

Biochar as a soil amendment for the immobilization of copper,
zinc, cadmium and lead on former sewage fields

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Ein jüdisches Sprichwort besagt:

“wenn Du Gott zum Lachen bringen willst, mache einen Plan...”

Im Laufe meiner Dissertation habe ich somit Gott, wenn es ihn gibt,
ausgiebig zum Lachen gebracht...

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Abstract

The mobilization of heavy metals from anthropogenically contaminated sites such as sewage fields poses a risk to the environment and human health in many regions of the world. The objective of this study was to assess the suitability of pyrolytically and hydrothermally produced biochars (pyrochar and hydrochar) as soil additives for *in situ* immobilization of metals. The immobilizing effect was investigated in a combination of pot and field experiments in which plant growth, metal uptake by plants, concentrations of metals in the soil solution and their speciation as well as leaching losses with drainage water were determined after addition of 0, 1, 2.5 and 5% ($\text{g } 100 \text{ g}^{-1}$) biochar to sewage field soil.

In the pot experiments, addition of hydrochar reduced biomass production and had no effect on metal mobility. The negative effect on biomass yields may be attributable to decreased N availability but toxic effects cannot be excluded. Therefore, the effect of hydrochar was not further studied in the field experiments.

In both the pot and field experiments, pyrochar addition increased biomass production and reduced concentrations of Zn and Cd in plant biomass. In the pot experiments, however, total Zn and Cd concentrations were not reduced or even increased in the $0.45 \mu\text{m}$ -membrane-filtered soil solution indicating the presence of non-plant-available Zn and Cd species. Thermodynamic modelling of chemical equilibria suggests the precipitation of Zn phosphates as a result of increasing pH and P concentrations with increasing pyrochar addition but does not indicate the formation of Cd mineral phases. The colloidal proportion of Zn determined by comparison of filtered and ultra-centrifuged samples of the soil solutions was high and the proportion of colloidal Cd was low which is in accordance with modelling calculations. Microprobe analysis of centrifugation residues supports the assumption of Zn phosphate precipitation since high concentrations of both elements were localized at the same site. In the field experiments, Zn and Cd concentrations in the soil solution decreased since colloids were excluded by the suction plates used for sampling. The cumulative leaching fluxes of Zn and Cd detected with ion exchange resins (SIAs) decreased as well. This is attributable to reduced concentrations in the soil solution and an increased water-holding capacity and thus reduced drainage caused by pyrochar addition. However, the reduction of the cumulative leaching fluxes was lower than expected on the

basis of soil solution concentrations and reduced drainage. An enhanced colloidal transport with pyrochar addition recorded with the SIAs but not with the suction plates may explain this finding.

In the pot and in the field experiments, Cu concentrations in plants remained constant or even increased after pyrochar addition. Copper and also Pb concentrations in the soil solutions increased as well. The results of the pot experiments suggest transport of Cu in the dissolved fraction only and for Pb, the formation of Pb phosphates and a colloidal transport which seems to account for a considerable proportion of the cumulative leaching fluxes determined with the SIAs also in the field experiments. Correlations of Cu and Pb with DOC concentrations in the pot and in the field experiments suggest mobilization by organic complexation. This mobilization might be a transient phenomenon since DOC, Cu and Pb concentrations in the soil solution decreased in the course of the field experiments. Despite the higher Pb and Cu concentrations with pyrochar addition, the cumulative leaching fluxes remained constant due to an increased water-holding capacity and therefore reduced drainage.

The use of pyrochars as soil amendments on former sewage field soils has the potential to reduce the mobility and availability of heavy metals, in particular Zn and Cd. Additional benefits may be an increased water-holding capacity and reduced cumulative leaching fluxes which compensate the possibly short-term mobilization of Cu and Pb. Further research should address the potential re-mobilization of Zn and Cd after exhaustion of the buffer capacity of the ash contained in the pyrochar and the related decrease in soil pH as well as the long-term mobility of colloids and organic-metal complexes.

Kurzfassung

Die Mobilisierung von Schwermetallen auf anthropogen belasteten Standorten, wie beispielsweise ehemaligen Rieselfedern, stellt ein Risiko für die Umwelt und die menschliche Gesundheit dar. Ziel dieser Arbeit war es, die Eignung von pyrolytisch und hydrothermal hergestellter Biokohle (Pyrochar und Hydrochar) für die *in situ* Immobilisierung zu testen. Die Immobilisierung von Schwermetallen wurde in einer Kombination aus Topf- und Feldversuchen untersucht, wobei das Pflanzenwachstum, die Aufnahme von Schwermetallen in die Pflanzen, die Konzentrationen der Schwermetalle in der Bodenlösung und ihre Spezierung sowie die Auswaschungsraten mit dem Sickerwasser bei Zugabe von 0, 1, 2,5 and 5% ($\text{g } 100 \text{ g}^{-1}$) Biokohle bestimmt wurden.

In den Topfversuchen reduzierte die Zugabe von Hydrochar die Biomasseproduktion und hatte keinen Einfluss auf die Schwermetallmobilität. Die negativen Effekte auf das Pflanzenwachstum sind vermutlich auf eine reduzierte N-Verfügbarkeit zurückzuführen, aber auch toxische Effekte können nicht ausgeschlossen werden. Daher wurde der Effekt von Hydrocharzugabe nicht weiter im Feld untersucht.

Sowohl in dem Topf- als auch in dem Feldversuch steigerte Pyrocharzugabe die Biomasseproduktion und reduzierte die Zn- und Cd-Konzentrationen in den Pflanzen. In den Topfversuchen war in der durch $0,45 \mu\text{m}$ Membranfilter filtrierte Bodenlösung jedoch keine Reduktion oder sogar eine Zunahme der Zn- und Cd-Gesamtkonzentrationen festzustellen, was auf das Vorhandensein von nicht-pflanzenverfügbaren Zn und Cd Spezies schließen lässt. Thermodynamische Gleichgewichtsberechnungen lassen eine Ausfällung von Zinkphosphatmineralen durch eine Erhöhung des pH-Wertes und der P-Konzentrationen aber keine Bildung von Cd-Mineralphasen vermuten. In Übereinstimmung mit diesen Berechnungen war der kolloidale Anteil, bestimmt durch den Vergleich von filtrierten und ultrazentrifugierten Proben für Zink hoch und für Cd gering. Die Analyse der Zentrifugenrückstände mit der Elektronenstrahlmikrosonde unterstützt die Annahme einer Ausfällung von Zn-Phosphatmineralen, da beide Elemente an der gleichen Stelle hohe Konzentrationen aufwiesen. In den Bodenlösungen des Feldversuchs sanken die Zn- und auch die Cd- Konzentrationen, da Kolloide mit den eingesetzten Saugplatten nicht erfasst wurden. Die kumulativen Auswaschungsraten von Zn und Cd, bestimmt mit Ionenaustauscherharzboxen (SIAs), nahmen ebenfalls ab. Dies ist auf eine Reduzierung der Bodenlösungskonzentrationen und eine gesteigerte Wasserspeicherkapazität und damit

einhergehende Verringerung der Sickerwassermenge, die durch die Pyrocharzugabe erreicht wurde, zurückzuführen. Allerdings war die Reduzierung der kumulativen Auswaschungsraten geringer als auf Basis der Bodenlösungskonzentrationen und der geringeren Sickerwassermenge zu erwarten gewesen wäre. Ein vermehrter colloidalen Transport mit Zugabe von Pyrochar, der mit den eingesetzten SIAs, nicht aber mit den Saugplatten erfasst wurde, könnte dieses Ergebnis erklären.

In den Topf- und den Feldexperimenten blieben die Cu-Konzentrationen in den Pflanzen nach Zugabe von Pyrochar konstant oder stiegen sogar an. In der Bodenlösung stiegen die Cu- und auch die Pb-Konzentrationen ebenfalls an. Die Ergebnisse des Topfversuchs legen für Kupfer einen Transport nur in gelöster Form nahe und für Pb die Bildung von Bleiphosphaten und einen kolloidalen Transport, der auch im Feldversuch einen beträchtlichen Anteil der ausgewaschenen kumulativen Fracht auszumachen scheint. Korrelationen der Cu- und Pb- mit den DOC-Konzentrationen in den Topf- und den Feldversuchen legen eine Mobilisierung durch organische Komplexbildung nahe. Diese Mobilisierung könnte nur ein vorübergehender Effekt sein, da die DOC-, Cu- und Pb-Konzentrationen im Lauf des Feldversuchs abnahmen. Trotz höherer Pb- und Cu-Konzentrationen in der Bodenlösung bei Zugabe von Pyrochar blieben die Auswaschungsraten konstant, was auf die erhöhte Wasserspeicherkapazität und die reduzierte Sickerwasserrate zurückzuführen ist.

Der Einsatz von Pyrochar als Bodenadditiv zeigt ein Potential für die Verringerung der Schwermetallmobilität und -verfügbarkeit vor allem für Zn und Cd auf ehemaligen Rieselfeldböden. Zusätzliche Vorteile ergeben sich aus einer gesteigerten Wasserspeicherkapazität und damit reduzierter Sickerwasserraten, die eine eventuell kurzfristige Mobilisierung von Pb und Cu kompensiert. Weitere Forschungen sollten eine potentielle Remobilisierung von Zn und Cd nach Erschöpfung der Pufferkapazität der in der Biokohle enthaltenen Asche und den damit verbundenen sinkenden pH-Werten berücksichtigen. Darüber hinaus sollte die langfristige Mobilität organischer Schwermetallkomplexe und der Kolloide genauer untersucht werden.

1 General Introduction

1.1 Background and rationale

The use of arable land for bioenergy production is discussed highly controversially due to the competition with food production. A high demand for food and energy leads to a high pressure on the productivity of soils and the utilization of available agricultural areas. This phenomenon will increase in the future due to an increasing population and a higher standard of living in the developing countries. Remediation of polluted soils and use of contaminated areas for energy crop production are two of the possible answers (Lal, 2010).

In 25 different regions of Germany, a programme entitled “Bioenergie-Regionen” has been initiated by the Federal Ministry of Food, Agriculture and Consumer Protection (BMELV) with the aim to develop sustainable networks and structures for bioenergy production. The research presented in this thesis was performed in the context of this programme and supported by the “Bioenergie-Region Ludwigsfelde” in order to find out whether the former sewage fields located in this region can be used for energy crop production thus avoiding the “food or fuel” dilemma.

Due to prolonged irrigation with wastewater, nutrients but also high amounts of heavy metals have accumulated in the sewage field soils so that food production is not admissible at the present time (LUA 1997). Energy crop production might be an alternative land use which can benefit from the high nutrient contents of these fields and may provide financial profits which can be reinvested in the remediation of contamination hotspots. Additionally, the uptake of heavy metals by plants contributes to their removal from the soil in the long run (Tack & Meers, 2010).

After the cessation of wastewater irrigation, heavy metal mobility has been increasing due to the lack of alkaline and organic inputs resulting in decreasing pH and contents of organic matter which is the major sorbent for heavy metals in the sandy soils (Grunewald, 1994). If bioenergy crops are cultivated on these soils, a further increase in the mineralization of organic matter is expected along with soil tillage. Annual plants require frequent soil tillage and leave bare soil which is exposed to wind erosion thus presenting the risk of inhalation and dermal uptake of contaminated soil particles by the population. In order to avoid increasing mineralization and wind erosion, perennial plants may be a better choice. However, even for cultivation of perennial plants, soil tillage is considered

necessary at least in the phase of establishment. Energy crop production itself only contributes to a long-term extraction of the heavy metals and does not reduce the risk of heavy metal leaching. Moreover, increasing heavy metal concentrations in the soil solution have detrimental effects on plant growth and may reduce yields of energy crops. Therefore, a concomitant measure to be taken to minimize metal mobility might be reasonable.

Biochar addition to soils has recently been discussed under the aspect of metal immobilization (Beesley et al., 2011) and has originally been known to promote yields in the Terra Preta soils of the Amazon Basin in combination with organic waste such as bones and faeces (Glaser & Birk, 2012). On the former sewage fields organic waste has already accumulated. Increased yields and reduced heavy metal mobility are highly desired for energy crop production and groundwater protection. Additionally, the input of biochar may contribute to carbon sequestration and may help to meet the climate targets (Lehmann, 2006). My findings should help to assess the chances and risks of biochar amendment for the immobilization of heavy metals accumulated in the soils by prolonged wastewater irrigation.

1.2 The study site, geographical settings and history of irrigation with wastewater

The former sewage fields investigated in this study are located on the “Teltow” ground moraine plane about 10 km south of Berlin in the administrative district Teltow-Fläming (Figure 1.1). Mean annual temperature is 9.3° C and mean annual precipitation 525 mm a⁻¹ (climate data from the measuring station at Berlin-Schönefeld, <http://www.dwd.de>). With about 300 mm a⁻¹ of rainfall in the vegetation period between May and October, the study area is situated in one of the driest regions of Germany.

The investigation area belongs to the wastewater irrigation district of Großbeeren and is one of the oldest sewage fields in the vicinity of Berlin. This area received wastewater from 1890 to 1994. Until the 1980ies it had a size of approximately 746 ha. The highest application rates were about 20 million m³ per year in the 1970ies (LUA 1997). Before distribution on the fields, the wastewater conducted to the irrigation area in pressure pipes was collected at the highest point and led to a sedimentation tank where the coarse materials were separated by sedimentation which was the only pretreatment of the sewage water. The sediment was removed from the sedimentation tanks, dried on special areas and used as a fertilizer in the first years of irrigation. Later the sediment was desposited in a

landfill due to increasing contamination (LUA 1995). From the sedimentation tank the liquid phase was distributed to the fields in irrigation channels. The individual fields had a size of approximately 2500 m² which were separated by dykes. About 2 m below the surface of the sewage fields, a system of drainage pipes installed beforehand collected the drainage water and led it to drainage trenches and from there to the receiving surface water.

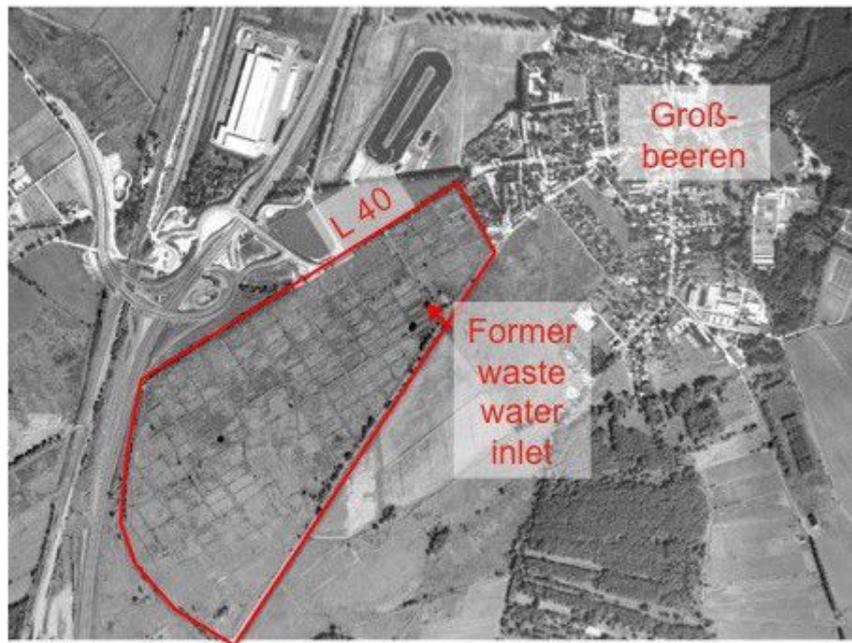


Figure 1.1 Aerial photograph of the municipality of Großbeeren with added marking of the investigation area (Landesbetrieb für Landvermessung und Geobasisdaten)

The ground moraine plane was formed in the Weichselian glacial period at a height of 45 m above sea level. In this quaternary substrate, four aquifers have formed which are partly in contact due to breaks in the confining layers. The first aquifer is unconfined and considerably influenced by wastewater irrigation. Investigations of the groundwater carried out in the 1990ies (Scheytt, 2000) have revealed high concentrations of nitrogen, phosphorus, salts and dissolved organic carbon but only low heavy metal concentrations. Also in the second aquifer the influence of wastewater irrigation was detectable. Due to irrigation the groundwater level has risen. After termination of irrigation, this level sank to its natural level which is now between 4 and 10 m. The mean rate of groundwater recharge is between 85 and 110 mm/a (Scheytt, 2000).

In the investigation area, the dominating soils are Albeluvisols and Cambisols according to the WRB classification (Fahlerden and Braunerden according to the German soil classification system) which have developed on loamy sandy substrates of the glacial till covered with silty to loamy sand layers in the periglacial Holocene (LUA 1997). In the south-west of the investigation area Regosols and Anthrosols according to the WRB classification (Regosole and Kolluvisole according to the German soil classification system) have formed during the establishment and operation of the sewage fields (Figure 1.2).

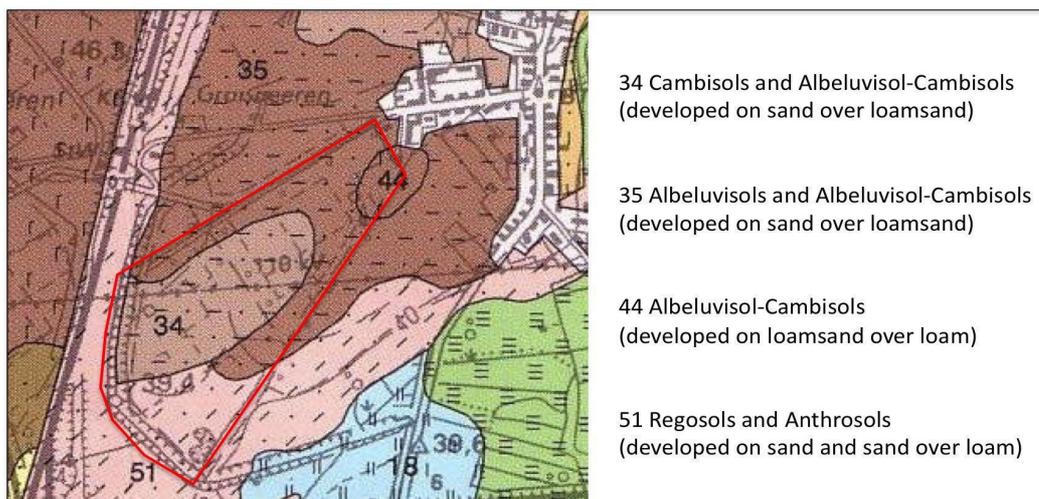


Figure 1.2 Soil map of the investigation area (Bauriegel, A.; Kühn, D. & Hannemann, J (1997): Bodengeologische Karte des Landes Brandenburg, Blatt Potsdam)

Due to prolonged irrigation with wastewater, the process of clay translocation which is usually negligible in this region has intensified. Partly, this process has led to decreased drainage, temporarily water-logged conditions and the formation of a characteristic gleyic colour pattern. The nutrient contents of the sandy soils in this region are usually very low but with the wastewater large amounts of organic matter and nutrients have accumulated in the soils. Especially contents of phosphorus, a non-renewable and scarce resource, are very high (LUA 1995).

With proceeding industrialization, the amount of wastewater and the proportion of industrial wastewater has increased. Thus, in addition to nutrients also large quantities of contaminants were distributed on the fields (Ritschel & Kratz, 2000). The main contaminants are cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) (Grunewald, 1996). Contamination hotspots which are usually small, i.e. former sedimentation tanks and

irrigation channels also show high contents of organic contaminants such as polychlorinated biphenyls (PCBs), poly-aromatic hydrocarbons (PAHs) and dichlorodiphenyltrichloroethane (DDT). The irrigated fields which account for about 80% of the whole irrigation area show moderate contamination with a heterogeneous pattern of heavy metal concentrations (Grunewald, 1996). Depending on the duration and amount of wastewater applied, levels of nutrients and contaminants differ widely. Fields with a high infiltration capacity received much more wastewater than those with a low infiltration capacity (Kulla, 2006) and thus show higher contamination levels. Within a single field, the contents of heavy metals and organic substance decrease from the wastewater inlet to the outlet area in a concentric form since heavy metals co-sedimented with particulate matter (Grunewald, 1994). The contamination of the subsoils is more homogeneous and lower compared to the topsoils (Grunewald, 1996).

After the termination of irrigation with wastewater the risk of leaching of heavy metals into groundwater has increased. Some studies have shown that, under long-term sewage sludge application, a rebound of the solubility of heavy metals in the soils occurred years or even decades after termination of sudge application due to acidification processes caused by mineralization involving N and S oxidation reactions (McBride, 2003). On the former sewage fields around Berlin, the lack of organic and alkaline inputs from the wastewater and, possibly, N and S oxidation reactions have resulted in decreasing pH levels and concentrations of organic carbon after the termination of wastewater application (LUA 1995). Since organic substance is the main sorbent for the heavy metals accumulated on sandy soils, the mineralization of organic matter together with decreasing soil pH led to the mobilization of heavy metals (Grunewald, 1994). An increase in their mobility enhances the risk of leaching into groundwater and also increases their toxicity to microorganisms and plants.

At present, measures to avoid human exposure taken by the Environmental Agency of the Land Brandenburg include restrictions of landuse such as the ban on food and feed production to avoid contamination of the food chain. An all-year coverage of the soil with perennial plants is required to avoid displacement of contaminated soil by wind erosion and thus inhalation and dermal uptake of contaminants by the population. However, these measures do not reduce the increasing risk of leaching and toxicity of heavy metals with decreasing soil pH and mineralization of organic substance. Moreover, any beneficial use

of the accumulated nutrients is prevented. Therefore, measures to be taken for immobilization of the heavy metals become increasingly important and may eventually allow crop production in the future.

1.3 Remediation of large-scale heavy metal-contaminated sites

The former sewage field soils show near-surface, moderate but large-scale contamination patterns. Since heavy metals are not degradable, biological degradation techniques cannot be used for remediation. For this kind of contamination, the established *ex situ* remediation techniques such as thermal desorption, soil washing or “dig and dump” which means excavation of the soil and its deposit in a landfill may also not be practicable due to the high costs involved. Moreover, these methods leave a “clean” but unfertile site as a result of the removal or treatment of the topsoil. Also the practice of containment where caps and/or horizontal linings are installed to prevent leaching of contaminants is quite expensive and not practicable for large-scale moderate contamination.

In situ methods are usually less expensive. At present, two strategies for a cost-effective reduction of heavy metal emissions are available for this kind of contamination: (1) phytoremediation and (2) *in situ* immobilization. The term “phytoremediation” usually applies to all processes such as extraction, complexation, volatilization and degradation of contaminants. In the context of this thesis, however, only the extraction and uptake of metals by plants are considered for which decades of experience are available (Salt et al., 1998; Tack & Meers, 2010). One of the advantages compared to immobilization is the de-facto removal of the metals from the soil. Partly, a recovery of the metals accumulated in the plants can be practised (Garbisu & Alkorta, 2001). The main disadvantage is still the low efficiency of the method since plants which accumulate metals usually produce only small amounts of biomass and plants which produce high yields usually do not accumulate metals in high concentrations (Tack & Meers, 2010). Investigations carried out by Salt (1988) on the sewage fields of Karolinenhöhe (Berlin Spandau) showed that decontamination of the soils by phytoremediation would take several hundred years with the plants growing already on the fields. Research on plants meeting both high biomass production and high metal accumulation is in progress (Tack & Meers, 2010). When the plants are intended for non-food use such as bioenergy production, high yields are also required for economic reasons. However, the plants have to be able to tolerate high metal concentrations in the soils. Metal concentrations in plants have already reached critical levels (Salt, 1988) and increasing metal mobility might further reduce plant growth.

For immediate reduction of the risk emanating from such contaminated sites, especially with regard to groundwater pollution and toxicity to plants, immobilization of heavy metals is the other option. For this purpose, substances are added to the soil leading to the precipitation of solid phases of metals or providing sorption capacity, so that heavy metal mobility is reduced (O'Day & Vlassopoulos, 2010). However, this technique does not remove the metals from the soil. These immobilizing additives might be of organic or inorganic nature. Out of the group of inorganic additives, carbonates are widely used to increase soil pH and concurrently the formation of negatively charged functional groups thus reducing the mobility of heavy metals by their sorption to oxides, silicates and organic substance or due to precipitation of metal carbonates and hydroxides. The effect of soil pH on metal mobility on former sewage field soils was investigated in several studies (Alloway & Jackson, 1991; Marschner et al., 1995). On the basis of these studies, liming of former sewage fields was suggested as a measure to immobilize metals. However, liming is supposed to increase microbial activity and leaching of dissolved organic carbon (DOC) (Andersson & Nilsson, 2001) thus promoting the formation of soluble organo-Pb complexes (Sauvé et al., 1998). Also, the release of metal-containing colloids might increase with increasing pH as shown for Pb by Klitzke et al. (2008). Hoffmann (2002) has shown that heavy metal mobility in the soil solution was not efficiently reduced by liming but by application of glacial till on former sewage field soils north of Berlin. The combination of lime and clay from glacial till increases soil pH and provides additional sorption capacity on aluminosilicates. Aluminosilicates such as montmorillonite, vermiculite and zeolite are widely used for filtration and water treatment. The underlying mechanism of metal immobilization is adsorption or ion exchange on their large negatively charged surfaces (O'Day & Vlassopoulos, 2010). However, glacial till was available in large amounts during the construction of the Berlin subway in the 1990ies but does not accrue in large quantities at present and pure aluminosilicate minerals are considered to be too expensive for remediation of former sewage field soils (Wessolek & Fahrenhorst, 1994).

