to offer if you are not mobile. The public transportation system was very badly structured compared to Vienna. Busses often went only once an hour; on the weekends they did not go at all. Hence one has to have a car or at least a bike to be able to run errands. Therefore it turned out very well for me at the end because I

met a lovely friend who had a car and offered to pick me up and drive me home whenever we met. The people I met take friendships very seriously and I am convinced that we will keep contact in the future.

I am deeply thankful that I was given the opportunity to experience life abroad with a scientific background. I was able to significantly improve my scientific English. Working in the Lab was challenging at first because there were a lot of expressions that I did not know, such as beaker, Erlenmeyer flasks, ect., which is necessary when you work in an English speaking lab. I am now more able to speak English when talking about scientific research; also my English writing has improved a lot. I am convinced that the improvement of my speaking will be of much advantage in near future once I am done with my PhD.

8. Acknowledgments

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9. Literature

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