Many studies conducted mainly in the past ten years have shown that application of iron, manganese and aluminum oxides and hydroxides to soils contaminated with heavy metals leads to a long-term reduction of metal extractability (Komárek et al., 2013). The underlying mechanisms are specific or non-specific adsorption of metals on the relatively large surface areas of iron (Fe), aluminum (Al) or manganese (Mn) oxides (including hydroxides, hydrous oxides, oxyhydroxides etc.) or co-precipitation and incorporation of

contaminants along with the formation of secondary oxides. Most of the studies focus on iron oxides. Pure iron oxides or their precursors such as iron grit or iron sulfates are relatively expensive for large-scale application and, therefore, the use of iron-containing byproducts of industrial processes such as water treatment residues or red mud has frequently been discussed (Komárek et al., 2013). However, these byproducts themselves may contain high levels of trace elements which may be released into the environment. Another disadvantage might be an excessive fixation of phosphorus thus leading to a reduction of soil fertility and plant growth (Römer, 2003; Brown et al., 2005) along with a reduction of the uptake of heavy metals by plants.

Phosphate-based amendments induce the formation of relatively stable phosphate minerals with divalent metals (Kumpiene et al., 2008). Phosphate (P) concentrations in the soil solution of former sewage field soils are already high so that leaching of P is considered to cause eutrophication when drainage water from the fields is entering surface water (Driescher & Gelbrecht, 1993). After addition of phosphate-based amendments leaching of P might increase. For example, Dermatas et al. (2008) reported on P leaching at concentrations $>300 \text{ mg l}^{-1}$ after addition of P amendments.

Out of the group of organic sorbents, activated carbon is the most common additive which adsorbs contaminants on a large reactive surface area but is too expensive for large-scale treatment. As cost-effective organic amendments, municipal organic waste, paper mill sludge or biosolids can be used as sorbents for heavy metals after a sanitation process if the waste itself is not contaminated with heavy metals (Jones & Healey, 2010). These organic materials immobilize heavy metals by different processes: (1) by providing sorption capacity on negatively charged surfaces, (2) by complexation with organic substance with a high molecular weight and (3) by increasing the pH of the soil inducing precipitation of mineral phases and increasing the amount of negatively charged surfaces. Additionally, they provide nutrients for plant growth and enhance soil properties such as water-holding capacity, aeration of the soil and biological activity. This may also have a positive effect on the degradation of organic co-contaminants. Another advantage of these organic amendments is that they are renewable resources and close the nutrient cycle. Their use as amendment may also reduce waste streams. However, the application of organic amendments bear the risk of release of dissolved organic matter (DOM) leading to organic complexation and thus mobilization of metals especially Cu and Pb which have a high affinity to organic substance. Also, the organic amendments will mineralize with time and the immobilized metals will be released again. Some of the organic amendments are

subject to a sanitation process before application consisting mainly in composting or fermentation, leading to a stabilization of the organic material since easily degradable organic material is consumed by microorganisms. However, the success of soil remediation is restricted to a period of years or decades since these organic materials are still further degradable (Jones & Healey, 2010).

Recently, biochar has been proposed as a cost-effective amendment for metal immobilization in soils (Beesley et al., 2011). The term “biochar” is used for biomass converted by a pyrolytic process into a stable, less biodegradable carbon (C) form for the purpose of soil improvement. In contrast to activated carbon, biochar has not been subject to any activation process and is therefore less expensive. Initially, biochar has been known as a “key ingredient” of the very fertile Terra Preta soils in the Amazon Basin (Glaser & Birk, 2012) and has been proposed as an amendment to soils to increase biomass production, *e. g.* by increasing their water-holding capacity and nutrient retention (Jeffery et al., 2011). Additionally, biochar can be used for carbon sequestration in soils (Lehmann, 2007). All these aspects are highly desired for the former sewage fields.

Another way to produce stable C forms is via hydrothermal carbonization which is similar to the natural coalification process and leads to coal-like substances in a liquid phase by high pressure and high temperature. In order to differentiate between the two types of processes, the term “pyrochar” is used for biochar produced by pyrolysis and “hydrochar” is used for the product obtained by hydrothermal carbonization. The term “biochar” in this thesis refers to any kind of carbonized material without regard to the conversion process.

1.4 Immobilization of heavy metals by biochar - state of the art

Pyrochars have a highly condensed aromatic structure with a large specific surface area in the range of hundreds of $\text{m}^2 \text{g}^{-1}$ (Downie et al., 2009). Several studies have shown that the cation exchange capacity (CEC) of the Terra Preta soils is much higher than that of the surrounding soils (Liang et al., 2006; Glaser & Birk, 2012) leading to the assumption that pyrochar added to these soils is providing negatively charged surfaces for ion exchange which are responsible for the ability to sorb nutrients and also heavy metals. However, freshly produced pyrochars do not show a high CEC (Singh et al., 2010) and technical methods to oxidize the biochar surface by an activation process will lead to high costs. Oxidation of the pyrochar surface will occur also naturally by microbial degradation but is assumed to be a very slow process (Kuznyakov et al., 2009). Adsorption of humic

substances containing functional groups themselves to the pyrochar surface has also been suggested to provide negatively charged functional groups (Lehmann et al., 2005; Liang et al., 2006). Prost et al. (2013) have recently shown that CEC increased due to sorption of compost-derived organic matter after a relatively short process of composting. Therefore also adsorption of soil-borne DOC might increase CEC.

Another mechanism for the immobilization of heavy metals might be an increase of the soil pH attributable to the high ash content of pyrochars leading to an increase in the sorption capacity of functional groups of variable charges or precipitation of mineral phases especially P minerals as has been shown for Pb in a study by Cao et al. (2009). Various studies have shown that the mobility of metals in soils and their uptake by plants can be reduced (Namgay et al., 2010; Fellet et al., 2011; Park et al., 2011). However, the effects of pyrochar addition are not uniform and the mechanisms of immobilization are not yet well understood (Beesley et al., 2011).

With respect to groundwater protection, the cumulative leaching fluxes are of higher relevance than element concentrations. An increased water-holding capacity has also been reported for pyrochar (Jeffery et al., 2011). Therefore, it can be assumed that not only sorption or precipitation of mineral phases but also reduced drainage water may decrease cumulative heavy metal leaching fluxes.

Compared to pyrochar, hydrochars have smaller surface areas in the range of tens $\text{m}^2 \text{g}^{-1}$ but high proportions of functional groups capable of exchanging ions and offer an option to be used as soil amendment (Mumme et al., 2011; Libra et al., 2011). Some studies have shown that hydrochar can sorb metals from aqueous solutions (Liu & Zhang, 2009; Liu et al., 2010). As in the case of pyrochar, an increased water-holding capacity has been reported with addition of hydrochar to sandy to loamy soil (Abel et al., 2013). However, little is known about the effects on plant growth (Gajic & Koch, 2012). A study by Busch et al. (2012) even reported toxic effects of hydrochar on plants.

1.5 Objectives of this thesis

It was the aim of this thesis to find out whether the use of pyrochar and hydrochar as soil amendments is suitable for the immobilization of heavy metals accumulated in the former sewage field soils. In a first step, a laboratory study was conducted to investigate the following questions:

- Does biochar (pyrochar and hydrochar) addition reduce heavy metal concentrations in plants and the soil solution and is there a positive effect on biomass yields?
- Which processes lead to the immobilization of heavy metals present in the soil?

To answer these questions, I conducted pot experiments with *Avena sativa* grown on soil from former sewage fields. The working hypothesis was that **addition of pyrochar and hydrochar immobilizes heavy metals due to the precipitation of mineral phases and/or adsorption and thus increases biomass production**. The results of these experiments are presented in Chapter 2: Suitability of biochars (pyro- and hydrochars) for heavy metal immobilization on former sewage field soils.

In a second step, I conducted field experiments to quantify the immobilizing potential of pyrochar under field conditions. Since the hydrochar used had shown negative effects on plant growth in the pot experiments it was excluded from the field experiments. The questions to answer were:

- Do the positive effects of increasing biomass production and reduced heavy metal concentrations in plants with pyrochar addition also occur under field conditions?
- Is the metal mobility influenced in the same way as in the pot experiments?
- Does pyrochar addition reduce the risk of groundwater contamination?
- How long-lasting are these effects?

In Chapter 3 (Biochar addition enhanced growth of *Dactylis glomerata* and immobilized Zn and Cd but mobilized Cu and Pb on a former sewage field soil), I focused on the concentrations of heavy metals in the soil solution and their uptake by plants under field conditions. On the basis of the results of the pot experiments, I hypothesized that **addition of pyrochar increases yields and immobilizes Zn due to precipitation of Zn mineral phases and Cd due to increased sorption with increasing soil pH. For Cu and Pb, I hypothesized that addition of pyrochar increases Cu and Pb mobility due to organic complexation**. In Chapter 4 (Biochar reduces Zinc and Cadmium but not Copper and Lead

leaching on a former sewage field), I focused on the effect of pyrochar addition on the leaching of heavy metals into groundwater. Some studies have shown that pyrochar addition to soils increases their water-holding capacity, in particular on sandy soils. Thus **I hypothesized that Zn and Cd leaching is reduced by pyrochar addition not only as a consequence of reduced concentrations in the soil solution but also as a consequence of reduced drainage of water attributable to the increase in the water-holding capacity. For Cu and Pb, I hypothesized that the increased water-holding capacity compensates increased Cu and Pb concentrations so that biochar addition will have no effect on Cu and Pb leaching.**

2 Suitability of biochars (pyro- and hydrochars) for heavy metal immobilization on former sewage field soils ¹

2.1 Summary

Mineralization of organic material and decreasing pH is expected to increase bioavailability and leaching of metals in soils formerly contaminated by irrigation with wastewater. Biochar has recently been proposed as a sorbent for metals, although the effects described in the literature available are still inconsistent. Therefore, we conducted pot experiments to study the effects of the application of two different biochars to a sewage-field soil on growth and nutrition of oat (*Avena sativa* L.) as well as on the mobility of zinc (Zn), copper (Cu), cadmium (Cd) and lead (Pb) in the soil solution. Poplar-derived hydrochar (obtained by hydrothermal carbonization) and maize-derived pyrochar (obtained by pyrolysis) were mixed with the soil at concentrations of 0, 1, 2.5 and 5% (g 100 g⁻¹). Soils were leached after two, three and five weeks with deionized water. Hydrochar reduced biomass production and had almost no effect on metal concentrations in plants and leachates. The negative effect on biomass yield may be attributable to decreased nitrogen (N) availability. Pyrochar increased biomass production and reduced plant Zn and Cd concentrations. In contrast, metal concentrations in soil leachates generally increased. Comparison of ultra-centrifuged and filtered samples, microprobe analysis of centrifugation residues and Visual Minteq calculations suggest colloidal transport of Zn precipitates whereas Cu is transported in the dissolved fraction. We conclude that the tested hydrochar is not suitable for metal immobilization. In the case of pyrochar, further research on colloidal transport of metal precipitates is needed to assess its suitability for soil remediation, despite positive effects on plant growth and the reduced uptake of Zn and Cd.

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2.2 Introduction

Mining, processing and use of metals have caused diverse and wide-spread environmental pollution with traces of various metals such as lead (Pb), copper (Cu), cadmium (Cd) and zinc (Zn). These elements are recovered in the wastewater collection system, especially of urban and industrial areas (Nicholson *et al.*, 2003). The former sewage-fields south of Berlin received mixed wastewater for decades and are highly contaminated with organic pollutants and metals so that food production is not allowed at the present time. These soils also have large contents of nutrients, especially of phosphorus (P), and they are rich in organic matter. Upon completion of the wastewater irrigation process, however, the concentration of organic matter and soil pH have been decreasing. Since organic matter is mainly responsible for the sorption capacity of these sandy soils, its further mineralization and decreasing pH will increase both bioavailability and leaching of metals (Grunewald, 1994). Thus strategies are needed which utilize the nutrients accumulated in the soils, for example for energy crop production, without initiating metal leaching after soil cultivation.

Kumpiene *et al.* (2008) reviewed the literature on the immobilization of metals through soil amendments. Clays, carbonates, phosphates and iron oxides are effective amendments for the fixation of Cu, Pb and Zn. Also numerous organic amendments such as sludges, compost or paper mill waste are suitable for the reduction of the mobility of metals (Zhou & Haynes, 2010). Recently, biochar has been proposed as a cheap amendment for polluted soils (Fuentes *et al.*, 2010; Beesley *et al.*, 2011). At the same time, biochar is expected to improve soil fertility and to contribute to C sequestration (Glaser & Birk, 2012). Other studies have shown that biochar may reduce the mobility of metals in soils and their uptake by plants (Namgay *et al.*, 2010; Fellet *et al.*, 2011). However, the effects are not uniform and the mechanisms of fixation are not well understood (Beesley *et al.*, 2011). One of the main uncertainties is that the chemical and physical properties of biochar may vary depending on feedstock and charring conditions (Fellet *et al.*, 2011).

The term 'biochar' is used as a new term for biomass converted into a stable C form, mainly by pyrolytic processes. However, another way to produce stable C forms is by hydrothermal carbonization which is similar to the natural coalification process and leads to coal-like substances in a liquid phase by high pressure and high temperature. In order to differentiate between the two types of processes, we use the term 'pyrochar' for biochar

produced by pyrolysis and 'hydrochar' for the biochar obtained by hydrothermal carbonization. For hydrochar, little is known about the effects on plant growth (Gajic & Koch, 2012) and the effects on metal immobilization (Liu & Zhang, 2009).

In the present study, pot experiments were conducted to examine the potential of both types of biochar for reducing metal leaching and uptake by plants. We hypothesized that addition of pyrochar and hydrochar to nutrient-rich former sewage-field soils will decrease the concentrations of metals in soil solutions and plant tissues through the (i) sorption or (ii) precipitation of metals and thus will increase yields.

2.3 Materials and methods

2.3.1 Soil

We collected soil from a former sewage field south of Berlin (Großbeeren, 52°21'0.36" N, 13°17'54.8304" E) to study the effects of biochar addition on metal leaching and uptake by plants. Between 1884 and the beginning of the 1980s, an area of approximately 750 ha had received about 20 million m³ wastewater per year (LUA, 1997). Precise data about spatial distribution on the individual fields and metal concentrations of the wastewater are not available. Since metals are co-sedimented with particulate matter, the contamination pattern shows large concentrations in the inlet area decreasing with increasing distance to the outlet area in a concentric form (Grunewald, 1994). Samples were taken from the top-soil (0–30 cm) at five sampling points located at a distance of about 10 m from the former wastewater inlet where contamination was expected to be greatest. Moist field samples were homogenized cautiously with a rotary stirrer in a plastic container. Stones >10 mm and wastewater debris were removed by hand.

2.3.2 Biochars

Pyrochar was produced in a Pyreg reactor using *Zea mays* L. as feedstock heated to 750°C for around two hours (Pyreg GmbH, Dörth, Germany). Hydrochar was produced from poplar (*Populus sp.*) wood chips applying approximately 200° C and 20 bar for two hours (Sun Coal Industries GmbH, Ludwigsfelde, Germany). In order to exclude the possibility that differences between hydrochar and pyrochar were attributable to differences in feedstock, we repeated the experiment with a hydrochar produced from *Zea mays* silage by applying 200° C and 20 bar for ten hours (Addlogic Labs, Jettingen, Germany). Any wood

pieces in the hydrochar made from poplar wood which were not fully carbonized were removed by hand. The biochars were forced through a 2-mm stainless steel sieve before they were mixed with the soil.

2.3.3 Characterization of soil, biochars and plants

Aliquots of the homogenized soil and biochars were air-dried and sieved to 2 mm. The pH was measured in a 0.01 M CaCl₂ suspension (soil:solution ratio 1:2.5 g g⁻¹, biochar:solution ratio 1:5, ml ml⁻¹ (inoLab pH/Cond Level 1, SenTix 41 electrode, WTW, Weilheim, Germany). Additionally, the electrical conductivity of the biochars was determined (inoLab pH/Cond Level 1, TetraCon 325 electrode, WTW, Weilheim, Germany) in a filtered suspension (biochar:solution ratio 1:5, ml ml⁻¹) with distilled water. For analysis of element concentrations, specific surface area and porosity, the biochars, soil and plants were ground in tungsten carbide vessels (MM200, Retsch, Haan, Germany). Total carbon (C), N and sulphur (S) of biochars, soil and plants were measured with an elemental analyser (Vario EL III, Elementar, Hanau, Germany). Potassium (K), calcium (Ca), magnesium (Mg), P, Cu, Zn, iron (Fe), manganese (Mn), aluminium (Al), Cd and Pb in soils were determined after digestion with *aqua regia*. Plants and biochars (approximately 50 mg each) were digested with 10 ml 69% HNO₃ (Rotipuran, Roth, Karlsruhe, Germany) at 180°C and maximal 20 bar for 15 min in a microwave pressure apparatus (Mars Xpress, CEM, Kamp-Lintfort, Germany). Elemental concentrations were determined by flame atomic absorption spectroscopy (1100B, Perkin Elmer, Waltham, Massachusetts, USA) for K, Ca, Mg, Fe, Mn, Al, Cu and Zn and graphite furnace atomic absorption spectroscopy (SpectrAA 880Z, Varian, Darmstadt, Germany) for Cd and Pb. Phosphate was measured as dissolved reactive P according to Murphy & Riley (1962) using a continuous flow analyser (SAN Plus, Skalar, Breda, Netherlands). All samples were analysed in duplicate.

The specific surface area (SSA) and micro-porosity of the biochars were measured by gas adsorption in an Autosorb-1 (Quantachrome, Odelzhausen, Germany) using N₂ and CO₂ as adsorbate. Prior to analysis, the samples were degassed under vacuum at 20° C until the pressure increase was below 10 micron per minute. For determination of the specific surface area, N₂ adsorption isotherms at 77 K were evaluated using the BET equation (ISO 9277:1995) in the relative pressure range P/P₀ of 0.05–0.3. In addition, the micro-pore volume (MPV) and micro-pore surface area (MPSA) were determined by applying the Dubinin-Radushkevich method (DIN l66135-3) to the N₂ isotherms in the relative pressure range P/P₀ of 0.00001–0.08. Because of the low temperature of 77 K, the diffusion of N₂ in

pores <0.7 nm is kinetically limited (Lowell *et al.*, 2010). Therefore, isotherms using CO_2 as an adsorbent were measured at 273 K and micro-pore surface and volume were determined by applying the Dubinin-Radushkevich method to the isotherms in the same relative pressure range as for the N_2 isotherms. All samples were analysed in duplicate.

2.3.4 Pot experiments

Substrates for the pot experiments were produced by mixing 0, 1, 2.5 and 5% of the respective biochars to the field-moist sewage field soil ($\text{g } 100 \text{ g}^{-1}$, dry mass). The mixtures were gently homogenized with a rotary stirrer. The pH in each substrate was measured as described for soil. We filled 290 cm^3 pots (diameter 7.5 cm) with 200 g of substrate, corresponding to 158 g dry mass. According to Kalsch *et al.* (2006), a volume of about 500 cm^3 is sufficient for growing eight plants per pot for seven to eight weeks. Since we grew only three plants per pot for five weeks, we assumed that the volume of our planting pots was suitable. Filter papers (MN 615, Macherey-Nagel, Düren, Germany) were placed on the bottom of the pots to avoid loss of substrate. For self-watering, two glass fibre wicks per pot were drawn through the filters and substrates. Each pot was placed on a water storage vessel which was filled with water up to 4 cm under the rim. Pots were placed in a climate chamber kept at 20° C with 16 hours of artificial daylight and eight hours of darkness. Regularly, the water storage vessels were refilled and pots were rearranged to avoid spatial effects. Ten seeds of oat (*Avena sativa* L.) were sown per pot. After ten days, the plants were thinned to three plants per pot. The shoots were harvested after 35 days and fresh weight was determined immediately. The plants were washed with deionized water and dried at 60° C for 24 hours before dry mass was determined. All treatments were carried out in four replicates. Elemental uptake was calculated as the concentration multiplied by the dry mass of the above-ground plant material and is given in μg or mg per pot.

2.3.5 Leachates

All pots received additional 50 ml deionized water after two, three and five weeks which caused leaching of soil solution. The leachates were collected and frozen after measurement of pH (inoLab pH/Cond Level 1, SenTix 41 electrode, WTW, Weilheim, Germany). For further analysis, the leachates were defrosted slowly and filtered through a $0.45\text{-}\mu\text{m}$ membrane (DIAFIL, polyvinylidene fluoride, 25 mm, DIA-Nielsen, Düren,

Germany). In order to stabilize the solutions, the filtrates were brought to a pH of <3 by addition of HCl. Elemental concentrations were determined as described for *aqua regia* digests.

For determination of the colloidal proportion of metals contained in the filtrates of the two-week leachates, aliquots of the replicates of each treatment were mixed and ultra-centrifuged (Optima L-90K, rotor 70Ti, Beckmann Coulter, Krefeld, Germany) at 160 000 *g*. Calcium, Cd, Cu, Pb and Zn were measured in the supernatant by ICP-OES (CAP 6000 Series, Thermo Scientific, Waltham, Massachusetts, USA). In the same solution we measured the concentration of dissolved organic carbon (DOC) with a TOC analyser (TOC-5050A, Shimadzu, Duisburg, Germany). Centrifugation residues were dried in petri dishes for microprobe analysis.

2.3.6 Electron microprobe analysis (EMPA)

Dried centrifugation residues were redispersed in 10 ml deionized water using ultrasound and further diluted with deionized water at a ratio of 1:100. This dispersion was dropped onto pieces of silicon wafer material and scanned with a field emission electron probe micro-analyser (JXA-8530F, Jeol, Eching, Germany). This analysis combines a very sensitive element analysis with high spatial resolution X-ray spectroscopy and was shown to be suitable for the detection and characterization of P-rich mineral particles in sediments (Zanini *et al.*, 1998). Images and element mappings were obtained at 15 kV and 20 nA on a section of 9.6x 8.4 μm with 240 x 210 pixels. Time of measurement per pixel was 200 ms.

2.3.7 Metal speciation modelling

In order to assess whether metal colloids could form, the mean concentrations of Zn, Cd, Pb and P as well as the pH value in the filtrates of the 5% treatments were used for modelling of speciation with Visual Minteq 3.0. The concentration of DOC was not included in the modelling since no information on complexing properties of biochar-associated DOC was available. However, in accordance with literature, we considered the affinity of Cd and Zn to form organic complexes to be poor compared with that of Cu (Bradl, 2004). Also the formation of Pb phosphates was considered to over-ride organic complexation reactions (Hashimoto *et al.*, 2009).

2.3.8 Statistics

Data from yields, element concentrations of plants and leachates did not meet the requirements for an ANOVA (normal distribution and homoskedasticity). For at least one of the elements in the leachates even log transformation did not reach near-normal distribution. Therefore, we used the Kruskal-Wallis test (Statistica 6.0) at the 5% level of significance which is the non-parametric complement to an ANOVA. This test is based on ranks instead of means and does not require normal distributions.

2.4 Results and discussion

2.4.1 Characterization of soil and biochars

The soil of the former sewage field had a pH of 5.4 and was rich in organic matter (Table 2.1). Phosphorus and metal concentrations (Table 2.2) were above the German limit values fixed as a precautionary measure for sandy soils. Pyrochar itself was rich in all nutrients except N, but was still poor compared with commercial fertilizers. Metal concentrations in pyrochar were small (Tables 2.1 and 2.2). In addition, because of large ash contents, nutrient concentrations from the group of alkali and alkaline earth metals were large leading to high pH and electrical conductivity (Amonette & Joseph, 2009). In contrast, both hydrochars were acidic and generally poor in nutrients. In the hydrochar from poplar wood, however, Fe concentrations were large resulting from Fe addition as a catalyst during the production process. Small nutrient concentrations and low pH values are in line with data reported by Fuertes *et al.* (2010) for hydrochars.

Table 2.1 PH, electrical conductivity (EC) as well as carbon and nitrogen concentrations and their ratios of sewage field soil, pyrochar and hydrochars (feedstock).

Sample	pH	EC	Organic C	Total N	C:N
		/ mS cm ⁻¹	/ %	/ %	ratio
soil	5.4	n.d. ^a	4.4	0.4	11
pyrochar (<i>Zea mays</i>)	9.3	3.7	65.9	1.6	41
hydrochar (<i>Populus</i>)	4.3	0.6	55.6	0.2	281
hydrochar (<i>Zea mays</i>)	3.6	n.d. ^a	62.2	1.5	42

^a not determined

Table 2.2 Element concentrations of sewage field soil, pyrochar and hydrochars (feedstock).

Sample	Element concentration									
	/ mg kg ⁻¹									
	K	Ca	Mg	P	Fe	Mn	Cu	Zn	Cd	Pb
soil	1332	4719	1218	4651	8869	173	306	472	7.5	268
pyrochar (<i>Zea mays</i>)	29762	10271	6576	8413	1917	168	13	103	0.1	4.6
hydrochar (<i>Populus</i>)	676	1537	133	17	3695	36	27	24	0.1	2.8
hydrochar (<i>Zea mays</i>)	804	2226	693	538	163	12	10	47	<LoD ^a	<LoD ^a

^a Limit of Detection

The specific surface area and micro-pore volume of the pyrochar (Tab. 2.3) were in the range reported by Downie *et al.* (2009) for pyrochars obtained at 750° C. In contrast to pyrochar, our hydrochars from poplar wood and maize silage showed a very small specific surface area and micro-pore volume which is in line with Mumme *et al.* (2011). When determined with CO₂ as an adsorbent, micro-pore volume and surface area of hydrochar and pyrochar were much larger than when determined with N₂. This indicates that the proportion of small micro-pores of less than 0.7 nm is large (Lowell *et al.*, 2010).

Table 2.3 Specific surface area (SSA), micropore volume (MPV) and surface area (MPSA) of pyrochar and hydrochars (feedstock) analysed with N₂ and CO₂ as adsorbents.

Sample	SSA (N ₂)	MPV	MPSA	MPV	MPSA
	/m ² g ⁻¹	(N ₂)	(N ₂)	(CO ₂)	(CO ₂)
		/cm ³ g ⁻¹	/m ² g ⁻¹	/cm ³ g ⁻¹	/m ² g ⁻¹
pyrochar (<i>Zea mays</i>)	222.9	0.0481	139	0.184	529
hydrochar (<i>Populus</i>)	2.8	0.0005	1.27	0.018	52
hydrochar (<i>Zea mays</i>)	6.3	0.0014	3.86	n.d. ^a	n.d. ^a

^a not determined

2.4.2 Plant yield, element concentration and total uptake of elements

Addition of hydrochar from poplar wood resulted in a significantly reduced fresh ($P = 0.015$) and dry matter ($P = 0.016$) production of up to 50% (Figure 2.1). Since the N concentration of this hydrochar was much smaller and the C:N ratio of 280 was extremely

large compared with pyrochar, the experiment was repeated with hydrochar made from maize silage to exclude the possibility that the smaller N content in poplar-wood hydrochar was the explanation for the negative effects on biomass production. Nitrogen concentration and C:N ratio of maize-silage hydrochar were similar to those of pyrochar. However, hydrochar from maize silage had the same negative effect on fresh matter production ($P = 0.001$; data not shown). Since the condensation grade, and therefore stability, is less for hydrochars than for pyrochars (Kuzyakov *et al.*, 2009; Steinbeiss *et al.*, 2009), an increased microbial availability of hydrochar C may lead to N limitation, after immobilization in microbial biomass, and thus explain decreasing yields with hydrochar addition. This is in line with Gajic & Koch (2012) who attributed growth inhibition effects of hydrochar on sugar beet grown on arable soil to N limitation. Smaller N concentrations in above-ground biomass with increasing hydrochar addition support this hypothesis (Table 2.4). However, since toxic substances such as 5-hydroxymethyl-furfural-1-aldehyde (HMF) and furfural are intermediates in the hydrothermal conversion process and thus could have been present in our hydrochars (Titirici *et al.*, 2008), a toxic impact of hydrochar also cannot be ruled out, as shown in toxicity tests by Busch *et al.* (2012).

In contrast, addition of pyrochar increased fresh and dry matter production by up to about 60% compared with the control (Figure 2.1). This increase was highly significant for fresh ($P = 0.006$) and almost significant for dry matter ($P = 0.050$) production. At the 5% addition, the variability of yields was much greater than with all other treatments. This may be because of water stress since short-term drying of the soils of the 5% addition treatments was observed during the course of the experiment, despite self-watering with glass fibre wicks. One explanation for this phenomenon could be that hydrophobic compounds contained in the pyrochar (Knicker, 2011) accumulate on glass fibre wicks, a process which would most probably occur at the greatest rate of pyrochar added and restrict water flow.

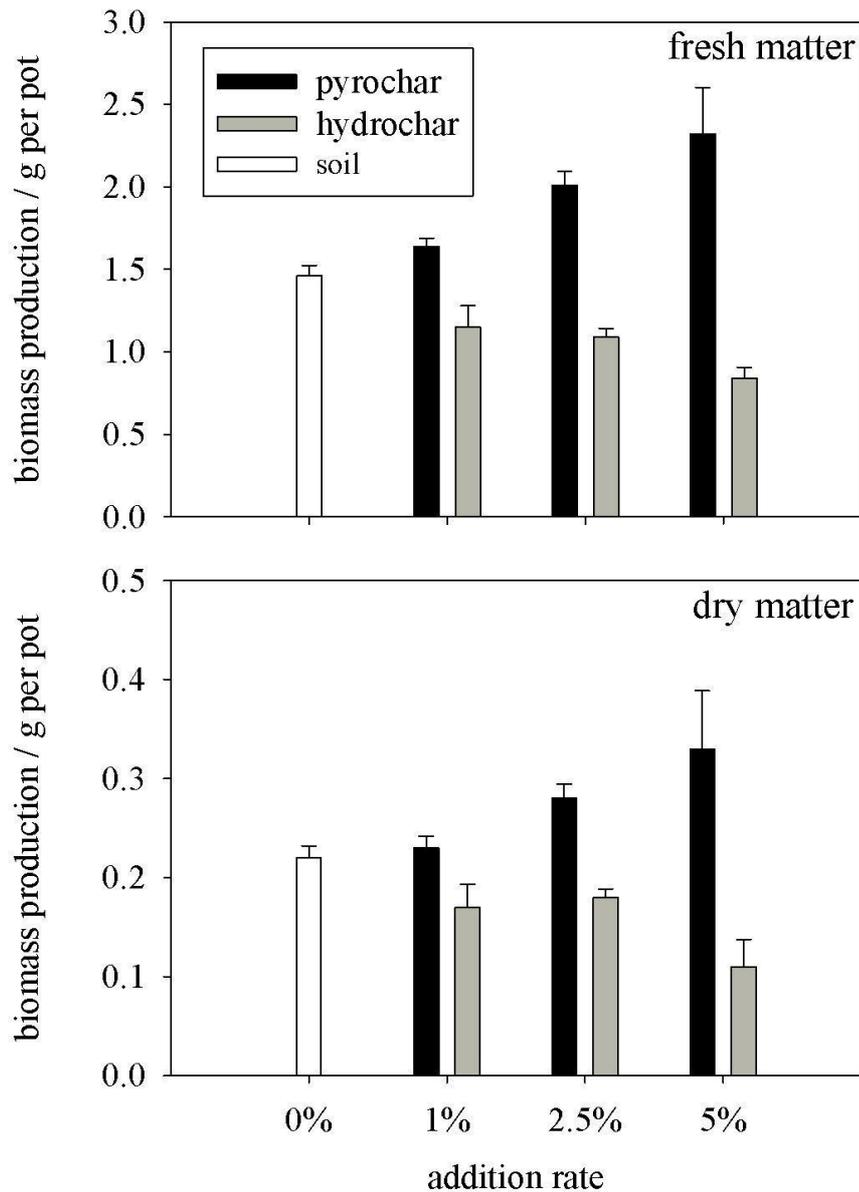


Figure 2.1 Effects of increasing pyrochar and hydrochar addition to a sewage field soil on above-ground biomass of *Avena sativa* (values are means of four replicates \pm standard error)

In arable soils without metal contamination, increased yields caused by pyrochar addition were mainly attributed to an improved water holding capacity of the soil along with a liming effect and improved nutrient availability (Jeffery *et al.*, 2011). Since P, K and Ca concentrations in the control plants (Table 2.4) of our experiments were above the plant optima (Fink, 2007), additional nutrients contained in the pyrochar are probably not responsible for increased yields. However, reduced trace element concentrations in plant biomass may be responsible for increasing biomass production (Table 2.4).

Addition of hydrochar made from poplar wood significantly ($P = 0.005$) reduced N concentrations in plants to less than 1%. With hydrochar from maize silage, plant N concentrations were also significantly ($P = 0.006$) reduced to about 1% (data not shown). All other nutrients except Mg were also reduced with hydrochar from poplar wood (Table 2.4). Hydrochar addition had no effect on the concentrations of Cd ($P = 0.12$) and Fe ($P = 0.24$), whereas the concentrations of Cu ($P = 0.041$) and Zn ($P = 0.008$) were reduced. Lead in all plant tissues was below the detection limit.

In contrast to hydrochar, the addition of pyrochar had no significant effect ($P = 0.45$) on plant N concentrations and, despite relatively large P, K, Ca and Mg contents of the pyrochar itself, P ($P = 0.93$), K ($P = 0.18$) and Mg ($P = 0.31$) concentrations of plant tissues were also not significantly altered. However, Ca concentrations were significantly ($P = 0.014$) reduced to 0.41% in the 5% treatment. With increasing addition of pyrochar, the concentrations of Fe ($P = 0.003$), Zn ($P = 0.003$) and Cd ($P = 0.014$) were significantly reduced to near the plant optima. Copper ($P = 0.092$) and Mn ($P = 0.012$) concentrations showed a considerable decrease already with the addition of 2.5% pyrochar. Our results are in line with those of Park *et al.* (2011) who found significantly reduced Cd concentrations in Indian mustard shoots with the addition of chicken manure and greenwaste-derived biochar (pyrochar) to contaminated shooting-range soil. The authors also found no significant effect on Cu concentrations in plants. However, Namgay *et al.* (2010) reported decreasing Cd and Cu contents in maize shoots and inconsistent effects on Zn concentrations which were attributed to the large intrinsic Zn contents of the pyrochar used.

Antagonistic and synergistic effects may alter element concentrations in plants. Unusually large concentrations of K in the soil solution with pyrochar addition (Figure 2. 2) may cause antagonistic effects and contribute to decreasing Ca concentrations (Jakobsen, 1993). Interactions between major nutrients and metals or between different metals (Siedlecka, 1995) may also change the elemental concentrations.

Along with decreased yields of hydrochar-treated plants, the total uptake of N decreased by about 66% (data not shown). We observed a similar reduction (61–74%) of the uptake of all other elements except for Mn (41%) and Mg (49%), and we interpret this as an indication that no relevant immobilization of metals occurred by hydrochar addition. In contrast to hydrochar, addition of pyrochar increased yields and the total uptake of N, P, K and Mg, while the total uptake of Ca, Zn, Cd and Fe decreased (Table 2.5). This indicates

that Zn, Cd and Fe were less bioavailable when pyrochar was present. In our study, the addition of pyrochar increased the initial pH from 5.4 to 5.5 with 1%, to 6.5 with 2.5% and up to 6.7 with 5% addition so that a reduced plant availability of Zn, Cd and Fe is possible. For Cu, our observations were different. Despite decreasing tissue concentrations, the total uptake of Cu was greater with 5% pyrochar addition than in the control. The reduced Cu concentration of plants, therefore, may be explained by dilution with increasing biomass production.

Table 2.4 N, P, K, Ca, Mg (%) and Fe, Mn, Cu, Zn and Cd (mg kg⁻¹) concentrations in above-ground biomass of *Avena sativa* grown on sewage field soil and soil amended with pyrochar and poplar-hydrochar: soil: soil alone; py 1%: soil + pyrochar (1%); py 2.5%: soil + pyrochar (2.5%); py 5%: soil + pyrochar (5%); htc 1%: soil + hydrochar (1%); htc 2.5%: soil + hydrochar (2.5%); htc 5%: soil + hydrochar (5%). Values are means of four replicates ± standard error.

	N	P	K	Ca	Mg	Fe	Mn	Cu	Zn	Cd
	/ %	/ %	/ %	/ %	/ %	/ mg kg ⁻¹				
soil	1.28 ±0.11	1.67 ±0.18	4.91 ±0.30	0.89 ±0.06	0.14 ±0.01	203 ±34.9	204 ±10.0	14.8 ±1.49	183 ±10.9	2.95 ±0.40
py 1%	1.25 ±0.06	1.82 ±0.29	5.37 ±0.47	0.69 ±0.10	0.17 ±0.02	118 ±16.1	178 ±18.1	12.2 ±1.11	108 ±16.2	3.03 ±0.67
py 2.5%	1.20 ±0.05	1.58 ±0.09	5.41 ±0.18	0.55 ±0.06	0.16 ±0.01	62 ±7.0	118 ± 3.8	9.0 ±0.67	58 ±7.2	1.65 ±0.24
py 5%	1.31 ±0.05	1.67 ±0.06	6.14 ±0.24	0.41 ±0.01	0.18 ±0.01	32 ±5.2	118 ±10.8	11.7 ±1.82	38 ±3.3	0.99 ±0.23
htc 1%	0.97 ±0.03	1.11 ±0.08	3.22 ±0.20	0.82 ±0.23	0.12 ±0.01	143 ±32.8	147 ± 5.5	10.4 ±1.31	124 ±8.1	2.69 ±0.27
htc 2.5%	0.82 ±0.03	0.89 ±0.04	2.87 ±0.03	0.54 ±0.03	0.11 ±0.003	147 ±13.7	165 ± 1.7	9.1 ±1.21	96 ±3.3	2.09 ±0.08
htc 5%	0.76 ±0.05	0.99 ±0.04	2.83 ±0.09	0.60 ±0.04	0.14 ±0.003	132 ±42.8	231 ±10.9	9.1 ±0.93	90 ±6.8	2.21 ±0.11

Table 2.5 Element uptake (µg or mg per pot) in above-ground biomass of *Avena sativa* grown on sewage field soil and pyrochar-amended soil: soil: soil alone; py 1%: soil + pyrochar (1%); py 2.5%: soil + pyrochar (2.5%); py 5%: soil + pyrochar (5%). Values are means of four replicates ± standard error.

	N	P	K	Ca	Mg	Fe	Mn	Cu	Zn	Cd
	/ mg	/ µg	/ µg	/ µg	/ µg	/ µg				
soil	3.10 ±0.25	3.59 ±0.43	10.55 ±0.9	2.38 ±0.45	0.31 ±0.03	44.2 ±9.2	44.1 ±3.8	3.17 ±0.32	39.4 ±3.5	0.63 ±0.09
py 1%	3.19 ±0.12	4.08 ±0.60	12.15 ±1.0	1.56 ±0.22	0.38 ±0.03	27.3 ±5.1	40.0 ±3.1	2.75 ±0.23	24.7 ±4.0	0.68 ±0.14
py 2.5%	3.82 ±0.28	4.43 ±0.40	15.16 ±1.1	1.55 ±0.26	0.44 ±0.03	17.4 ±2.3	33.2 ±2.5	2.51 ±0.15	16.5 ±2.5	0.47 ±0.08
py 5%	4.70 ±0.71	5.33 ±0.77	19.58 ±2.9	1.32 ±0.25	0.55 ±0.07	11.3 ±3.6	38.6 ±8.4	3.56 ±0.51	11.7 ±1.3	0.29 ±0.04

2.4.3 Soil solution concentrations

In the two-week leachates of all hydrochar treatments, the concentrations of nutrients and trace elements were in the range of the control treatment (Figures 2.2 and 2.3). In the five-week leachates (data not shown) K, Ca and Mg concentrations increased significantly with hydrochar addition (K, $P = 0.005$, Ca, $P = 0.03$, Mg, $P = 0.05$). Concentrations of K increased to about 6.9 mg l^{-1} , Ca to 20 mg l^{-1} and Mg to 1.5 mg l^{-1} . Increasing concentrations of these elements may have been caused by the reduced uptake by plants or increased mobility because of the acidic pH of the hydrochar which decreased soil pH slightly from 5.4 to 5.2. Copper and Zn concentrations were not affected by hydrochar while Pb ($P = 0.001$) and Cd ($P = 0.02$) concentrations increased slightly to about $9 \text{ } \mu\text{g l}^{-1}$ and $7 \text{ } \mu\text{g l}^{-1}$, respectively, in the 5% treatment. This is in line with the plant uptake and confirms our assumption that no immobilization of the metals by hydrochar occurred. In contrast to our results, Liu *et al.* (2010) and Liu & Zhang (2009) found a large sorption capacity of hydrochars made from pinewood and rice husk for Cu and Pb. The hydrochars used in their study were washed with acetone prior to the sorption experiments so that soluble organic compounds contained in the hydrochar may have been removed. In our study washing of hydrochars was not performed. The soluble organic compounds may have increased complexation of Cu and Pb and to a lesser extent also Zn and Cd (Bradl, 2004) and, therefore, may have contributed to large solution concentrations. It remains to be demonstrated how long-lasting these effects are.

Addition of pyrochar increased P, K and Mg concentrations in the two-week leachates (Figures 2.2 and 2.3). The increase was significant for P ($P = 0.01$) and K ($P = 0.004$) and only just significant for Mg ($P = 0.06$). In the five-week leachate, the increase was still significant for K ($P = 0.003$) but not for Mg ($P = 0.08$) and P ($P = 0.33$). In contrast to reduced concentrations of Ca, Cd, Zn and Fe in plants, the leachates of pyrochar-amended soil did not show the expected reduction in solution concentrations. The concentrations of Ca and Zn were not affected by pyrochar addition neither in the two-week (Ca, $P = 0.44$, Zn, $P = 0.10$) nor in the five-week leachate (Ca, $P = 0.13$, Zn, $P = 0.20$). The Cd, Pb, Fe and Cu concentrations were even increasing with increasing pyrochar addition in the five-week leachate (Cd, $P = 0.01$, Pb, $P = 0.007$, Fe, $P = 0.01$, Cu, $P = 0.01$). This clearly indicates that Ca, Cd, Zn and Fe must have been present in the filtrates in a colloidal or complexed form which was not plant-available. Copper was not significantly reduced in plants indicating that it must have been present in the leachate in a partly plant-available

form. In the soil solution, Cu is usually present almost completely in the organic fraction irrespective of the pH (Sauve *et al.*, 1997) and soluble organic Cu complexes may partly contribute to Cu uptake (Parker *et al.*, 2001). Lead concentration was below the detection limit in plants so that no statement on plant availability can be made.

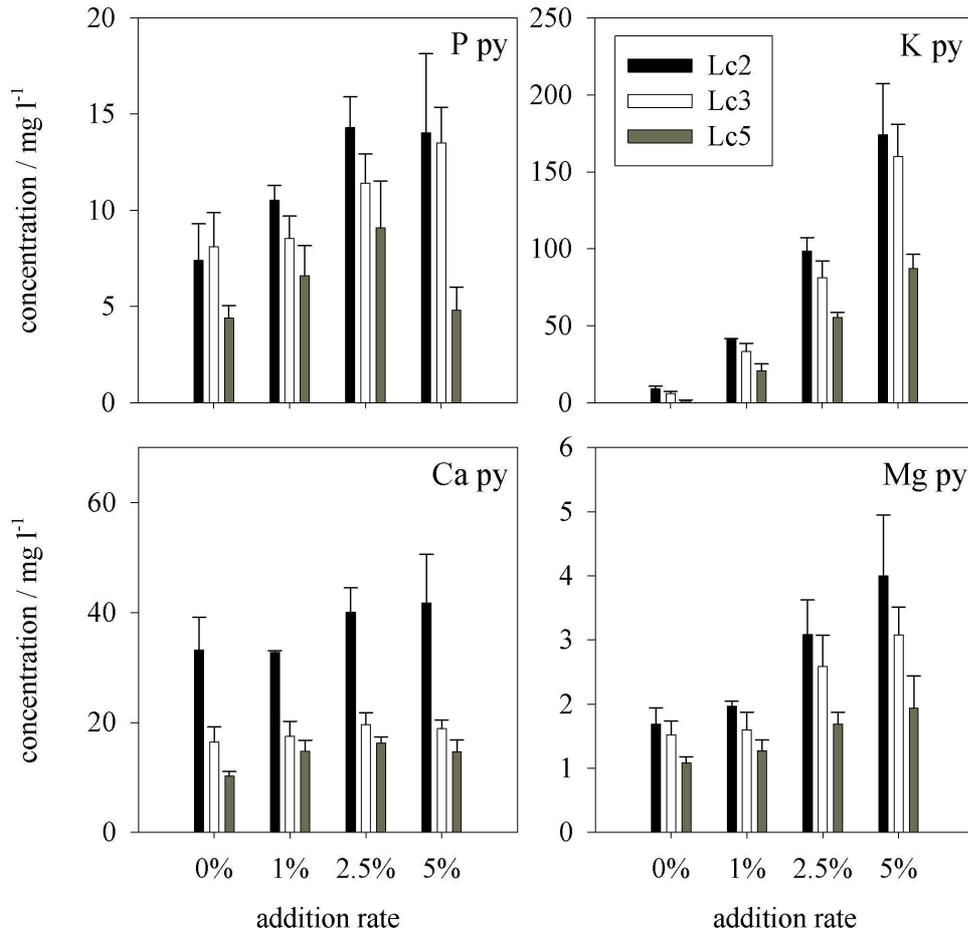


Figure 2.2 Effects of increasing pyrochar addition on the P, K, Ca and Mg concentrations in leachates collected 2 (Lc 2), 3 (Lc 3) and 5 weeks (Lc 5) after starting the pot experiment (values are means of four replicates \pm standard error)

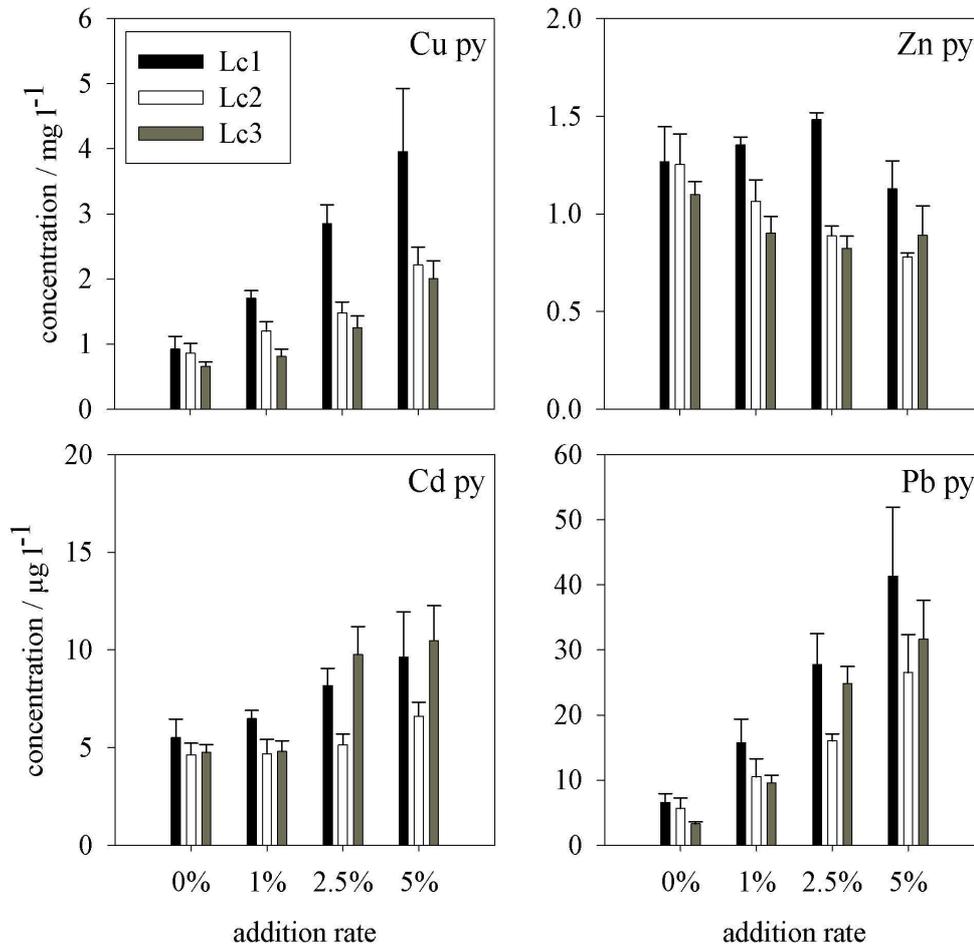


Figure 2.3 Effects of increasing pyrochar addition on the Cu, Zn, Cd and Pb concentrations in leachates collected 2 (Lc 2), 3 (Lc 3) and 5 weeks (Lc 5) after starting the pot experiment (values are means of four replicates \pm standard error)

For the quantification of the colloidal metal fraction, we ultra-centrifuged a mixed sample of the two-week leachates to separate colloids (which pass the 0.45 μm filters) and related the concentration obtained after ultra-centrifugation to that obtained after filtration (0.45 μm). As shown in Figure 2.4, approximately 30–50% of Zn, Pb and Ca was colloidal in the leachate of the control soils (0% pyrochar) while Cd and Cu were almost completely dissolved in this leachate. Increasing pyrochar addition increased the colloidal fractions of Zn and Pb by up to about 80%. Colloidal Cd was also formed with increasing pyrochar addition. In contrast, Cu remained almost completely dissolved even at the largest rate of hydrochar addition and we assume that this is mainly because of complexation by dissolved organic substances (Bradl, 2004). The addition of pyrochar increased the pH in

the leachates from 6.3 in the controls to 7.2 in the 5% treatment. Moreover, P concentrations in the controls were already large and additional P was added with pyrochar. According to Visual Minteq Speciation (3.0) calculations for the 5% treatment, the solution was oversaturated with respect to $Pb_5(PO_4)_3OH$ (hydroxypyromorphite) and $Zn_3(PO_4)_2 \cdot 4H_2O$ (hopeite) while there was no indication of any precipitation of a Cd mineral. For Pb this is in line with the findings of Inyang *et al.* (2012) who reported that the immobilization of Pb by pyrochar resulted from the precipitation of mineral phases such as hydroxypyromorphite, cerrusite and hydrocerrusite. According to the Visual Minteq calculations, 87% of the Zn and 98% of the Pb should have been present as precipitates in our filtrates. For Zn this is very close to the colloidal proportion identified after ultra-centrifugation (81%) in our study. For Pb we measured a smaller colloidal proportion (77%) than calculated by Minteq. This may result from a stronger interference of Pb with organic matter than with Zn (Bradl, 2004).

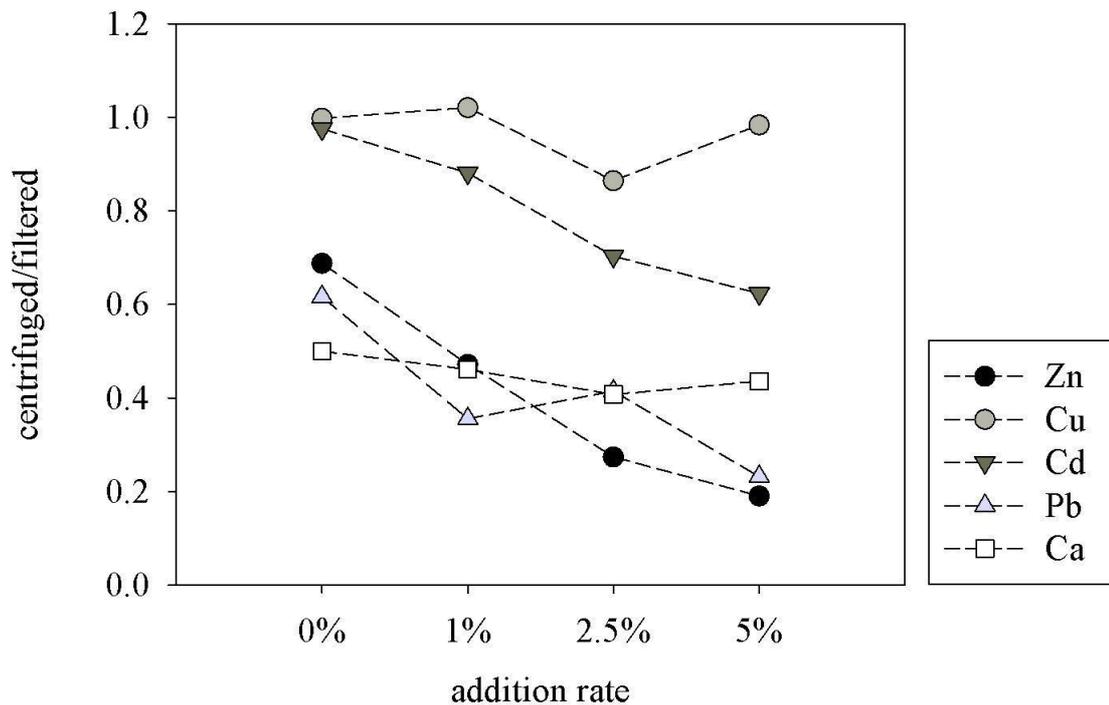


Figure 2.4 Colloidal fraction of Cu, Zn, Cd, Pb and Ca in the two-week leachate, expressed as the element concentration in ultra-centrifuged leachates divided by that in the original leachates

In the presence of DOC, the growth of minerals is impaired and the mineral colloids formed remain smaller than 450 nm (Lang & Kaupenjohann, 2003). In our study, mean concentrations of DOC increased from 65 mg l⁻¹ in the control to 207 mg l⁻¹ in the leachates with addition of 5% pyrochar. As shown for Pb by Klitzke *et al.* (2008), monovalent cations such as K⁺ enhance colloidal stability in contrast to the divalent Ca²⁺. In our study, the concentrations of K in the leachates increased with increasing amounts of pyrochar added from less than 10 mg l⁻¹ up to 174 mg l⁻¹. In summary, our results suggest that the addition of pyrochar resulted at least in the formation of small and stable Zn and Pb colloids which are mobile in the pore system of the soil but which are not plant-available.

Electron microprobe images and element mappings of the particles which we obtained by ultra-centrifugation support the hypothesis of precipitation of Zn phosphates. Element dot-maps showed aggregates of small particles with large P and Zn concentration (Figure 2.5). Drying and sample preparation may have induced the aggregation of these particles. Copper also appeared to accumulate along with P, however, much less than Zn. Lead was not detected, probably because concentrations in the soil solution were smaller than those of Cu and Zn. Moreover, the detection limit for Pb with EMPA is three times less than that for Zn.

In contrast to our results, Beesley *et al.* (2010) reported decreasing concentrations of Zn and Cd in soil pore water after the addition of a compost-biochar mixture. These authors used rhizon samplers (Eijkelkamp Agrisearch, Giesbeek, Netherlands) to collect the soil solution. These samplers have a standard pore size of 0.15 µm. Thus, the amount of colloidal Zn and Cd collected in that study was probably smaller than that collected in ours. With Cu, Beesley *et al.* (2010) found increasing concentrations as a result of biochar addition to soils and attributed this to the formation of organic Cu complexes. This is in line with our results: the Cu and the DOC concentrations in the ultra-centrifuged solutions were strongly correlated ($R^2=0.98$).

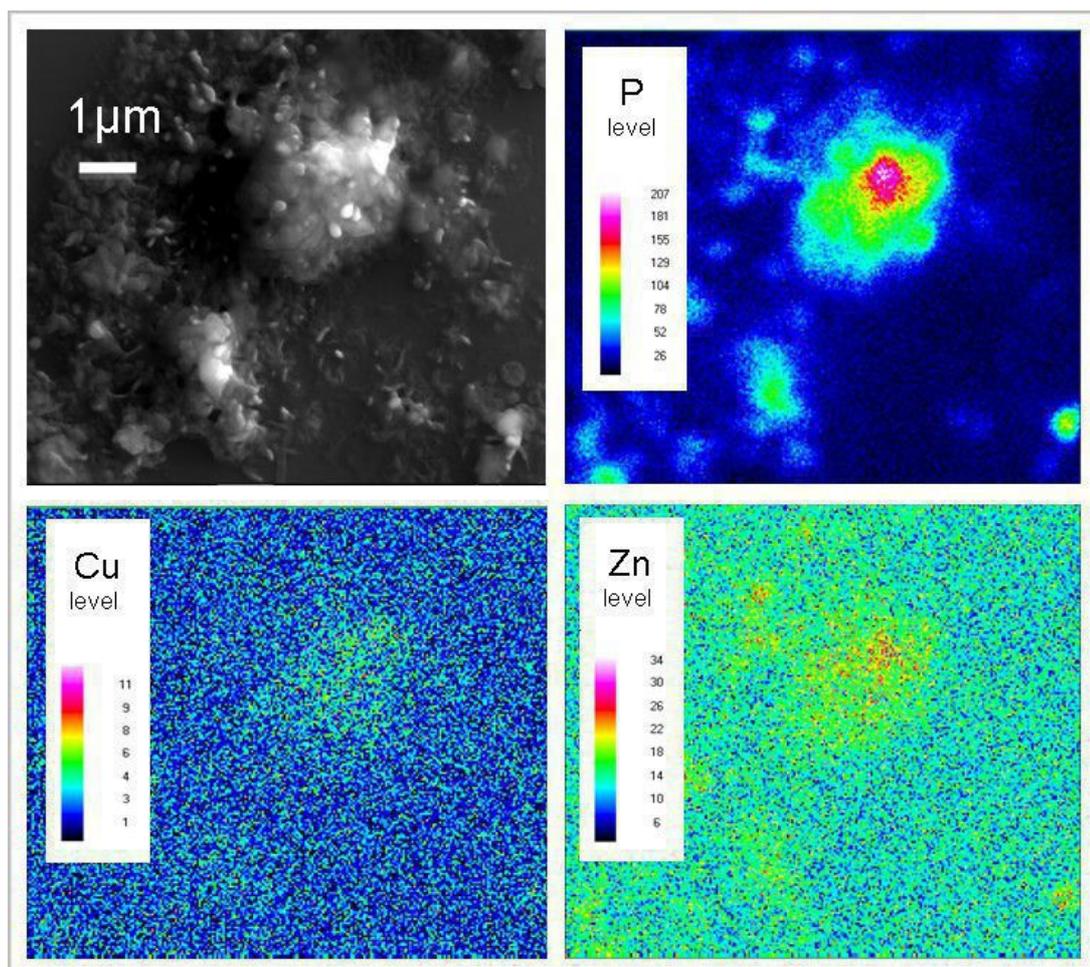


Figure 2.5 Micro-probe images and element mappings of ultra-centrifugation residues obtained at 15 kV and 20 nA; higher wavelengths (warmer colours) represent larger concentrations, the level gives X-ray quantum per pixel

2.5 Conclusions

We showed that the hydrochar used in this study does not immobilize metals in soils and is not suitable for soil remediation as long as negative effects on plant growth are not eliminated. Further investigations should concentrate on the question whether toxic effects or N immobilization is responsible for reduced plant biomass production. It cannot be ruled out that alteration of the process parameters of hydrochar production could result in hydrochars which are able to immobilize metals without exhibiting negative effects on plant growth.

In contrast, pyrochar may have positive effects on metal-contaminated sites since it reduces the plant availability of metals. However, this effect was element-specific and most pronounced for Zn. With respect to groundwater protection, the mobilization of metals

after pyrochar addition through organic complexation or formation of mobile colloids has to be considered. The conditions for the formation and the mobility of these substances should be studied in more detail and under field conditions. Our results were obtained shortly after the addition of fresh pyro- or hydrochars and long-term effects may differ widely. Thus, the field experiments should be designed as long-term studies.

2.6 Acknowledgements

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3 Biochar addition enhanced growth of *Dactylis glomerata* and immobilized Zn and Cd but mobilized Cu and Pb on a former sewage field soil²

3.1 Summary

The mobility and bioavailability of heavy metals in soils contaminated by irrigation with wastewater increases with increasing mineralization of accumulated organic substance and decreasing pH. In laboratory experiments, biochar has shown to reduce heavy metal availability to plants and enhance plant growth. However, literature from field trials is scarce. Therefore, we conducted a two-year field experiment with orchard grass (*Dactylis glomerata*) to study the effects of miscanthus-derived biochar amendment to sewage field soil on biomass production and concentrations of zinc (Zn), copper (Cu), cadmium (Cd), lead (Pb) and various nutrients in plants and in the soil solution. Biochar was mixed into the contaminated topsoil (30 cm) with addition rates of 0, 1, 2.5 and 5% based on dry weight (g 100g⁻¹). Soil solution was collected using suction plates installed at a depth of 30 cm. Addition of biochar increased biomass production, reduced Zn and Cd concentrations in the soil solution. Zn concentrations were also reduced in plants. This effect seems to be attributable to pH increase caused by biochar addition. In contrast, Pb and Cu concentrations in the soil solution generally increased and correlated with the concentrations of dissolved organic carbon (DOC). Similarly, Cu concentrations increased also in the plants, however, only at the beginning. Our data indicate that increased concentrations of DOC, Cu and Pb in the soil solution might be a transient effect. Therefore, further research is needed to determine the long-term effect of biochar amendment on element immobilization and leaching into groundwater.

² Submitted to European Journal of Soil Science (20.09.2013), Wagner, A. & Kaupenjohann, M.

3.2 Introduction

Wastewater used for irrigation purposes provides nutrients for crop production. Especially in urban and industrial areas, however, high levels of contaminants in wastewater, *e.g.* heavy metals, lead to soil pollution (Singh *et al.*, 2004). The former sewage fields south of Berlin, consisting mainly of sandy soils, received mixed wastewater from industry and private households for decades. Consequently, the soils are highly contaminated with heavy metals but also show high contents of nutrients and organic matter. After termination of wastewater irrigation, there was no further input of organic and alkaline compounds so that organic matter and soil pH have been decreasing. Organic matter is mainly responsible for the sorption capacity of sandy soils. Its further mineralization and decreasing soil pH will increase both bioavailability and leaching of heavy metals (Grunewald, 1994). At present, food and feed production is not allowed on the contaminated soils. Energy crop production might be an alternative land use thus utilizing the high nutrient contents. However, strategies are needed to reduce heavy metal leaching which might be intensified along with soil cultivation.

Clays, carbonates, phosphates and iron oxides as well as various organic materials, *i.e.* sludges, compost or paper mill waste, are effective soil amendments for the fixation of Cd, Cu, Pb and Zn (Kumpiene *et al.*, 2008) (Zhou & Haynes, 2010). Recently, also biochar known as a “key ingredient” of the very fertile Terra Preta soils in the Amazon Basin (Glaser & Birk, 2012) has been proposed as a cheap amendment for polluted soils, concurrently increasing biomass production (Beesley *et al.*, 2011). The term “biochar” is used for biomass which has been converted, mainly by a pyrolytic process, into a stable, less biodegradable C form for the purpose of soil improvement, *e. g.* by increasing its water holding capacity, nutrient retention and carbon sequestration (Jeffery *et al.*, 2011). In contrast to activated carbon, biochar has not been subject to any activation process and is therefore less expensive.

Several short-term laboratory studies and pot experiments have shown that biochar may reduce the mobility of heavy metals in soils and their uptake by plants depending on metal type and biochar properties (Beesley *et al.*, 2011). In recent pot experiments, biochar addition to sewage field soils reduced Zn, Cd and Cu concentrations in plants. In the leachates, however, concentrations of Zn remained the same whereas Cu and Cd concentrations even increased along with biochar addition (Wagner & Kaupenjohann, 2014). Comparison of ultracentrifuged and filtered samples, microprobe analysis of

centrifugation residues and Visual Minteq equilibrium calculations suggested colloidal transport of Zn precipitates and transport of Cu as dissolved organic complexes. Since short-term pot experiments do not reflect the ambient hydrologic conditions, field experiments were conducted to examine the potential of biochar to reduce the concentrations of Cu, Pb, Cd and Zn in the soil solution and the uptake of these elements by plants under field conditions. On the basis of our pot experiments (Wagner & Kaupenjohann, 2014) we hypothesized that the application of biochar to nutrient-rich former sewage field soils will lead to a decrease of Zn and Cd concentrations in soil solutions and plant tissues caused by the precipitation or sorption of these metals and in an increase of Cu and Pb concentrations due to organic complexation.

3.3 Materials and Methods

3.3.1 Field site

In April 2011, a field experiment was established on a former sewage field near Großbeeren (52°21′0.36″ N, 13°17′54.8304″ E) about 10 km south of Berlin. An area of approximately 750 ha had received about 20 million m³ wastewater per year between 1884 and the beginning of the 1980s (LUA, 1997). Precise data about spatial distribution of the wastewater on the individual fields are not available. The sewage fields show heterogeneous patterns of contamination with heavy metals. Within a single field, the contents of heavy metals and organic substance decrease from the wastewater inlet to the outlet area in a concentric form (Figure 3.1) since heavy metals co-sedimented with particulate matter (Grunewald, 1994). Mean annual temperature is 9.3° C and mean annual precipitation 570 mm a⁻¹ (climate data from the measuring station at Berlin-Schönefeld, <http://www.dwd.de>). With about 300 mm a⁻¹ of rainfall in the vegetation period between May and October the study area is situated in one of the driest regions of Germany.

3.3.2 Preparation of the field experiment

In the area of a former wastewater inlet, four plots (A, B, C, D) were prepared as shown in Figure 3.1. Separately for each plot, the sod (approximately 5 cm) was removed and the remaining soil was excavated to a depth of 30 cm with a mini-digger. The soil material was sieved through an open mesh flooring (mesh size 31x31 mm, rotec GmbH, Berlin, Germany) and deposited on sub-floor panels (OSB-oriented strand board) in the form of a cone. For further homogenization, the soil was relocated and heaped up to a cone with a

mini-digger again. For basic soil characterization, six aliquots were taken from the cone and united to a single sample. The cone was flattened and divided into four aliquots which were mixed with 0, 1, 2.5 and 5% biochar based on dry weight ($\text{g } 100\text{g}^{-1}$). The weight of the soil was calculated from the volume using a soil density of 1.2 g cm^{-3} for the first 30 cm based on measurements of the regional authority of Brandenburg for Mining, Geology and Raw Materials (LBGR) for this area. The soil-biochar mixtures were deposited onto a cone and relocated twice to obtain a homogeneous distribution of the added biochar. For determination of pH and organic carbon concentrations after biochar addition, six aliquots were taken from each biochar-soil mixture and united to a single sample. The plots were divided into four subplots by aluminium sheets. Each subplot was refilled with the soil and corresponding soil-biochar mixtures. During the refilling process, the soil material was evenly trodden down three times in each subplot in order to achieve soil compaction. The plots A, B, and C had a size of 4 m^2 with 1 m^2 subplots for each treatment. In the D plot, the 0 and the 5% treatments were doubled to a size of 2 m^2 for intensive measurements. Before refilling, eight suction plates (diameter 90 mm; bubble point 1000 hP; pore size 1-1.6 μm ; ecoTech, Bonn, Germany) were embedded at a depth of 30 cm for the collection of soil solution on both intensive-measurement subplots (Figure 3.2). In October 2011, suction plates were connected to a suction control system (SCS 8, UMS, Munich, Germany) and suction was adjusted for each treatment to a mean value from three tensiometers (T4-40, UMS, Munich, Germany) installed at the same depth as the suction plates plus an offset of 10 hPa. Soil solutions were collected in glass bottles and removed every week or every two weeks, depending on the weather conditions from October 2011 to March 2012.

In August 2011, orchard grass (*Dactylis glomerata*) seeds were sown with an amount of 20 kg ha^{-1} on the plots. During the germination period, the plots were repeatedly moisturized and evaporation was reduced by covering them with a clear-transparent foil. Herbaceous plants and quitch (*Agropyron repens*) were ripped out but left on the plots to avoid nutrient loss.

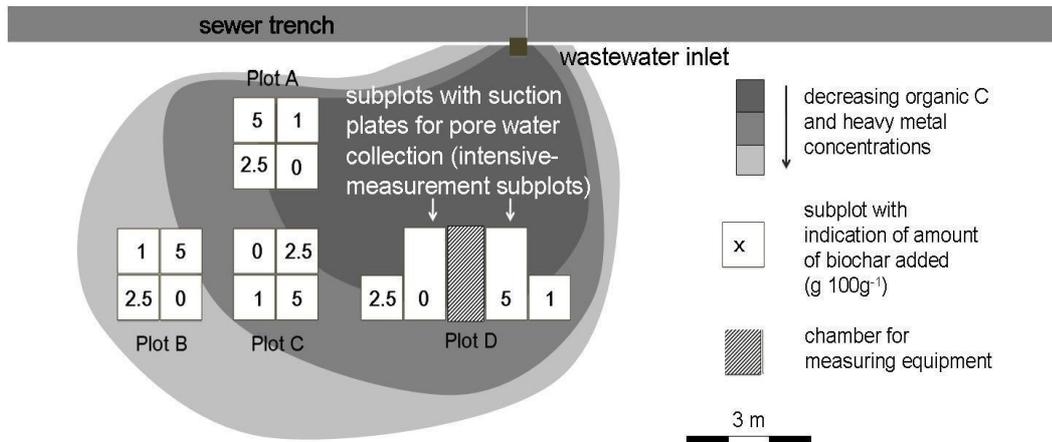


Figure 3.1 Alignment of the plots on the former sewage field

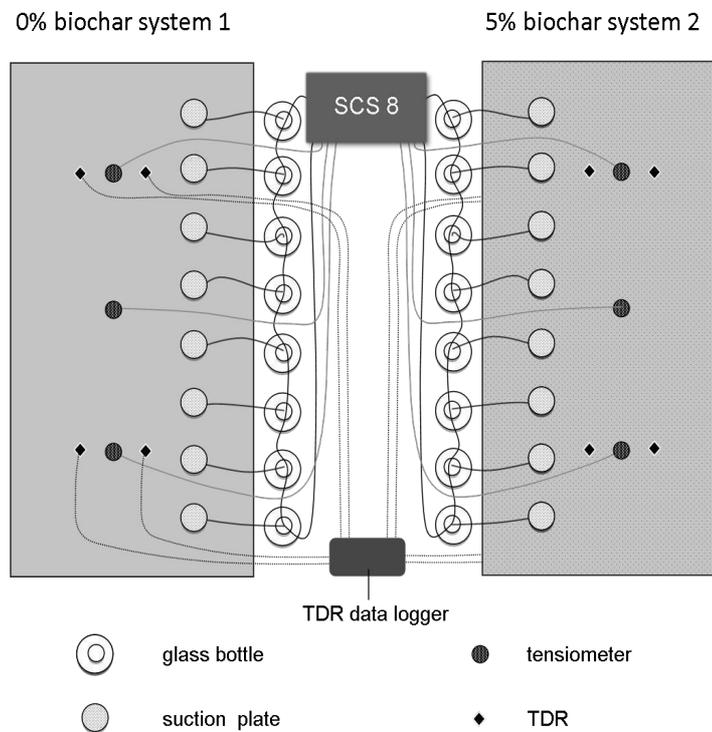


Figure 3.2 Position of suction plates, tensiometers and TDRs on intensive-measurement subplots with 0 and 5% biochar addition

3.3.3 Biochar and soil

The biochar used in this study was produced in a Pyreg reactor (Pyreg GmbH, Dörth, Germany) using *Miscanthus* as a feedstock. The mean residence time of the material in the reactor was about 30 min at a temperature of $860\pm 20^\circ\text{C}$.

For determination of the basic biochar (Table 3.1) and soil properties of each plot (Table 3.2), aliquots of the homogenized soil, biochar and biochar-soil mixtures were air-dried and sieved to 2 mm. The pH was measured in duplicate in a 0.01 M CaCl_2 suspension with a soil/solution and soil-biochar mixture/solution ratio of 1:2.5 (g ml^{-1}) and a biochar/solution ratio of 1:5 (ml ml^{-1}) (inoLab pH/Cond Level 1, SenTix 41 electrode, WTW, Weilheim, Germany). For analysis of element concentrations all samples were ground with a planetary ball mill (PM 400, Retsch, Haan, Germany) in agate vessels. Total carbon (C) and nitrogen (N) concentrations were measured using an elemental analyzer (Vario EL III, Elementar, Hanau, Germany). Carbon and N concentrations in biochar and soil were analyzed in duplicate. Carbon concentrations in biochar-soil mixtures were determined in quadruplicate so that the heterogeneity of the biochar particle distribution could be quantified. Phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb) in soils were determined after digestion with *Aqua regia* (suprapur, Roth, Karlsruhe, Germany). Biochar (50 mg) was digested with 10 ml 69% HNO_3 (suprapur, Roth, Karlsruhe, Germany) for 15 min at 180°C in a microwave pressure apparatus (Mars Xpress, CEM, Kamp-Lintfort, Germany). All samples were digested in duplicate. Concentrations of all elements in soil digests and of P, K, Ca, Mg, Fe and Mn in biochar digests were determined using inductively-coupled plasma optical emission spectrometry (iCAP 6000 ICP Spectrometer, Thermo Fisher Scientific, Dreieich, Germany). Copper, Zn, Cd and Pb in biochar digests were analyzed using graphite furnace atomic absorption spectroscopy (SpectrAA 880Z, Varian, Darmstadt, Germany).

3.3.4 Sampling of plant material and determination of yields

In October 2011 the plants were harvested for the first time. In 2012 the plants were harvested on 25 May, 23 July and 26 September. The plants of each subplot were cut about 5 cm above the soil surface with garden scissors and stored in plastic bags. For determination of the yields, the total biomass was air dried and the dry weight was determined. Despite continuous weeding, some other *poaceae*, quitch (*Agropyron repens*)

and meadow grass (*Poa pratensis*) which could not be distinguished at their early stage had grown on the plots in October 2011 and May 2012, but in July and September only few weeds were found. For determination of the yields, weeds were included. For determination of element concentrations, ten leaves of orchard grass per subplot were cut with a ceramic knife before harvesting the total biomass in May and September 2012 and stored in paper bags. Only in October 2011 when plants were still at their early stage, an aliquot of the total biomass was used for determination of element concentrations. In the laboratory, plant material was washed with deionized water and dried for 24 hours at 60° C.

3.3.5 Element concentrations of plants

For analysis of element concentrations, dried plants were ground in tungsten carbide vessels (MM200, Retsch, Haan, Germany). Total C and N were measured using an elemental analyzer (Vario EL III, Elementar, Hanau, Germany). Phosphorus, K, Ca, Mg, Cu, Zn, Cd and Pb concentrations were determined after digestion of 250 mg plant material with 10 ml 69% HNO₃ (suprapur, Roth, Karlsruhe, Germany) for 15 min at 180° C in a microwave pressure apparatus (Mars Xpress, CEM, Kamp-Lintfort, Germany). Element concentrations were determined using inductively-coupled plasma optical emission spectrometry (iCAP 6000 ICP Spectrometer, Thermo Fisher Scientific, Dreieich, Germany). All samples were analyzed in duplicate.

3.3.6 Element concentrations of the soil solution

Soil solutions were sampled regularly and the amount of solutions in each glass bottle was determined. Aliquots of each sample were stored in glass vessels for determination of pH and dissolved organic carbon (DOC) and in acid-purged polyethylene vessels for element concentrations. The pH was determined immediately after returning from the field on a pH meter with a glass electrode (inoLab pH/Cond Level 1, SenTix 41 electrode, WTW, Weilheim, Germany). Samples for the determination of DOC and element concentrations were acidified to a pH of ~3 by adding 2 M HCl, stored in a refrigerator and measured within two weeks after sampling. The concentration of DOC was measured as non-purgeable organic carbon with a TOC analyzer (TOC-5050A, Shimadzu, Duisburg, Germany). Phosphorus, K, Ca, Mg, Cu, Zn, Cd and Pb concentrations were determined as described for plants. In order to determine the colloidal fraction in the soil solutions,

aliquots of all soil solution samples collected on 4 January 2012 were ultracentrifuged (Optima L-90K, rotor 70Ti, Beckmann Coulter, Krefeld, Germany) at 160 000 *g* and all elements were again measured in the supernatant using ICP-OES.

3.3.7 Statistics

Data were not normally distributed or heteroscedastic for at least one element in each dataset of yields, element concentrations of the plants and the soil solutions considered separately for each sampling date. Therefore, we used parameter-free statistical tests which are based on ranks instead of means and do not require normal distributions. For significance testing of soil solution concentrations in the intensive-measurement subplots (0 and 5% treatment) Mann-Withey U tests were done for each date of sampling. This test is the non-parametric complement to the students *t* test. For yields and element concentrations of plants we used the parameter-free Kruskal-Wallis test after setting yields and element concentrations of the plants from each 0% subplot as 100% and relating increasing or decreasing yields and concentrations as percentage to this standard. This was necessary to overcome the great differences in the initial heavy metal and organic carbon concentrations of the soils of the plots and, consequently, in the yields and element concentrations of plants depending on the distance from the former wastewater inlet. The Kruskal-Wallis test is the non-parametric complement to an ANOVA. Mann-Whitney U and Kruskal-Wallis test were performed using Statistica 6.0. Additionally, regressions were done using all single measurements of the 0 and 5% treatments for Cu, Pb, Zn and Cd with pH or DOC in Sigmaplot 11.0. For this purpose, one DOC value was eliminated after it was identified as an outlier applying the Q-test. For each regression a pair of at least 25 measurements was available. Results are reported as significant at the 5% level of significance.

3.4 Results & Discussion

3.4.1 Effects of biochar addition on soil properties

As has been expected for biochars, pH and the total concentrations of alkali and alkaline earth metals were large while the total concentrations of heavy metals were small (Table 3.1). Total heavy metal and nutrient concentrations of the soil before biochar addition were elevated as compared to non-irrigated soils and C concentrations were larger than usual for sandy soils in this region (Table 3.2). Contamination levels and C

concentrations in the plots decreased with increasing distance from the former wastewater inlet in accordance with Grunewald (1994). Due to the high pH and C content of the biochar, its addition significantly increased pH and C concentrations (both $p=0.003$) in the biochar-soil mixtures. Mean pH (standard error in paranthesis) increased from 5.1 (0.05) to 5.3 (0.05) with 1%, 5.5 (0.03) with 2.5% and 5.9 (0.09) with 5% biochar addition. Mean C increase was 1.23 (0.137) with 1%, 2.35 (0.137) with 2.5% and 3.76 (0.222) with 5% biochar addition. Altogether this amounted to a total recovery of 133% of the added biochar C. This excessive recovery rate may be attributable to evaporation during the one-day period between determination of the water content and weighing of the biochar for the mixtures, overestimation of the actual soil density or variability of C determination. The standard error for the determination of mean C concentrations tripled in samples with biochar compared to samples without biochar (data not shown) because of the great differences in C concentrations between biochar particles and the soil.

Out of eight suction plates, seven on the 0% subplot and only four on the 5% subplot were collecting soil solution during the whole measuring period. Whether heterogeneous water flow with biochar addition or damaged suction plates are responsible for this failure could not be ascertained without destroying the experimental setup. Soil solution from the 5% subplot could be collected for the first time about 6 weeks later than from the 0% subplot. This may be attributable to increased water holding capacity with biochar addition.

Table 3.1 PH and element concentrations of the biochar

pH	C	N	P	K	Ca	Mg	Fe	Mn	Cu	Zn	Pb	Cd
	/ %		/ mg kg ⁻¹									
8.7	73	0.39	1478	12 032	4367	1636	812	142	21	52	4.1	0.182

Table 3.2 PH and total element concentrations (Aqua regia) of the soil of the plots before biochar addition

Plot	pH	C	N	P	Ca	K	Mg	Fe	Mn	Cu	Zn	Pb	Cd
		/ %		/ mg kg ⁻¹									
A	5.0	4.93	0.46	4869	5698	1599	1352	9710	118	387	780	249	9.6
B	5.2	2.58	0.24	1885	2744	1362	933	5904	171	220	368	153	6.8
C	5.1	3.46	0.33	3210	4014	1439	1138	7536	125	293	553	198	9.0
D	5.0	4.41	0.41	4154	5031	1588	1252	8458	144	357	697	220	9.9

3.4.2 Effects of biochar addition on element concentrations in the soil solution

The pH in the soil solution of the control and the 5% treatment was higher by about one pH unit than that measured in the 1:2.5 suspensions (Figure 3.3 and Table 3.2). This may be explained by the process of degassing of CO₂ from the field-collected soil solution when coming into contact with the atmosphere leading to an increased pH (Kaupenjohann & David, 1996). As in the 1:2.5 suspensions, the pH of the soil solution of the 5% treatment was about one pH unit higher than without biochar addition. This was significant ($p < 0.05$) for all sampling dates between 7 December 2011 and 11 May 2012.

Mean DOC concentrations in the controls were 70 mg l⁻¹ and remained relatively constant over the sampling period (Figure 3.3). These DOC concentrations are large compared to ranges reported by (Kindler *et al.*, 2011) for European topsoils under different landuse. This may be attributable to sewage treatment-induced large C concentrations in our soil and an increased mineralization after intensive homogenization of the soil at the beginning of the experiment. Addition of 5% biochar significantly ($p < 0.05$ for all dates) increased the DOC concentrations by up to approx. 4 times. It is likely that the additional DOC in the soil solution is biochar-borne. Laboratory experiments by Lin *et al.* (2012) and Bruun *et al.* (2012) have already shown that, depending on charring conditions, biochar can release DOC into the soil solution. In a lysimeter study under field conditions, Bell & Worrall (2011) also found increasing DOC concentrations of arable soils at biochar application rates of 62 500 kg ha⁻¹ and 87 500 kg ha⁻¹. However, a portion of the increased DOC concentrations after addition of biochar may also be soil-borne since increased pH along with biochar addition leads to deprotonated functional groups of organic matter (-COOH and -OH) and thus increased negative charge and decreased sorption of DOC to the soil matrix (Kalbitz *et al.*, 2000). Increased microbial activity in biochar-amended soil may further contribute to increased DOC concentrations since pH increase and reduced metal toxicity increases microbial activity leading to an increased turnover of soil organic matter. In a two-year field study on a Typic Haplustox, Major *et al.* (2010) have also shown that biochar addition induced leaching of non-biochar-derived DOC, however, the mean DOC concentrations of 2.76 mg l⁻¹ were much smaller than those obtained in our study. Major *et al.* (2010) related these findings to increased biomass production and microbial activity leading to an increased turnover of plant biomass and non-biochar-derived DOC leaching, rather than mineralization of soil organic matter. In our study, no increase in biomass production was observed in October 2011 and May 2012 (see *Effects of biochar addition*

on biomass production), suggesting that DOC is soil organic matter-derived rather than plant biomass-derived. However, the biochar-induced increase in DOC concentrations may be a transient effect. Jones *et al.* (2012) reported that there were no significant differences in DOC concentrations between biochar-amended plots and controls after three years of a field trial. In our study as well, DOC concentrations decreased over the period from 7 December 2011 to 11 May 2012.

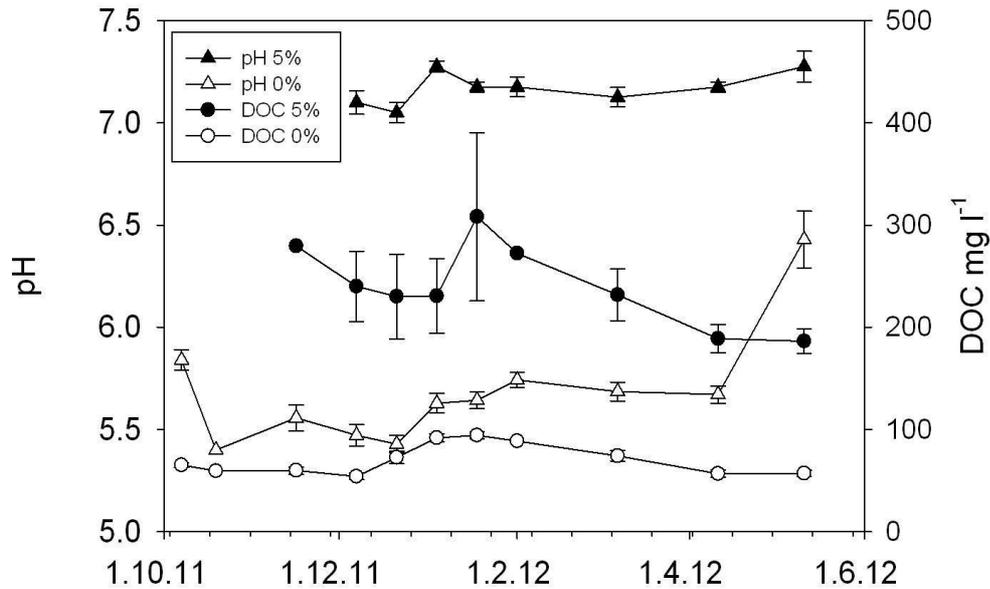


Figure 3.3 DOC concentrations and pH in the soil solutions of the intensive-measurement subplots with 0 and 5% biochar addition

Copper concentrations in the soil solutions of the control subplot were approx. 0.5 mg l⁻¹ at the beginning of the sampling period and increased in the winter months to approx. 1.2 mg l⁻¹ (Figure 3.4). With addition of biochar the concentrations increased to approx. 1.5 mg l⁻¹. This increase was significant (p < 0.05) for all sampling dates, except for the winter months where the concentrations in the controls increased. Mean Pb concentrations in the controls were below 10 µg l⁻¹ and remained relatively constant over the whole sampling period. Biochar addition increased Pb concentrations significantly at all sampling dates (p < 0.05) which amounted to 48 µg l⁻¹ at the beginning and decreased to about 20 µg l⁻¹ in May 2012.

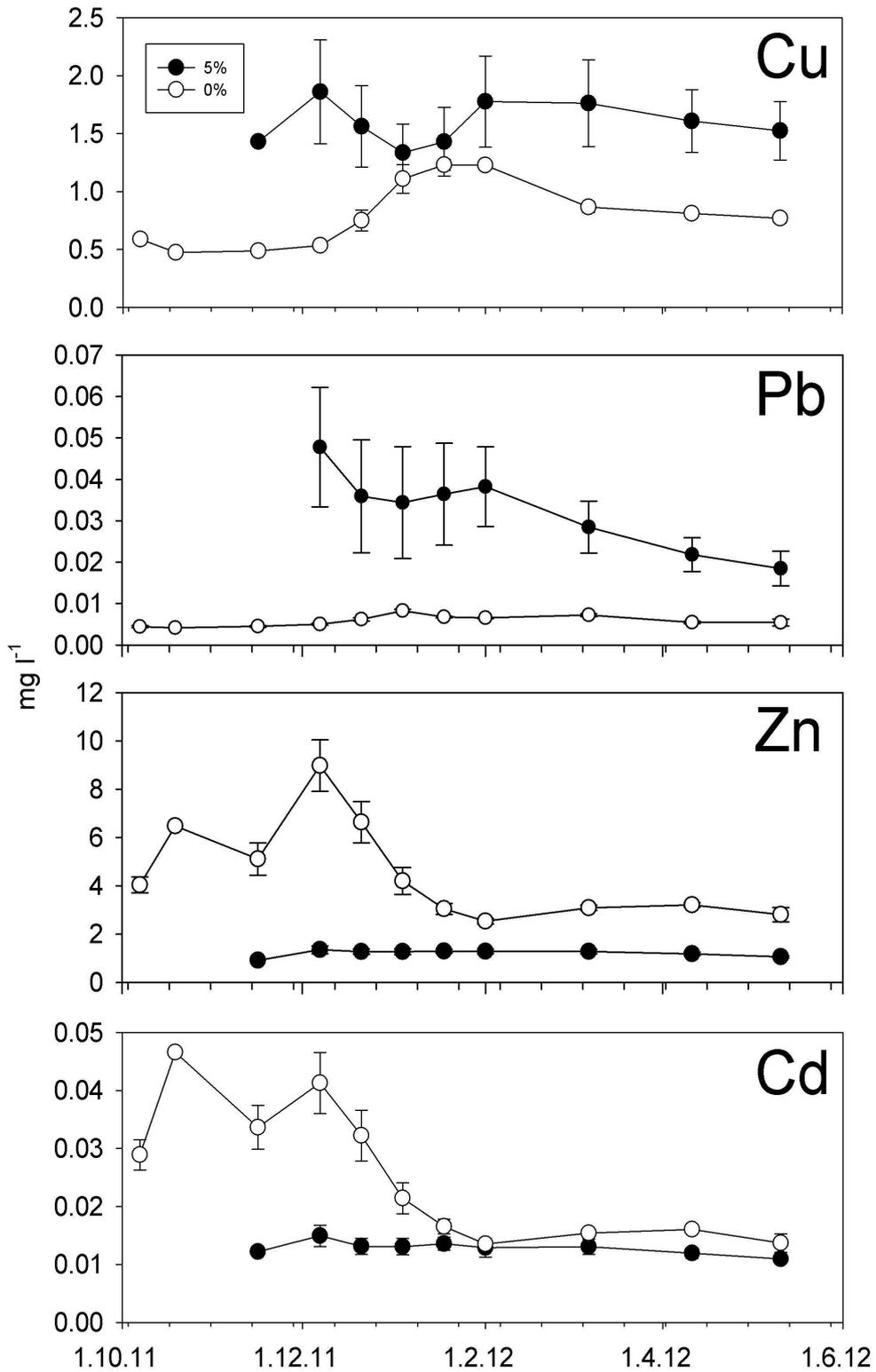


Figure 3.4 Zn, Cu, Cd and Pb concentrations of the soil solutions in the intensive-measurement subplots with 0 and 5% biochar addition

Apart from pH, heavy metal mobility is dependent on the presence of organic substance and especially Cu and Pb have a high affinity to functional groups of humic substance (Bradl, 2004). Thus, on the one hand, biochar might sorb Cu and Pb. Karami *et al.* (2011) reported decreased Cu and Pb concentrations in soil pore water after addition of biochar and Buss *et al.* (2012) reported decreased Cu concentrations in NaNO₃ extracts which are considered to represent the bioavailable fraction. However, Borchard *et al.* (2012) found a rather low Cu sorption to biochar surfaces previously washed for sorption experiments. On the other hand, Cu and Pb might be mobilized by DOC. In our study, Cu and Pb concentrations in the soil solution of the 0% and the 5% treatments were significantly correlated with DOC concentrations (Figure 3.5 A and B) but not with pH (0%: Cu $R^2=0.02$, Pb $R^2= 0.02$, both $n=60$, 5%: Cu $R^2=0.003$, Pb $R^2= 0.0003$, both $n=26$). For Cu, this correlation is in line with Beesley *et al.* (2010). Ashworth & Alloway (2004) have shown that sewage sludge-derived dissolved organic matter (SSDOM) increased Cu desorption from contaminated soil. The authors gave two possible explanations for this finding. Either, the added SSDOM acted as an extractant for Cu in the soil or, as Kaiser & Zech (1997) have shown, the added hydrophobic DOM was bound to the solid phase and hydrophilic native soil DOM was concurrently released into the soil solution. This native DOM may have already been associated with Cu. This may also be true of DOC derived from biochar applied to contaminated soil. These mechanisms may also be responsible for increased Pb concentrations in the soil solution. However, as can be seen from the slopes of the regression lines (Figure 3.5 A and B), complexation of DOC with Cu seems to be lower in the 5% treatment compared to the control but higher with Pb, indicating that the composition of DOC differed between the two plots.

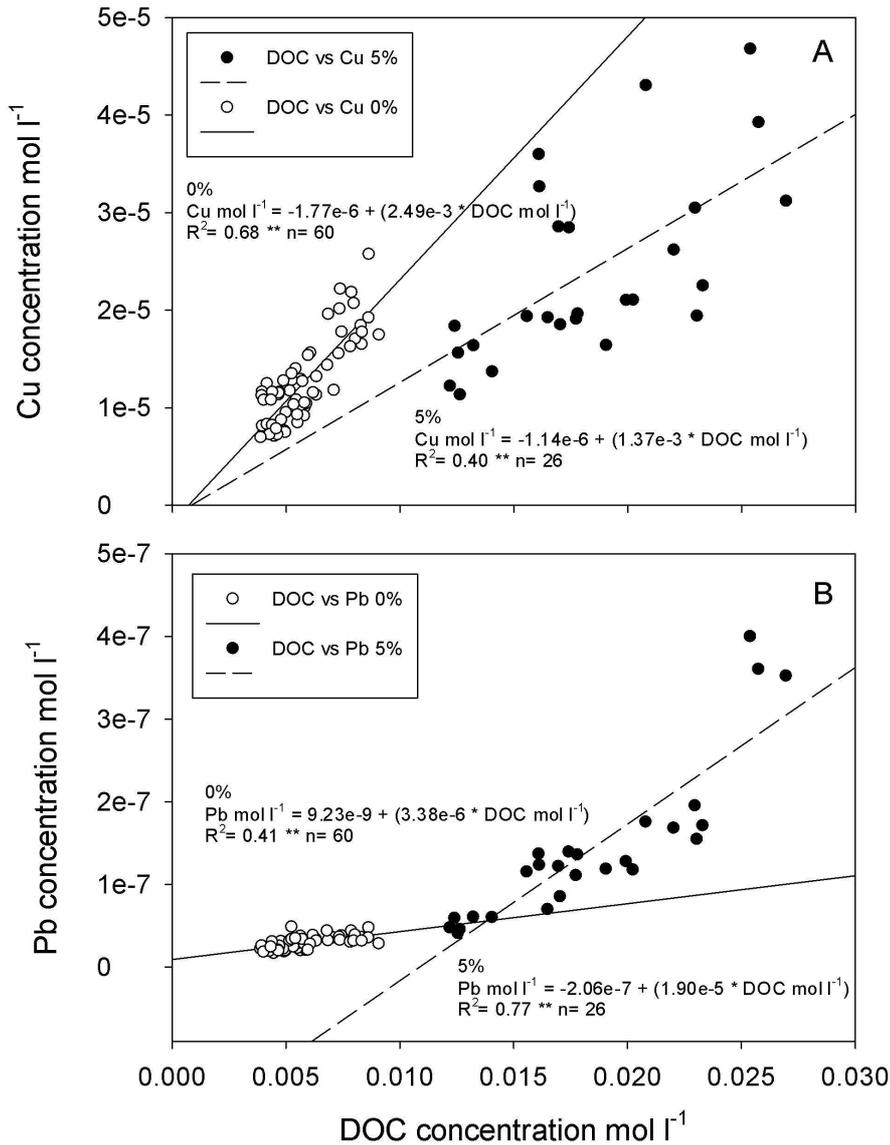


Figure 3.5 Correlations between DOC and Cu (A) and Pb (B) concentrations in the soil solutions of the intensive-measurement subplots with 0 and 5% biochar addition. The lines represent linear regressions (Sigmaplot 11.0; ** : $p < 0.001$; * : $p < 0.05$; n.s.: not significant)

Bolea *et al.* (2006) have shown that in compost leachate Pb is complexed primarily by DOC with a high molecular weight (>300-100 kDa) and Cu mainly by DOC with a molecular weight of less than 10 kDa. The fact that mobilization of Pb is more effective compared to Cu leads to the assumption that biochar-derived DOC is of high molecular weight. In our former pot experiments (Wagner & Kaupenjohann, 2014) we also found increasing Pb concentrations in the leachates with increasing addition of biochar. However, this increase was at least partly related to an increase of the colloidal fraction indicating the formation of precipitates. Inyang *et al.* (2012) also found decreased Pb concentrations due

to precipitation of mineral phases like hydroxypyromorphite, cerrusite and hydrocerrusite along with the addition of biochar in laboratory experiments. Element concentrations measured in the supernatant of an ultracentrifuged set of samples were similar to concentrations measured in the soil solution thus confirming that colloids did not significantly contribute to the element concentrations in the soil solution. In this experimental setup, suction plates were used for the sampling of soil solutions which are usually not permeable for colloids in relevant amounts (Ilg *et al.*, 2007). Therefore, we cannot exclude the concurrent occurrence of both processes, *i.e.* the formation of precipitates and the organic complexation in the bulk soil. However, oversaturation with Pb in the soil solution of the 5% treatment with respect to hydroxypyromorphite which is the most stable mineral form and determined Pb concentrations in the controls suggests that organic complexation inhibits precipitation (Figure 3.6).

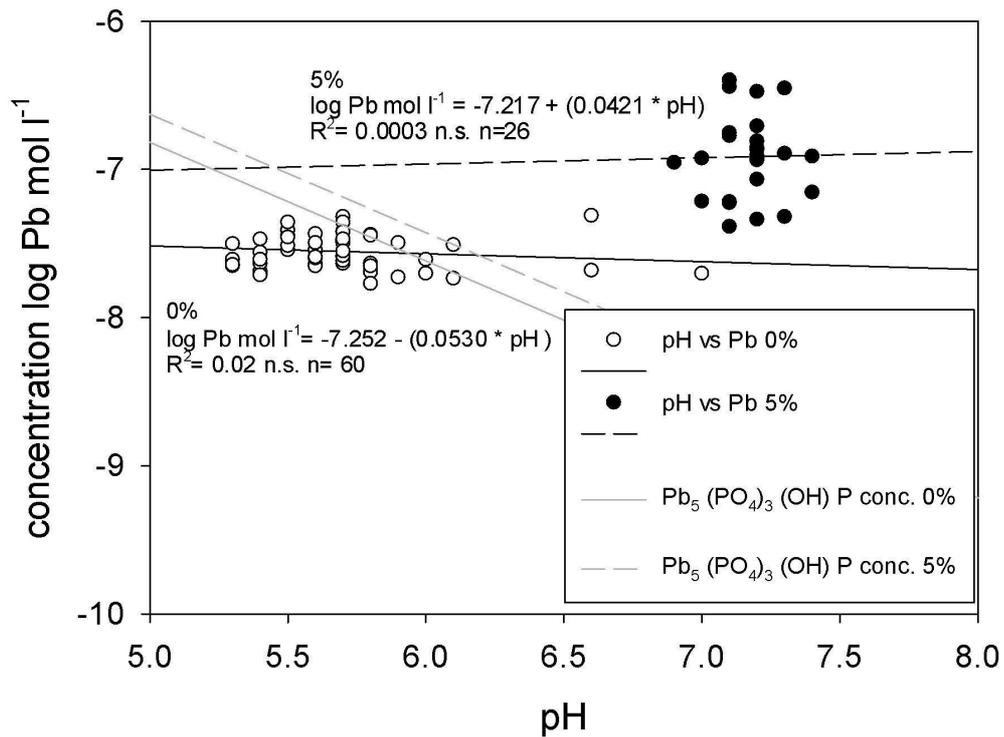


Figure 3.6 Correlation between pH and Pb concentrations in the soil solutions of the intensive-measurement subplots with 0 and 5% biochar addition. The lines represent linear regressions (Sigmaplot 11.0; ** : $p < 0.001$; * : $p < 0.05$; n.s.: not significant). Additionally the solubility lines for Pb phosphate are given at the levels of P concentrations in the 0 and 5% subplots

Zinc and Cd concentrations in the controls were up to 9 mg l⁻¹ and 45 µg l⁻¹, respectively, at the beginning and decreased to about 3 mg l⁻¹ and 15 µg l⁻¹, respectively, in the subsequent growing period (Figure 3.4). Addition of biochar significantly ($p < 0.05$) decreased Zn concentrations at all sampling dates to about 1 mg l⁻¹. Cadmium concentrations decreased to about 12 µg l⁻¹. However, this reduction was significant only for the period from 7 December 2011 to 4 January 2012 and for 11 April 2012.

Reduced Zn and Cd concentrations in the soil solution with biochar addition are in line with column experiments performed by Beesley & Marmiroli (2011). In another field study, decreasing Cd concentrations after biochar addition were also reported (Cui *et al.*, 2011). Both Zn and Cd concentrations in the controls were negatively correlated with pH (Figure 3.7 A and B).

The formation of Zn phosphates may control Zn concentrations. In our former pot experiments (Wagner & Kaupenjohann, 2014) we have shown that precipitation of Zn phosphates with the addition of maize-derived biochar is likely. Also in this study, the Zn concentrations in the control treatment are in line with the solubility limits of Zn phosphate. For Cd there was no indication of the formation of Cd minerals, neither Cd phosphates nor Cd carbonates. Thus, we assume that for Cd the reduction is caused by sorption to the soil matrix. However, in the solutions of the 5% treatment the reduction of Zn and Cd concentrations was not as pronounced as predicted on the basis of the pH-metal regressions obtained for the control treatment and no significant relation with pH was observed. Zinc and Cd are also known to form organic complexes but compared to Cu and Pb to a lesser extent (Bradl, 2004). In our study, also a minor complexation of Zn and Cd with DOC was observed for the 5% treatment, as can be taken from the significant regressions of the metals and DOC and the flat slope of the regression line (Figure 3.8 A and B). Thus, organic complexation may have reduced the efficiency of the biochar to decrease the concentrations of the metals in the soil solution.

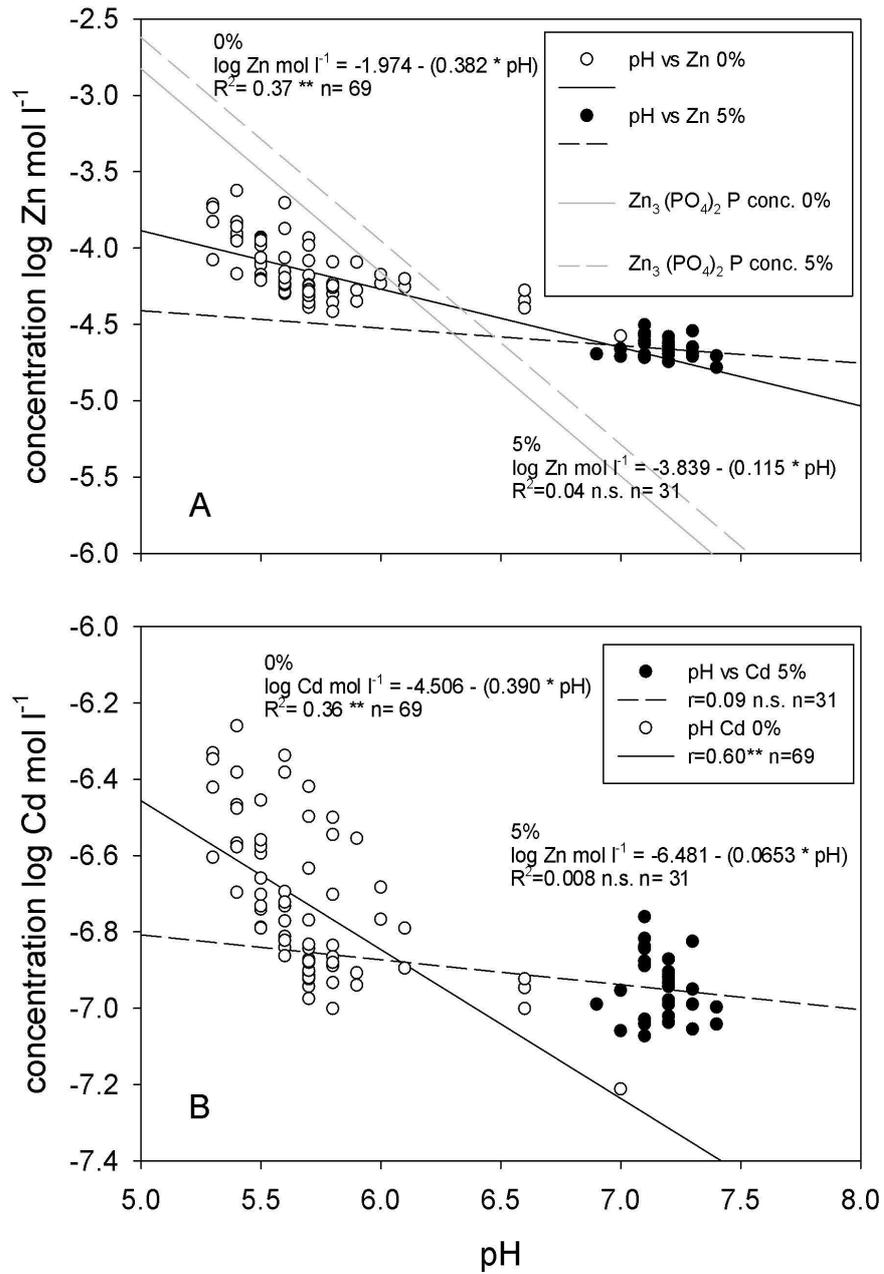


Figure 3.7 Correlation between pH and Zn (A) and Cd (B) concentrations in the soil solution of the intensive-measurement subplots with 0 and 5% biochar addition. The lines represent linear regressions (Sigmaplot 11.0; ** : p= <0.001; * : p=<0.05; n.s.: not significant). Additionally the solubility lines for Zn phosphate are given at the levels of P concentrations in the 0 and 5% subplots

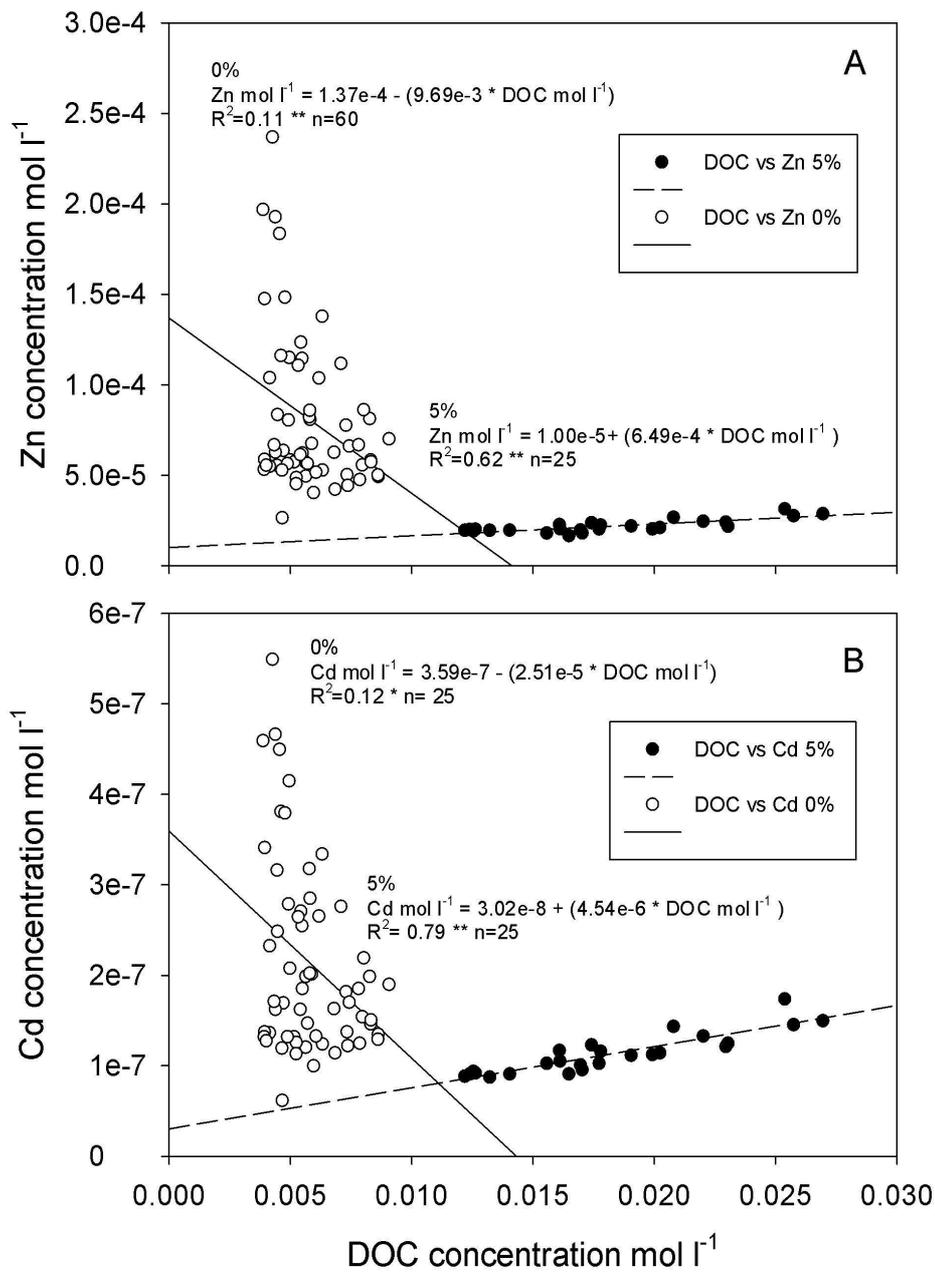


Figure 3.8 Correlations between DOC and Zn (A) and Cd (B) concentrations in the soil solutions of the intensive-measurement subplots with 0 and 5% biochar addition. The lines represent linear regressions (Sigmaplot 11.0; ** : p= <0.001; * : p=<0.05; n.s.: not significant)

Apart from trace element concentrations, the concentrations of nutrients like P, K, Ca and Mg were also altered by biochar addition (Figure 3.9). Phosphorus concentrations in the soil solution of the control subplot were between 3 and 5 mg l⁻¹ which is in the range of the concentrations found in soils receiving excessive P with manure application (Nelson *et al.*, 2005) and may be attributable to large total phosphorus concentrations in the soil after prolonged wastewater irrigation. With the addition of biochar, soil solution concentrations have significantly been decreasing at all sampling dates since 7 December, however, with about 2 mg l⁻¹ they were still very large. When reaching surface waters by interflow such concentrations in the soil solution will lead to eutrophication. Smaller P concentrations in the soil solutions of the 5% treatment than in those of the control treatment support the hypothesis of the precipitation of P-containing minerals. With increasing pH, Ca phosphates, especially hydroxyapatite (Ca₁₀(PO₄)₆OH₂) and other apatite forms substituted with various amounts of Cd, Zn and Pb or other impurities like Na or Mg found in natural apatites may form (Raicevic *et al.*, 2005).

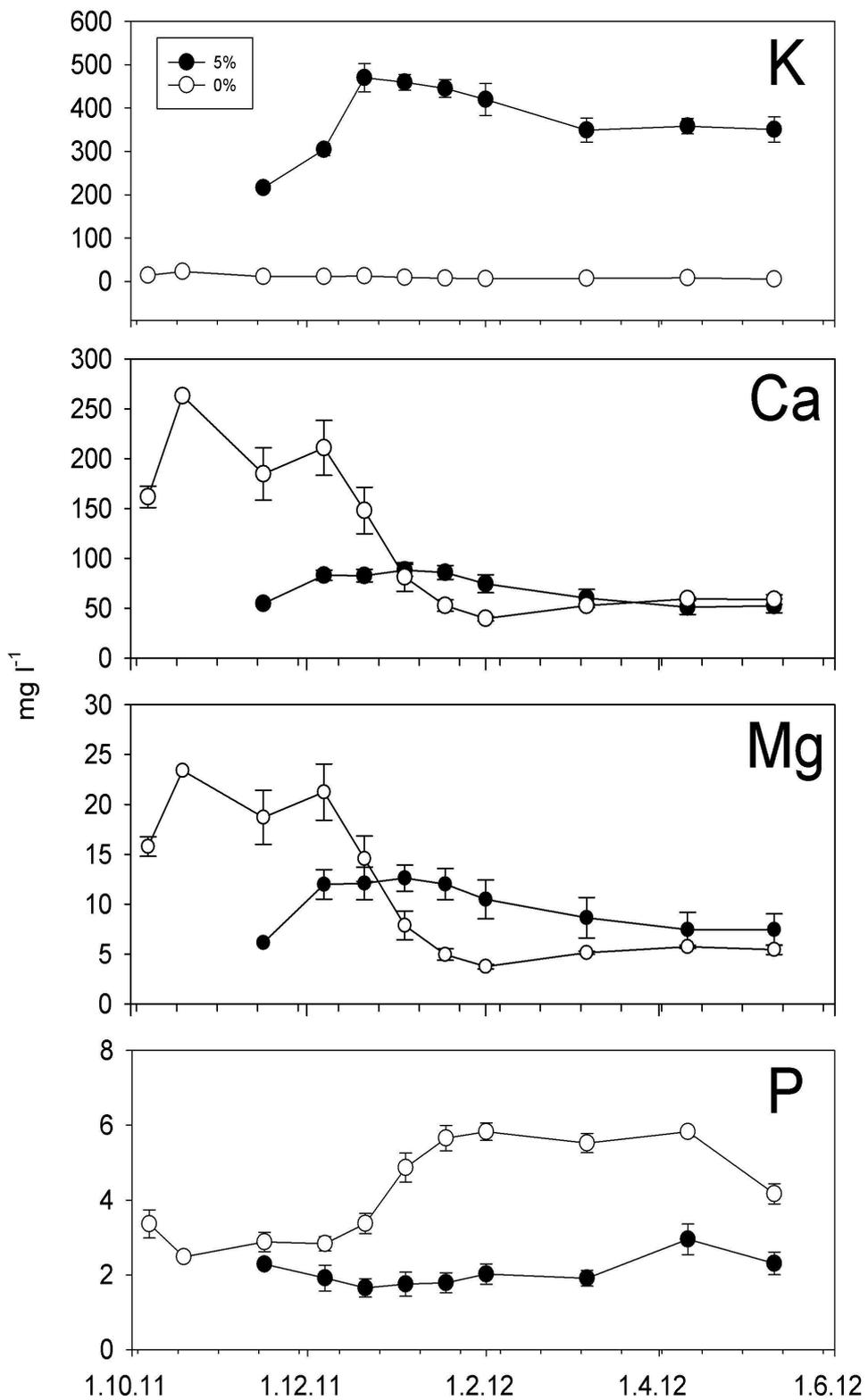


Figure 3.9 Potassium, Ca, Mg and P concentrations in the soil solutions of the intensive-measurement subplots with 0 and 5% biochar addition

Potassium concentrations in the soil solutions were 10.5 mg l^{-1} without biochar addition and significantly ($p < 0.01$) larger by approx. 35 times with biochar addition thus clearly exceeding common concentrations in arable soils. Potassium concentrations in the added biochar were about 10 times larger than in the soil so that a ready release from biochar is likely. Quilliam *et al.* (2012) also reported an increase of exchangeable K in this order of magnitude. Calcium and Mg concentrations in the soil solutions of the control and the 5% treatments were in an optimal range for plant nutrition at any sampling date. Biochar addition resulted in relatively stable Ca and Mg concentrations. Significantly smaller concentrations in the beginning and larger concentrations in the middle of the sampling period in the 5% treatment compared to the controls were attributable to changes in the concentrations of the controls, probably caused by initial mineralization. At the end of the sampling period no significant differences were observed.

3.4.3 Effects of biochar addition on element concentrations of plants

At the harvest in October 2011 the plants were still at an early stage of development and element concentrations in plant tissue were generally larger than in May or September 2012 (Table 3.3). This is due to a dilution effect which occurs with biomass production.

Plant Zn and Cu concentrations were exceeding toxic concentrations in October 2011 with up to 822 and 48 mg kg^{-1} , respectively (Fink, 2007). In May and September 2012 the plant Zn and Cu concentrations were below the toxic level. In general, the trace element concentrations in plants reflect the concentrations in the soil solution, except for Pb. Lead is usually accumulated in the roots and not transported to the shoots, especially when nutrient availability is good (Laperche *et al.*, 1997) and was detectable only in the first harvest in 2011 showing no significant effect of biochar addition ($p=0.093$). Copper concentrations in plants significantly increased in October 2011 ($p=0.022$). Since it is assumed that Cu is present in the soil solution mainly in an organically complexed form, these Cu complexes must have been plant-available. This is in line with Ashworth & Alloway (2007) who reported a similar uptake of Cu by plants from soil solution in its free ionic or organically complexed form. However, in May ($p=0.14$) and September ($p=0.21$) 2012 no significant differences between the treatments were observed. As in our pot experiments (Wagner & Kaupenjohann, 2014), Zn concentrations were reduced by 50% ($p=0.006$) at the first harvest which is below the toxic concentration given by Fink (2007). As in the case of Cu, this was a transient effect since in May ($p=0.11$) and September 2012 ($p=0.11$) no statistically significant differences were found between treatments. Cadmium

concentrations in plants were not influenced by biochar addition at any sampling date. The decreasing plant Zn and Cu concentrations suggest that the effect of biochar on element concentrations in the soil solution diminishes with time. This assumption, however, cannot be verified by soil solution data for the period between July and September 2012 since no concurrent sampling of the soil solution was possible because of low water contents in the growing period.

Nutrient concentrations in the plants of the controls were in the optimal range for plant growth at all sampling dates, except for Ca and Mg at the May harvest which were slightly below the level of deficiency (Fink, 2007). The concentrations of N and Mg were not significantly influenced by biochar addition at any sampling date and P only in May 2011 ($p=0.011$) with smallest concentrations for the 1 and 2.5% treatment. With increasing amounts of biochar, only Ca showed significantly decreasing concentrations at all sampling dates (October 2011 $p=0.004$, May 2012 $p=0.035$, September 2012 $p=0.003$). The Ca concentrations in the soil solutions of the 5% treatment were larger than or in the same range as the controls since the beginning of 2012. Therefore, significantly reduced Ca concentrations in the plants may be attributable to an antagonistic effect of K (Gunes *et al.*, 1998). Biochar is rich in K and, as shown above, K concentrations in the soil solution increased by a factor of 35 with 5% biochar addition. Potassium concentrations in the plants significantly increased in May 2012 ($p=0.008$) and September 2012 ($p=0.016$) but not in October 2011 ($p=0.21$) when the plants were harvested at an early stage.

Table 3.3 Mean element concentrations in plants grown on plots amended with biochar in concentrations of 0, 1, 2.5 and 5% (October 2011, May 2012 and September 2012)

	N	P	K	Ca	Mg	Zn	Cu	Cd	Pb
	/ %					/ mg kg ⁻¹			
2011									
Oct 0%	5.2 ±0.33	0.49 ±0.018	4.1 ±0.13	0.57 ±0.033	0.23 ±0.009	649 ±58.1	45 ±1.98	2.8 ±0.21	4.6 ±1.5
Oct 1%	5.1 ±0.33	0.53 ±0.024	4.6 ±0.29	0.51 ±0.011	0.24 ±0.012	591 ±43.1	44 ±2.56	2.5 ±0.29	2.5 ±1.23
Oct 2.5%	5.4 ±0.47	0.50 ±0.023	4.5 ±0.27	0.43 ±0.02	0.24 ±0.022	457 ±19	52 ±1.42	2.5 ±0.22	2.8 ±1.23
Oct 5%	5.5 ±0.26	0.54 ±0.013	4.9 ±0.2	0.33 ±0.018	0.23 ±0.015	338 ±44.9	55 ±2.48	2.1 ±0.45	2.9 ±1.08
2012									
May 0%	1.9 ±0.08	0.27 ±0.011	2.1 ±0.16	0.29 ±0.014	0.082 ±0.003	189 ±11.8	11.5 ±0.77	0.35 ±0.11	
May 1%	2.0 ±0.18	0.23 ±0.01	2.3 ±0.1	0.23 ±0.003	0.077 ±0.003	171 ±18.8	12.0 ±1.43	0.72 ±0.26	
May 2.5%	2.2 ±0.24	0.23 ±0.009	2.4 ±0.17	0.20 ±0.029	0.091 ±0.008	146 ±26.9	13.6 ±1.82	0.45 ±0.15	
May 5%	2.2 ±0.24	0.24 ±0.013	2.7 ±0.16	0.15 ±0.022	0.100 ±0.01	122 ±9.1	13.6 ±1.43	0.43 ±0.14	
Sept 0%	2.5 ±0.09	0.23 ±0.009	2.4 ±0.1	0.60 ±0.041	0.14 ±0.007	259 ±32.6	14.1 ±0.67	1.2 ±0.22	
Sept 1%	2.4 ±0.19	0.22 ±0.027	2.8 ±0.1	0.51 ±0.023	0.14 ±0.006	225 ±27.8	12.8 ±0.7	1.2 ±0.26	
Sept 2.5%	2.4 ±0.15	0.21 ±0.02	2.8 ±0.04	0.44 ±0.01	0.15 ±0.002	159 ±8.4	12.3 ±1.42	1.0 ±0.11	
Sept 5%	2.5 ±0.11	0.20 ±0.013	3.2 ±0.09	0.32 ±0.026	0.17 ±0.012	165 ±36.2	13.7 ±1.62	0.75 ±0.07	

3.4.4 Effects of biochar addition on biomass production

When biomass was harvested for the first time, the amount produced was negligible and not related to biochar addition ($p=0.82$) (Figure 3.10). In 2012, the mean total dry mass yields from 3 harvests from plots without biochar addition were 8.6 t ha^{-1} . This is above the regional mean yield for meadows which is about 5 t ha^{-1} (Statistical Office for Berlin-Brandenburg 2012). The high yields on our control plot may be attributable to the large organic carbon and nutrient concentrations in the former sewage field soil. With biochar addition, the mean total yields increased further with increasing addition of biochar ($p=0.021$) to 11.4 t ha^{-1} on the 5% subplots. This effect was most pronounced for the summer harvest ($p=0.008$) when the highest yields were obtained (Figure 10). Also in September, the yields had increased due to biochar addition ($p=0.015$). The first harvest in May did not show effects of biochar addition ($p=0.33$), probably because the grass culture was not yet established and frost damage had occurred during an unusually cold winter. The increased Cu and Pb concentrations in the soil solution after addition of biochar did obviously not have a negative effect on plant growth although the mean Cu concentrations in the soil solutions of the control exceeded median phytotoxic concentrations of 0.13 mg l^{-1} by a factor of 10 as reviewed by Kopittke *et al.* (2010) and further increased with biochar addition. Also the increased mean Pb concentrations in the 5% treatment were near to phytotoxic concentrations. The levels of phytotoxicity given by Kopittke *et al.* (2010) are based on the free ionic form which is assumed to be the most toxic form (Giller *et al.*, 1998). Since DOC concentrations in the soil solutions were large, organic complexation might have reduced Cu and Pb toxicity to plants. For Cu, Ashworth & Alloway (2007) reported lower toxicity of the organic-complexed Cu to plants compared to the free Cu ion. Also, antagonistic effects of K and Ca did not affect plant growth on the former sewage field soils which are still rich in nutrients. Increasing yields with addition of biochar are in line with the results from the pot experiments (Wagner & Kaupenjohann, 2014). Soil solution concentrations of Zn with up to 10 mg l^{-1} in the controls were clearly exceeding phytotoxic concentrations of 1.3 mg l^{-1} as reported by Kopittke *et al.* (2010) for the free ionic form and were reduced below the toxic level in the soil solution of the 5% treatment. Zinc concentrations in the controls were not correlated with DOC concentrations, indicating that a smaller portion was present in the organically complexed form. Therefore, the reduced Zn availability may have contributed to increased yields. Various beneficial effects of biochar addition on soil properties which are not the subject of

this paper may also have contributed to increased yields. Other authors conducting field studies on soils not contaminated with heavy metals also reported on increased yields after biochar application (Jeffery *et al.*, 2011).

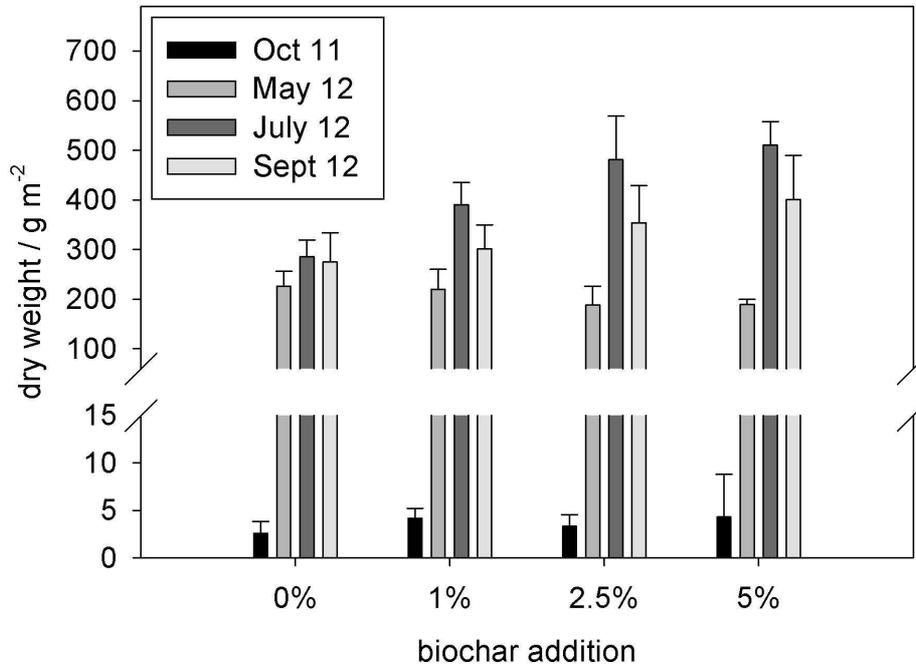


Figure 3.10 Mean biomass production on plots amended with biochar in concentrations of 0, 1, 2.5 and 5% (October 2011-September 2012)

3.5 Conclusions

This study confirms the results of our previous pot experiments and shows that, also under field conditions, the application of biochar reduces the plant availability and concentrations of Zn and, to a minor degree, also Cd and increases the concentrations of Cu and Pb in the soil solution. Knowledge of the properties of biochar responsible for the release of DOC seems to be important for the assessment of the suitability of biochars for the remediation of sites contaminated with Cu and Pb. However, due to organic complexation of Cu and Pb, their toxicity is reduced and does not affect plant growth. These results were obtained in the first year after the addition of fresh biochar. The release of DOC and the concurrent increase of Cu and Pb concentrations might have been transient effects. Therefore, long-term studies are needed to determine the risk of Cu and Pb leaching into the groundwater considering the possibly increased water-holding capacity of the biochar mixtures. Also, colloidal transport of metal precipitates should be studied with respect to

groundwater protection. With respect to plant nutrition, application of biochar might cause imbalances in element concentrations and therefore lead to growth depression in soils poor in nutrients.

3.6 Acknowledgement

This work has been financed by Berliner Stadtgüter GmbH. We wish to thank Carolin Schweiker for her valuable help with the field experiments, Sabine Dumke and Iris Pieper for excellent technical assistance in the laboratory and Elke Bauer for linguistic assistance.

4 Biochar reduces zinc and cadmium but not copper and lead leaching on a former sewage field³

4.1 Abstract

The leaching of heavy metals from anthropogenically contaminated sites such as sewage fields poses the risk of groundwater pollution. Biochar has recently been proposed as a soil additive to reduce heavy metal concentrations in the soil solution and increase water retention thus reducing drainage. However, effects of biochar addition on heavy metal leaching have not been studied so far. Therefore, we added 0, 1, 2.5 and 5 g 100 g⁻¹ of miscanthus-derived biochar to sewage field soil and examined water retention and cumulative leaching of Zn, Cd, Cu, and Pb in a two-year field study. Cumulative heavy metal leaching was determined by self-integrating accumulators (SIAs) based on ion exchange resins and compared with data calculated from mean concentrations in the soil solution collected with tension lysimeter plates and groundwater recharge rate. The highest rate of biochar addition increased water retention and thus reduced the amount of drainage water. Mean cumulative Zn and Cd fluxes decreased due to both reduced concentrations in the soil solution and reduced drainage. Although Cu and Pb concentrations in the soil solution increased with biochar addition, the reduced drainage resulted in similar fluxes in the biochar and the control treatment. The cumulative Zn, Cd, and Cu fluxes determined with SIAs were in the same range as the calculated values, while SIA-based Pb fluxes were much higher than those calculated. Since the suction plates excluded colloids, the high SIA-based Pb fluxes indicate colloidal transport and reveal the importance to elucidate the colloidal pathway for risk assessment.

³ Submitted to Journal of Environmental Quality (24.02.2014), Schweiker, C., Wagner, A., Peters, A., Bischoff, W.-A. & Kaupenjohann, M.

4.2 Introduction

Irrigation of arable land with wastewater provides nutrients for crop production thus reducing the use of fertilizers. While the establishment of wastewater treatment plants has substituted this practice in industrial countries, it is still common practice in developing countries. In urban and industrial areas, heavy metals contained in wastewater accumulate in the soils (Singh et al., 2004; Mapanda et al., 2005). This contamination poses a risk for food production and, even after the termination of wastewater irrigation, for leaching of heavy metals into groundwater.

Starting at the end of the 19th century until the 1990s, sewage fields located in surrounding areas of Berlin were used to purify untreated wastewater from private households and industry containing nutrients and organic matter as well as heavy metals, mainly Cu, Zn, Cd and Pb in high and other contaminants in minor concentrations which accumulated in the soils (Ritschel and Kratz, 2000). The soils irrigated with wastewater are mainly sandy soils poor in nutrients with a high infiltration but a low water retention capacity. The input of organic matter and alkaline elements into these sandy soils increased their sorption capacity for nutrients and heavy metals as well as their pH level and also their water retention capacity.

With the cessation of wastewater irrigation, the pH of the soils decreased and the accumulated organic matter partly underwent mineralization leading to a re-mobilization of heavy metals (Grunewald, 1994). Despite mineralization, the organic matter content of these soils is still unusually high. Water repellent properties of the organic matter as well as drying and wetting cycles (Täumer et al., 2005; Täumer et al., 2006) lead to a very high spatial variability of the water contents and cause preferential flow. Increasing heavy metal concentrations in the soil solution and preferential flow increase the risk of groundwater contamination. Therefore, measures to reduce leaching of heavy metals should be taken.

One method to reduce the mobility and thus leaching of heavy metals is the incorporation of immobilizing additives into the soil. Recently, biochar has been suggested for in-situ stabilization of heavy metals on contaminated sites (Uchimiya et al., 2010; Beesley et al., 2011). In this context, the term biochar refers to charred organic material obtained by pyrolysis which is produced with the purpose of soil improvement and/or carbon sequestration (Lehmann et al., 2006).

Biochar may contribute to a reduction of heavy metal leaching by (i) reducing heavy metal concentrations in the soil solution and/or by (ii) reducing percolated water masses. The former is achieved either by precipitation of mineral phases or by sorption of heavy metals as has been shown in several short-term laboratory studies and pot experiments (Beesley and Marmiroli, 2011; Karami et al., 2011; Cao et al., 2009). In line with these findings, a recent field study (Wagner and Kaupenjohann, 2014a) has shown that addition of biochar reduced Zn and Cd concentrations in the soil solution. However, Cu and Pb concentrations in the soil solution increased after biochar addition. Reduced Zn and Cd concentrations were explained by increased sorption after biochar addition and for Zn also by precipitation of Zn phosphate. Increased Cu and Pb concentrations correlated with increased concentrations of dissolved organic carbon (DOC).

Decreasing percolating water fluxes can be achieved by increasing water retention capacity of the soil. Several laboratory studies have shown a significantly increased water retention due to addition of biochar or biochar-compost-mixtures to loamy and sandy soils (Laird et al., 2010; Kinney et al., 2012; Briggs et al., 2012; Abel et al., 2013; Liu et al., 2012). For former sewage field soil, Abel et al. (2013) reported that there was no significant modification of the plant-available water content (AWC) with biochar addition but a change in the pore size distribution from large to more fine and medium-size pores which led to a higher water-holding capacity. However, literature about effects of biochar on water retention at a field scale is still scarce.

Based on the physical effect of biochar addition and findings of Wagner and Kaupenjohann (2014a), we hypothesized that addition of biochar (i) increases the soil water retention capacity on the field scale; (ii) reduces Zn and Cd leaching fluxes since both their concentrations in the soil solution and the amount of drainage water are reduced and (iii) has no distinct effect on Cu and Pb leaching fluxes since their concentrations in the soil solution are increased but the higher water retention capacity may compensate the increased concentrations.

4.3 Materials and Methods

4.3.1 Field site and preparation of the field experiments

The field site and the preparation of the field experiments are described in detail in Wagner and Kaupenjohann (2014a). In brief: In April 2011, the field study was established in the area of the wastewater inlet of a former sewage field near Großbeeren (52°21′0.36″ N,

13°17'54.8304'' E). An alkaline biochar made from *Miscanthus* was added in amounts of 0, 1, 2.5, and 5 g 100g⁻¹ (dry weight) to four plots (A, B, C, D, see Fig. 4.1) referred to as 0, 1, 2.5 and 5% in the following text.

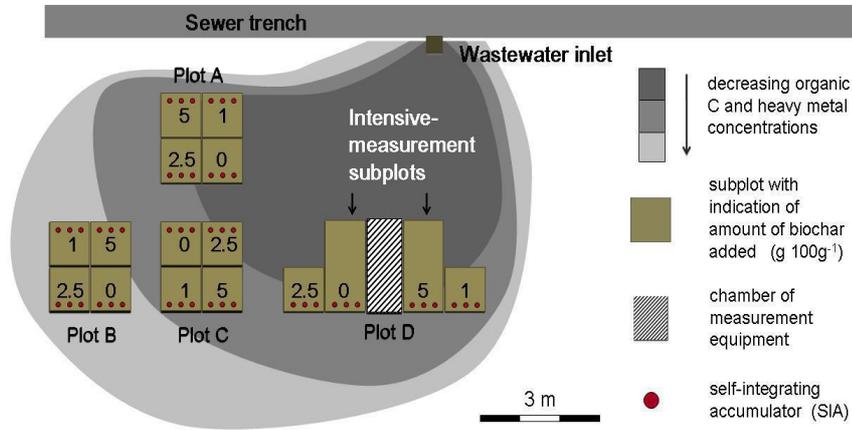


Figure 4.1 Alignment of the plots on the former sewage field (Wagner and Kaupenjohann 2014a, modified)

The contents of heavy metals and organic substance of the topsoil decrease with the distance from the wastewater inlet since heavy metals co-sedimented with particulate matter (Grunewald, 1994). In order to avoid a bias caused by differences of initial carbon and heavy metal contents within the subplots of each plot, the soil of each plot was homogenized before biochar addition. Therefore, the soil of each plot was excavated to a depth of 30 cm, passed through a 31 mm-meshed sieve and homogenized properly. The soil was then divided into four portions which were mixed with the corresponding amounts of biochar. Soil and soil-biochar mixtures were refilled and compacted. The plots showed different organic carbon and heavy metal concentrations depending on the distance from the former wastewater inlet (Wagner and Kaupenjohann, 2014a). Due to the low density of the added biochar compared to the soil, the surface level was approx. 5 cm higher with 5% biochar addition than that of the control. In August 2011, the soil was sown with orchard grass (*Dactylis glomerata*) to obtain a coherent vegetation cover. The plots were periodically harvested during the growth period. The size of the plots A, B and C was 4 m² with a size of 1 m² for each subplot. On plot D, the subplots with 0% and 5% biochar addition were 2 m² in order to install instruments for soil solution collection as well as for

measuring suctions and volumetric water contents (intensive-measurement subplots). Additionally, each subplot was equipped with SIAs in order to determine cumulative heavy metal fluxes for all treatments.

4.3.2 Determination of water retention characteristic and calculation of cumulative heavy metal fluxes

For collection of soil solution, the intensive-measurement subplots (plot D) were equipped with eight suction plates (SPs) at a depth of 30 cm (diameter 90 mm; bubble point 1000 hPa; pore size 1-1.6 μm ; ecoTech, Bonn, Germany) which were connected to a suction control system (SCS 8; UMS, Munich, Germany) (Fig. 4.2). For suction control, three tensiometers (T4-40; UMS, Munich, Germany) were installed on each subplot at a depth of 30 cm and the suction applied to the plates was set as the mean of three measured suctions with an additional offset of -10 hPa introduced to overcome the porous plate resistance (Morari, 2006). The soil solutions were collected in glass bottles. Depending on the weather conditions, the soil solutions were removed each week or each second week. During the investigation period, the number of SPs which collected soil solution varied depending on the precipitation. For each sampling date, the amount of leachate per SP was recorded and analysis of element concentrations in the soil solution was performed as described in detail in Wagner and Kaupenjohann (2014a).

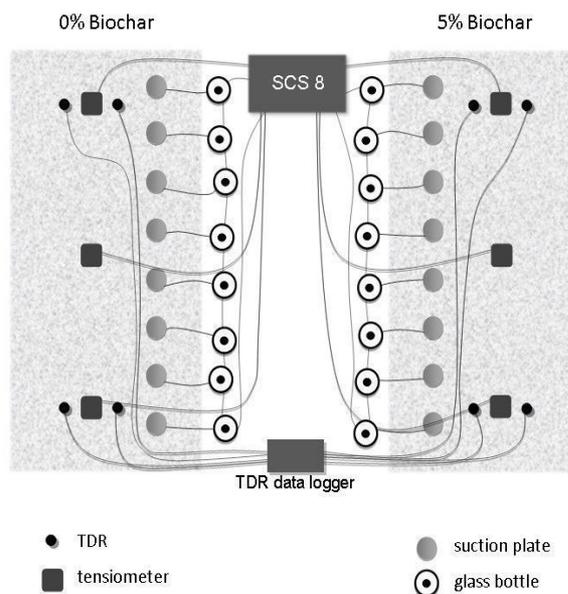


Figure 4.2 Position of suction plates, tensiometers and TDRs on intensive measurement subplots with 0 and 5% biochar addition (Wagner and Kaupenjohann 2014a, modified)

In order to detect the volumetric water contents between May 2012 and May 2013, we used four time domain reflectometry probes (TDR) (FP/mts; easytest, Lublin, Poland), installed at the same depth as the tensiometers. Together with the suctions recorded by the three tensiometers, water retention curves were determined in the investigation period of May 2012. This relatively short time period was used since reliable tensiometer readings were available for this period only. Thus it is to be noted that the water retention data were available only in a very limited suction range (Fig. 4.4). In order to determine the field capacity the van Genuchten water retention curve (van Genuchten, 1980) was fitted to the measured field data. The van Genuchten function is given by:

$$\Theta(h) = (\Theta_s - \Theta_r) [1 + (\alpha h)^n]^{1/n-1} + \Theta_r \quad \text{Eq. [1]}$$

where θ [-] is the volumetric water content, h [hPa] is the suction, α [hPa⁻¹] and n [-] are curve shape parameters and θ_s [-] and θ_r [-] are the saturated and residual water contents. Since addition of biochar should not reduce the fraction of fine and medium-size pores, the residual water content (θ_r) for the 5% subplot was chosen in a way to prevent intersection of the curves for the intensive-measurement subplots. This resulted in a value of approximately 0.08 for θ_r for the 5% subplot. AWC is given by the difference of volumetric water content at field capacity (63 hPa) and the water content at the permanent wilting point (10^{4.2} hPa).

To obtain an estimate of the cumulative heavy metal leaching fluxes for each element F_c^E [mg m⁻²] where the superscript E indicates the element), the weighted mean of concentrations C_{mean} [mg m⁻³] in the sampled soil solutions of the intensive-measurement subplots were multiplied with the groundwater recharge for one year, q_c (m). The groundwater recharge rate was calculated according to the hydro-pedotransfer function (HPTF) for grassland (Wessolek et al., 2008), whereas the C_{mean} is given by:

$$C_{\text{mean}} = \frac{\sum_{i=1}^o \sum_{j=1}^p C_{i,j} V_{i,j}}{\sum_{i=1}^o \sum_{j=1}^p V_{i,j}} \quad \text{Eq. [2]}$$

where o is the number of suction plates installed, p is the number of sampling dates and $C_{i,j}$ [mg m⁻³] is the measured element concentration in the soil solution collected with the i -th suction plate at the j -th sampling date and $V_{i,j}$ [m³] is the corresponding collected water volume. Thus C_{mean} is the total collected element mass divided by the total collected water volume. F_c^E is then given by:

$$F_c^E = C_{mean} \cdot q_c \quad \text{Eq. [3]}$$

The results were converted into kg ha^{-1} for comparison with fluxes determined with SIAs (see following section).

Data necessary for determination of the groundwater recharge rate with the HPTF according to Wessolek et al. (2008) are annual precipitation (597 mm), precipitation in summer (346 mm), annual potential evapotranspiration (ET_0) (754 mm) and plant-available water capacity in the effective root zone (AWCL). AWCL is given by AWC multiplied by the effective rooting depth (L [cm]). L was set to 30 cm, according to the installation depth of the measurement equipment. ET_0 was calculated with the Penman-Monteith equation (Monteith, 1965). The meteorological information for the calculation of ET_0 was provided by Leibniz-Institute of Vegetable and Ornamental Crops (IGZ), Großbeeren, Germany which is at about 700 m distance from our field site. Only the values of the barometric pressure were taken from the closest measuring station of the Deutscher Wetterdienst at Potsdam, Germany ($52^\circ 23' \text{ N}$, $13^\circ 03' \text{ E}$; <http://www.dwd.de/webwerdis>).

4.3.3 Determination of cumulative heavy metal leaching fluxes with self-integrating accumulators

For comparison we used a second method to quantify the cumulative heavy metal leaching fluxes. We installed PVC cartridges filled with a mixture of ion exchange resins (Table 4.1) and quartz in a sandy-silty-size fraction following the description of Predotova et al. (2011) and Lang and Kaupenjohann (2004). These cartridges function as self-integrating accumulators (SIAs; TerrAquat, Nürtingen, Germany) according to the infinite-sink-principle (Binkley, 1983) by sorption of heavy metals passing through the cartridges with soil water fluxes. The resin can be extracted after removal of the cartridges from the soil and give the cumulative leaching fluxes for the respective time period. On each subplot, three SIAs were installed at a depth of 30 cm and at a distance of 25 cm from the edge each. The SIAs were embedded vertically before refilling the soil and soil-biochar mixtures into the subplots and exchanged laterally from a trench dug to avoid disturbance of the mixtures above. With the biochar added and resulting elevation of the surface level a longer flow distance (from 30 to 35 cm) was achieved. This did not affect the calculation of the groundwater recharge rate determined with the HPTF since L was assumed to be

30 cm and TDRs and tensiometers were installed at a depth of approximately 30 cm from the surface for both the control and the 5% treatments. However, a minor effect on cumulative leaching fluxes determined with SIAs cannot be excluded.

Table 4.1 Chemical properties of the ion exchange resin used in the SIAs

	Mixed bed exchange resin	Heavy metal exchange resin
Product information	Purolite MB 400, volumetric ratio of cation and anion exchange resin 40/60	Amberlite IRC 748
Matrix	Gel polystyrene crosslinked with divinylbenzene	Macroporous styrene divinylbenzene
Exchange-ion form	H ⁺ / OH ⁻	Na ⁺
Total exchange capacity	0.55 eq/L	≥1.25 eq/L
Proportion of exchange resin	90%	10%

The SIAs were exchanged in Sept. 2011 and Sept. 2012 representing two different time spans, with 178 days for the first period from Apr. 2011 to Sept. 2011, referred to as investigation period 2011 and 358 days for the second period from Oct. 2011 to Sept. 2012, referred to as investigation period 2012. The precipitation in the study area for the investigation period 2011 was 436 mm with unusually heavy rainfall of 196 mm in July 2011 (data from IGZ). For the investigation period 2012 precipitation was 517 mm. The investigation periods were chosen due to similar precipitation amounts.

After removing the SIAs, the cumulative heavy metal fluxes were determined according to the instructions of TerraQuat Consultancy (Nürtingen, Germany). The resin-sand mixture of the SIAs was split into three layers (from top: A, B and C) and extracted separately. The A layer was used for determination of the cumulative heavy metal fluxes. The B layer in the middle was used as a blank and values determined were subtracted from those of the A layer. The C layer was necessary only for the prevention of metal diffusion into the B layer and was not analyzed. For extraction of the ion exchange resin, aliquots of the homogenized samples (15 g) were mixed with 50 ml 0.5 M H₂SO₄ (rotipuran; Roth, Karlsruhe, Germany) and shaken end-over-end for 30 minutes. The supernatant was decanted through a folded filter (no. 131; Munktell & Filtrak, Bärenstein, Germany). This

process was repeated with another 50 ml 0.5 M H₂SO₄. The heavy metal concentrations in the extracts were determined using inductively-coupled plasma optical emission spectrometry (iCAP 6000 ICP Spectrometer; Thermo Fisher Scientific, Dreieich, Germany). Each layer was analyzed in duplicate. The difference from the mean value of the two extractions was generally below 10% and reached 15% only in a few cases. Cumulative heavy metal leaching fluxes were calculated on the basis of the heavy metal concentration in the extract and the surface of the SIA box (81.67 cm²) and converted into kg ha⁻¹.

4.3.4 Statistics

To test whether biochar addition had a significant effect on heavy metal leaching fluxes determined with the SIAs, we performed linear regressions using Statistica 6.0 where the effectively added amount of C for each subplot (given in Wagner and Kaupenjohann, 2014a) was an independent and the cumulative flux of each element was a dependent variable. Data of the heavy metal fluxes from both investigation periods (2011 and 2012) were taken to increase the sample size to n=96. All data were log transformed and normalized to achieve a normal distribution of the residues. To the amount of C a surplus of 10 was added. The normalization of the values for each heavy metal (n_{HM}) was performed subtracting the respective average value (AV) divided by the standard deviation (SD) from each investigation period from the log transformed concentrations (\log_{HM}) of each heavy metal:

$$n_{HM} = \log_{HM} - \frac{AV_{HM}}{SD_{HM}} \quad \text{Eq. [4].}$$

4.4 Results and Discussion

4.4.1 Water budget and calculated cumulative heavy metal leaching fluxes

The water content in the control treatment varied between 5.3 and 36.5%, and in the 5% biochar treatment between 11.9 and 44.5% during the whole measuring period from May 2012 to May 2013 (Fig. 4.3). The differences in water contents were particularly pronounced in the first months (May to June 2012), where the water contents in the subplot with 5% biochar addition were higher by approximately 10-15% compared to the control subplot; from Sept. 2012 to Oct. 2012, they were higher by approximately 5-10%. In the summer of 2012, the water contents of both treatments were similar. After Oct. 2012, the

variability of water contents within the treatments increased and no distinct differences in water contents could be observed. However, the water contents in the 5% treatments tended to be higher from Feb. 2013 again.

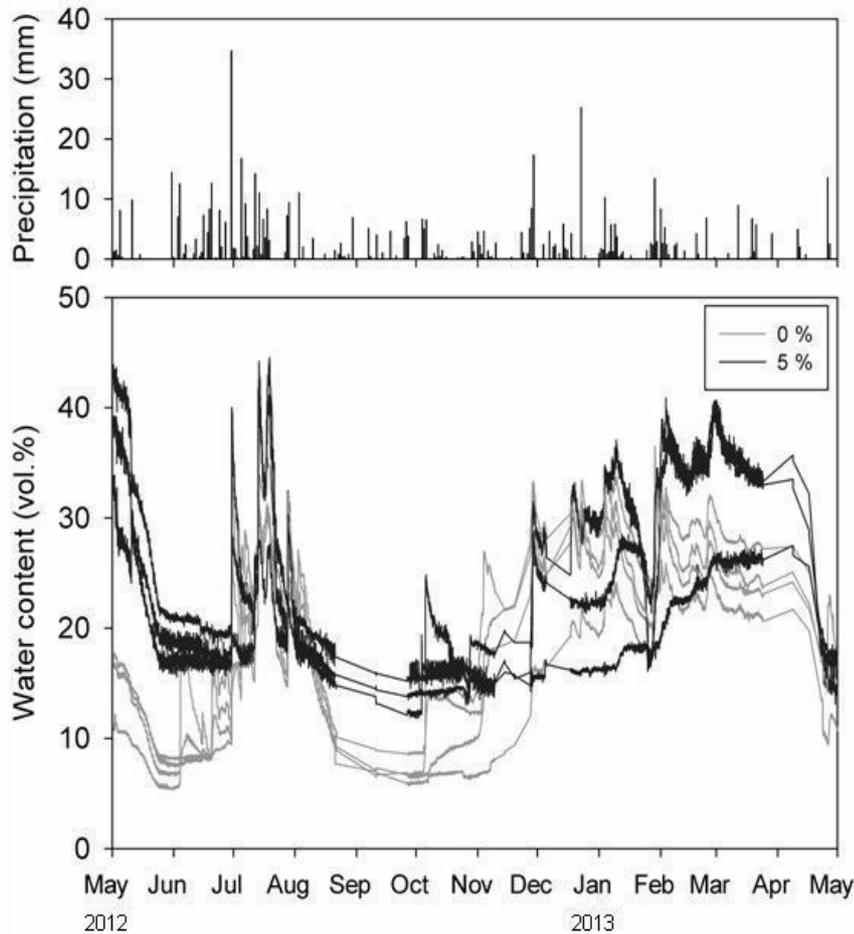


Figure 4.3 Soil water content (vol. %) with 0 and 5% biochar addition and daily precipitation between May 2012 and May 2013

Since biochar addition did not affect plant growth (Wagner and Kaupenjohann, 2014a) until May 2012, the water loss due to transpiration is assumed to be equal for both subplots. Therefore, the high water content of the 5% treatment at the beginning of our measurements is probably attributable to an increased water retention capacity due to biochar addition. Such an increased water retention can be explained by two processes: (i) an increase in the fine to medium-size pore fraction and (ii) a decrease of water repellency which is very pronounced on former sewage field soils (Täumer, et al., 2005, 2006). The former process has been reported by Abel et al. (2013) in a laboratory study. The latter is in accordance with findings of Kinney et al. (2012) who have shown that water repellency of biochars drastically decreased with increasing pyrolysis temperatures and the biochars

produced at temperatures higher than 500°C were non-repellent. Thus, a great volumetric fraction of non-repellent material with a potentially high water-holding capacity was added with the biochar.

Similar water contents in the summer months of 2012 can be explained by the higher biomass production after May 2012 on the 5% treatment subplot (Wagner and Kaupenjohann, 2014a) and the accompanying higher water loss due to transpiration. Furthermore, the summer months of 2012 were characterized by very humid conditions with frequent rainfall (Fig. 3) so that water-repellent spots in the control treatment have probably become non-repellent, which is in accordance with Täumer et al. (2006). In autumn 2012, the water content in the 5% subplot was again higher which is in agreement with the lower frequency and quantity of rainfall at that time and thus the higher probability of water repellency in the control treatment (see Täumer et al., 2006). The high variability of water contents within the treatments since Oct. 2012 reflects the high heterogeneity of potentially water-repellent spots which rewetted on very different time scales.

The water retention capacity in May 2012 was drastically increased by biochar addition (Fig. 4). The water content at field capacity (pF 1.8; $pF \equiv \log_{10}(\text{suction in cm})$) doubled from approximately 19% in the control to approximately 37% in the 5% treatment. Using the van Genuchten retention function, the water content at wilting point could be roughly estimated. The AWC increased from 13.3% in the control treatment to 28.8% in the 5% treatment. It is to be noted that the estimated saturated water content in the control subplot was lower than the measured water content in July and Aug. 2013. This discrepancy can be explained by non-static soil water retention characteristics due to time-variable water repellency. Thus, the determined water retention characteristics in Fig. 4.4 can only be regarded as a rough estimate. However, the increased water retention capacity determined in this field study is in accordance with results obtained in laboratory studies (Abel et al., 2013; Briggs et al., 2012; Liu et al., 2012).

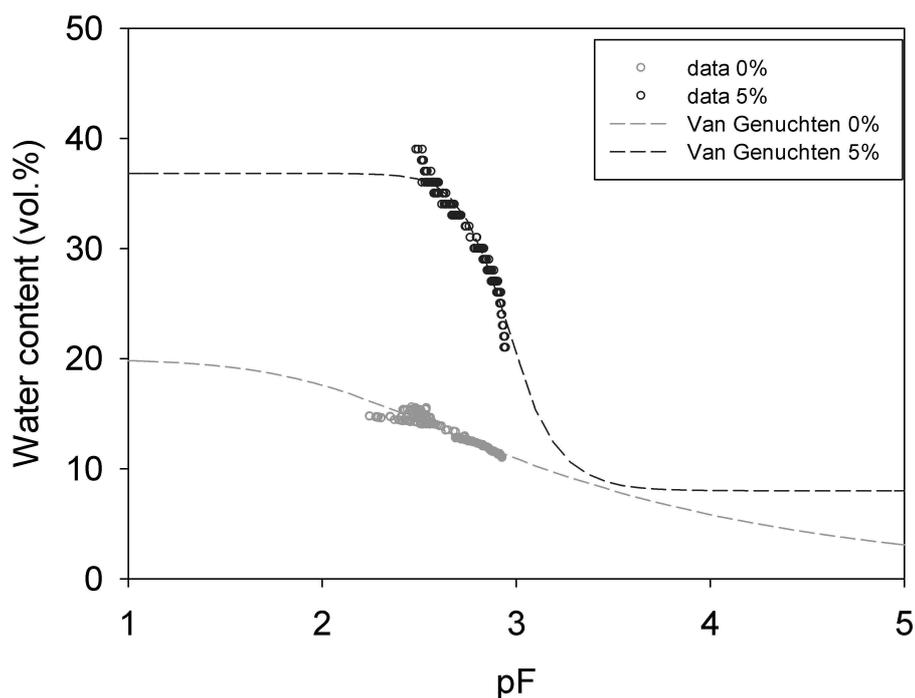


Figure 4.4 Water retention data for soils with 0 and 5% biochar addition (on the basis of data from May 2012) and fitted van Genuchten water retention function

The groundwater recharge rate calculated according to the HPTF was 112 mm a^{-1} for the control and 85 mm a^{-1} for the 5% treatment. In the soil solution of the intensive measurement subplots, the weighted mean Zn and Cd concentrations were reduced by biochar addition and decreased from 4.60 mg l^{-1} and 0.024 mg l^{-1} , respectively in the control to 1.21 mg l^{-1} and 0.012 mg l^{-1} , respectively in the 5% biochar treatment. Mean weighted concentrations of Cu increased with biochar addition from 0.85 mg l^{-1} in the control to 1.45 mg l^{-1} in the 5% biochar treatment and those of Pb from 0.006 mg l^{-1} to 0.028 mg l^{-1} . Increased water retention and reduced weighted mean Zn and Cd concentrations with biochar addition led to reduced cumulative leaching fluxes calculated for Zn and Cd. For Cu and Pb, the increased water retention capacity partly compensated the increased weighted mean concentrations so that the calculated cumulative leaching fluxes of Cu were similar and those of Pb were still higher (Table 4.2).

Table 4.2 Cumulative heavy metal leaching fluxes calculated on the basis of weighted mean concentrations and groundwater recharge rate (Eq. [3])

Biochar addition	Cumulative flux			
	Cu	Pb	Zn	Cd
0%	0.96	0.007	5.22	0.028
5%	1.25	0.024	1.04	0.011

4.4.2 Heavy metal leaching fluxes determined with SIAs

The mean cumulative Zn and Cd fluxes in 2011 were 2.94 and 0.025 kg ha⁻¹ in the control and decreased with increasing biochar addition to 1.48 and 0.021 kg ha⁻¹, respectively in the 5% treatment (Fig. 4.5). In 2012, the cumulative Zn and Cd fluxes in the controls and the biochar treatments were in the same range as in 2011. The reduction of these fluxes with biochar addition was significant for both metals (Zn $p=0.000002$, Cd $p=0.039$). However, the coefficient of determination was low (Zn $r^2=0.214$, Cd $r^2=0.045$) due to the high spatial variability. Mean cumulative Cu and Pb fluxes of the controls were 1 kg ha⁻¹ and 0.24 kg ha⁻¹, respectively in 2011 and in 2012 they were in the same range as in 2011 (Fig. 5). Biochar addition had no significant effect on cumulative Cu and Pb fluxes (Cu $p=0.576477$, $r^2=0.003$; Pb $p=0.379514$, $r^2=0.008$). For the cumulative heavy metal fluxes determined with SIAs we found a high spatial variability shown by the coefficients of variation (CVs) of 22-102% in 2011 and 23-59% in 2012 with no distinct differences between treatments. The CVs are much higher compared those (20%) reported for heavy metal fluxes determined with SIAs by Lang and Kaupenjohann (2004) under forest soils at a depth of 3-11 cm. The higher CVs in this study may be explained by preferential flow caused by the spatially and temporally variable extent of water repellency on sewage field soils (Täumer et al., 2005; Täumer et al., 2006) and the greater installation depth of 30 cm in our study. The latter can lead to a higher variability in water flow pathways and solutes (Flury et al., 1994; Flühler et al., 1996). In addition, different total metal contents of the plots A-D before biochar addition depending on the distance to the former wastewater inlet may contribute to the high variability of the heavy metal fluxes of the soils.

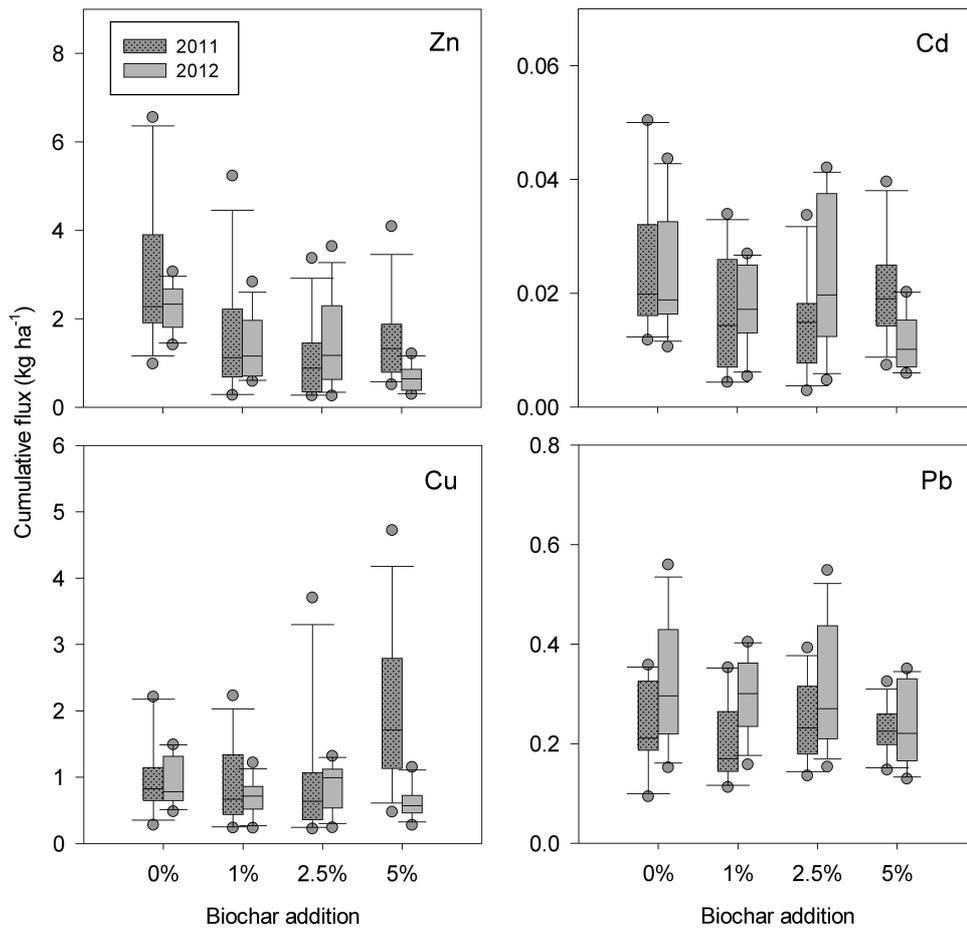


Figure 4.5 Cumulative heavy metal leaching fluxes determined with SIAs (2011 and 2012). The lower boundary of the box indicates the 25th percentile, the line within the box marks the median, and the upper boundary of the box indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. Outliers are presented as points.

The cumulative fluxes of Zn, Cd, and Cu determined with the SIAs (plot D) were generally in good agreement with those calculated on the basis of mean element concentration and groundwater recharge rate (Fig. 4.6). In contrast, the cumulative Pb fluxes of the 5% treatment and also of the control treatment determined with SIAs were 10 and 30 times, respectively higher than the calculated values. This may be attributable to the ability of the SIAs to sample Pb in an organically complexed and colloidal form at least partly as reported by Lang and Kaupenjohann (2004). Also Miller and Friedland (1994) reported that lysimeter studies underestimate Pb leaching fluxes compared to Pb leaching fluxes calculated on the basis of changes in the Pb quantities in the organic soil layer. The authors assumed that the colloidal transport may considerably contribute to Pb leaching fluxes but

is not included in lysimeter studies since lysimeters exclude particles and large organic molecules. High colloidal proportions of Pb in the soil solutions were also detected in the pot experiments by Wagner and Kaupenjohann (2014). For Cu, the ratio of reduction with biochar addition was similar for the SIA-detected and the calculated cumulative leaching fluxes. In the pot experiments, no colloidal transport of Cu was detected. This is assumed to be attributable to complexation with dissolved organic carbon. Bolea et al. 2006 have shown that Cu is mainly associated with DOC of low molecular weight (<10 kDa). Such small complexes seem to be collected by both sampling systems. For Zn and Cd, the reduction of the cumulative fluxes with biochar addition detected with SIAs was slightly lower than expected on the basis of the calculated values which might also indicate increased colloidal transport with biochar addition as already shown in the pot experiments by Wagner and Kaupenjohann (2014). The SPs used in this study have already shown to retain colloids (Ilg et al., 2007). However, little is known about the ability of SIAs to retain colloids of different nature.

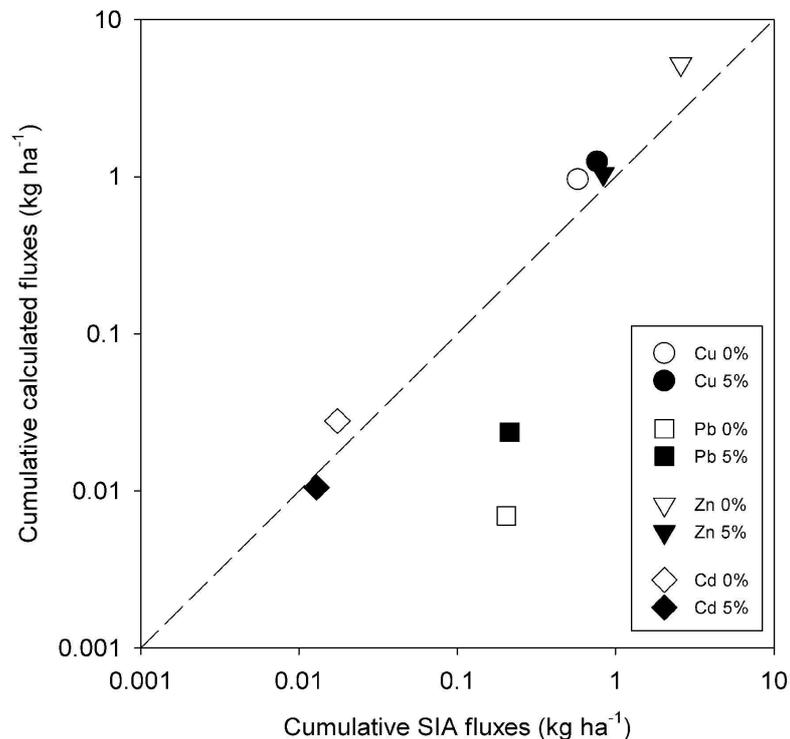


Figure 4.6 Comparison between cumulative Cu, Pb, Zn, and Cd fluxes determined with SIAs and calculated on the basis of mean weighted soil solution concentrations and groundwater recharge rates (dashed line represents 1:1 ratio)

4.5 Conclusions

This study shows that the application of biochar to sandy soils with high organic matter contents is suitable to increase their water retention capacity on the field scale. This is an additional benefit for plant growth and enhances the potential of biochar to reduce Zn and Cd fluxes not only due to reduced soil solution concentrations but also due to reduced drainage of water. The increased water retention compensates increased Cu and Pb concentrations with biochar addition so that, with respect to groundwater pollution, the negative mobilizing effect can be attenuated. Considerably higher Pb fluxes determined with SIAs compared to the calculated values indicate that with the SIAs also colloidal Pb is detected. This underlines the importance to determine also the colloidal pathway for risk assessment. However, the suitability of SIAs to detect different kinds of colloids should be studied in detail.

4.6 Acknowledgements

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5 Synthesis and Conclusions

5.1 Summarizing results with respect to the formulated hypotheses

5.1.1 Hydrochar

In the pot experiments, hydrochar addition had a negativ effect on plant growth and an immobilization of metals was not observed. Addition of poplar-derived hydrochar did not have an effect on Cu and Zn concentrations in any of the leachates sampled while Pb and Cd concentrations increased significantly in the five-week leachate from about 3 $\mu\text{g l}^{-1}$ and 5 $\mu\text{g l}^{-1}$, respectively, in the control to about 8 $\mu\text{g l}^{-1}$ and 7 $\mu\text{g l}^{-1}$, respectively, in the 5% treatment. This is in line with the element uptake by plants and leads to the assumption that no immobilization of the metals occurred with hydrochar addition. **Therefore, the hypothesis that hydrochar immobilizes metals and thus increases biomass production was not confirmed.** Whether toxic effects of hydrochar or N immobilization are responsible for reduced plant growth could not be answered in this thesis.

5.1.2 Pyrochar

Pyrochar addition may have a positive effect on metal-contaminated sites since it reduced Zn and Cd concentrations in plants and increased biomass production in the pot experiments. **Therefore, the hypothesis that pyrochar immobilizes metals and thus increases biomass production was confirmed for Zn and Cd.** For Zn, the formation of Zn phosphates seems to be possible, apart from a pH effect. Unexpectedly, reduced Zn concentrations in the plants were not accompanied by reduced leachate concentrations in the pot experiments. High colloidal Zn concentrations of about 80% may explain this contradiction since, in a colloidal form, Zn is not plant-available. Visual Minteq speciation calculations indicated precipitation of Zn phosphate for the 5% treatment and electron microprobe images of ultra-centrifugation residues showed that high concentrations of Zn and P are located at the same site which may also indicate the formation of Zn phosphates. In the field experiments, Zn concentrations in the plants and in the soil solution were reduced with pyrochar addition. However, the suction plates used do not allow the

sampling of colloids. The concentrations in the soil solution of the 5% pyrochar subplot were slightly higher than equilibrium concentrations in the presence of Zn phosphate. A partly organic complexation of Zn may be responsible for this finding.

For Cd, the decrease in plant element concentrations was not as pronounced as for Zn in the pot and the field experiments. Cadmium concentrations in the leachates of the pot experiments even increased. Visual Minteq speciation calculations did not indicate mineral formation and the colloidal proportion of Cd was considerably lower compared to that of Zn. In the field experiments, Cd concentrations of the plants were not influenced by pyrochar addition. In the soil solution, Cd concentrations decreased from $45 \mu\text{g l}^{-1}$ to about $15 \mu\text{g l}^{-1}$ but this decrease was not significant for all sampling dates. Cadmium concentrations in the 5% treatment did not correspond to equilibrium concentrations of any Cd mineral. The underlying mechanism for this reduction may, therefore, consist in an adsorption on functional groups with variable charges of the soil matrix which increased by pyrochar addition due to the alkaline nature of pyrochar. **Thus, the hypothesis that pyrochar addition immobilizes Zn due to the precipitation of Zn mineral phases and Cd due to increased sorption with increasing soil pH was supported.**

The reduction of Cd and Zn concentrations in the soil solutions and an increased water-holding capacity led to a significant reduction of Zn and Cd leaching, as shown by the SIA extractions and cumulative fluxes calculated on the basis of soil solution concentrations and amount of drainage water (Chapter 4). **Thus, the hypothesis that Zn and Cd leaching is reduced by pyrochar addition was supported.** However, the reduction of the cumulative leaching fluxes was lower than expected on the basis of the reduced soil solution concentrations and the reduced drainage caused by an increased water-holding capacity. An enhanced colloidal transport recorded by the SIAs but not with the suction plates may explain this finding.

For Cu- and Pb-contaminated or co-contaminated sites, pyrochar addition may have opposite effects. In the pot experiments, Cu concentrations of the plants did not decrease significantly and Pb was under the detection limit. Copper and Pb concentrations in the leachates increased by a factor of 4 to 5 with 5% pyrochar addition. For Cu, the colloidal proportion in the leachates was negligible and concentrations increased with increasing DOC concentrations. For Pb, a colloidal proportion (77%) in the leachates of the pot experiments indicated Pb mineral formation. However, the colloidal proportion (77%) of Pb was lower than predicted by Visual Minteq calculations (98%) related to $\text{Pb}_5(\text{PO}_4)_3\text{OH}$.

Therefore, the hypothesis formulated for the pot experiments (Chapter 2) that pyrochar addition immobilizes metals was not confirmed for Cu and Pb. This finding led to a new hypothesis for the field experiments that addition of pyrochar increases Cu and Pb mobility due to organic complexation. Copper concentrations in the soil solutions of the control subplot were approx. 0.5 mg l^{-1} at the beginning of the sampling period and increased with addition of biochar to approx. 1.5 mg l^{-1} . Mean Pb concentrations in the controls were below $10 \text{ } \mu\text{g l}^{-1}$ and biochar addition increased these concentrations to $48 \text{ } \mu\text{g l}^{-1}$ at the beginning of the sampling period. The Cu increase was significant for all sampling dates, except for the winter months where concentrations in the controls increased as well. Pb significantly increased at all sampling dates ($p < 0.05$). Copper and Pb concentrations correlated with DOC concentrations. **These findings support the hypothesis formulated for the field experiments that Cu and Pb is mobilized due to organic complexation.** However, the DOC, Cu and Pb concentrations decreased with time. Therefore mobilization of Cu and Pb may be a transient effect which is supported by the fact that Cu concentrations in plants had increased at the first harvest only. Lead concentrations in the plants were under the detection limit. Since plant biomass production was increased by pyrochar addition, although Cu and Pb concentrations in the soil solution exceeded phytotoxic levels, I concluded that Cu and Pb toxicity is reduced due to organic complexation. Copper and Pb concentrations in the soil solutions had increased considerably in the 5% treatment compared to the control, but the cumulative leaching fluxes of Cu and Pb were not enhanced with pyrochar addition as shown with the SIAs and fluxes determined on the basis of soil solution concentrations and amount of drainage water. **Thus, the hypothesis that an increased water-holding capacity compensates the increased Cu and Pb concentrations and that, therefore, biochar addition has no effect on Cu and Pb leaching was supported by our results.** The fact that cumulative Pb fluxes determined with the SIAs were considerably higher for the control and the 5% treatment compared to cumulative fluxes determined on the basis of soil solution concentrations and amount of drainage water suggest that colloidal transport is a major pathway for Pb.

5.2 Suitability of biochars as an amendment on former sewage field soils

In the pot experiments, hydrochar has shown to have a negative effect on plant growth. It can be excluded that differences in feedstock C/N ratio are responsible for this finding since negative effects occurred in both the poplar-derived and the maize-derived hydrochar. The latter has a C/N ration similar to that of pyrochar which had a positive effect on plant growth. However, the condensation grade and stability is considered to be lower for hydrochars than for pyrochars (Kuziyakov et al., 2009; Steinbeiss et al., 2009) so that microbial decomposition of hydrochar C may lead to N limitation. In this case, additional fertilization may compensate N deficiency. However, toxic effects cannot be ruled out and have been observed in toxicity tests by Busch et al. (2012). Therefore, both hydrochars tested do not seem to be suitable for any kind of soil remediation or carbon sequestration at the present time.

Pyrochar has shown a good potential to reduce Cd and Zn mobility and availability to plants, however, with respect to Pb and Cu, the considerable mobilization attributable to an increased release of DOC, even if this is a transient effect, may restrict its suitability. However, plant biomass production was not affected by increased Cu and Pb concentrations although concentrations in the controls were already exceeding toxic levels. This may be attributable to a reduced toxicity due to organic complexation. Also, the increased water-holding capacity with pyrochar addition prevented an increased Cu and Pb leaching into groundwater so that immediate negative effects were not detected. Since water availability is of vital importance for plant growth, pyrochar might provide an additional benefit making it superior to other soil additives such as lime or phosphate-based amendments, especially in a dry region such as the study site. Moreover, increased soil pH after liming is supposed to increase DOC concentrations and may therefore also lead to a mobilization of Cu (McBride et al., 1997) and Pb (Sauvé et al., 1998) and facilitate colloidal transport (Klitzke et al., 2008). Phosphate-based amendments may increase leaching of P leading to eutrophication of the receiving surface waters. However, no direct comparison with other remediation techniques was performed in this thesis making it difficult to assess the relative success of other immobilizing additives such as glacial till which may also increase the water-holding capacity of soils.

The pattern of contamination and the distribution of organic carbon on the former sewage field soils are heterogeneous. The organic carbon present in the investigated soils was very high and positive effects on yields may be partly attributable to the supply of N from the accumulated organic material. Chan et al. (2007) reported on increased yields only if biochar addition was accompanied by fertilization with mineral N on a nutrient-poor soil and own investigations (not published) have revealed growth depression with pyrochar applied to uncontaminated sandy soil typical of the region of Brandenburg. The high phosphorus concentrations found in the soil solutions also corresponded to the organic matter content and may have had an influence on the formation of mineral phases. Pyrochar addition to soils with low organic carbon contents may therefore be less effective. However, since heavy metal concentrations correlate with organic carbon contents (Grunewald, 1994), only sites with high organic carbon contents seem to require remediation.

Nutrient imbalances probably caused by high amounts of K released from pyrochar may also have detrimental effects on plant growth. In the plants of the field experiment, decreasing Ca concentrations with increasing addition of pyrochar were observed, however, they obviously did not have a negative effect on plant growth.

The results presented in this thesis were obtained shortly after the addition of fresh pyro- or hydrochars and long-term effects may differ widely. With respect to hydrochars, investigations of Busch et al. (2012) have shown that a hydrochar with initially toxic effects on plant growth had positive effects later which may be related to a degradation, leaching or volatilization of the harmful substance(s), offering the possibility to be used after pretreatment to reduce toxicity. For pyrochar, it remains to be elucidated how long-lasting the effect of Zn and Cd immobilization is since a decrease in soil pH after exhaustion of the buffer capacity of the ash contained in the pyrochar may remobilize these metals. Other processes may take place with time which may improve or reduce metal immobilization. On the one hand, oxidation of the surface of pyrochar or adsorption of organic matter to pyrochar may lead to an increase in the number of functional groups relevant for its cation exchange capacity (Nguyen et al., 2008; Liang et al., 2006) thus also improving metal immobilization with time. Adsorption of organic matter seems to be a relatively fast process as shown by composting experiments conducted by Prost et al. (2013). Therefore, adsorption of soil organic matter may have already increased the sorption capacity of pyrochar during the field experiment. Oxidation of the pyrochar surface due to microbial degradation is assumed to be a slow process (Kuzyakov et al.,

2009) so that the oxidation of the pyrochar surface might further increase metal sorption in the long run. On the other hand, decomposition of the accumulated organic substance together with an improved microbial activity due to pH increase by pyrochar addition may increase heavy metal leaching provided that the metal release exceeds the sorption capacity of the pyrochar added. Moreover, pore clogging by organic coating may also reduce the specific surface area (Mikutta et al., 2004) and could, therefore, reduce the sorption of heavy metals. However, studies by Prost et al. (2013) have shown that composting reduces the specific surface area of pyrochar by pore clogging but increases its cation exchange capacity which may be attributable to a lower number of functional groups in the core of pyrochar particles (Nguyen et al., 2008).

Copper, Cd, Pb and Zn are the main contaminants on former sewage field soils. However, various co-contaminants or organic pollutants such as As, Hg, Cr, PCB or PAH which have also accumulated in sewage field soils (Grunewald, 1996) and which have not been included in this study may also be influenced by biochar addition and may have adverse effects, for example, As may be mobilized due to pH increase (Masscheleyn et al., 1991) or organic contaminants may be mobilized due to increased DOC concentrations.

5.3 Challenges under conditions of practice

For an *in situ* treatment, the challenge consists in an adequate mixing of the sorbents to the soil to ensure stabilization of metal concentrations (O'Day & Vlassopoulos, 2010). The admixing of pyrochar to the soil for the pot and even for the field experiments was done by hand and very extensively to achieve a homogeneous distribution of the pyrochar particles. Under conditions of practice, such a homogeneous distribution may not be achieved and thus may reduce the efficiency of the method. Also, the heterogeneous contamination pattern of the soil may present an obstacle to the applicability of the method since a graded dosage may be needed depending on the contamination degree and content of organic carbon involving additional expenses for preliminary investigations.

In the phase of admixing of the biochar, wind erosion would pose the risk of drifting of the contaminated soil which can hardly be avoided since a homogeneous distribution of pyrochar in the soil is possible only by destroying the vegetation coverage. To avoid wind erosion in the long run, a coverage of the soil surface is needed which restricts the production of energy crops to perennial plants. At the moment, the former sewage fields

are a biodiversity hotspot since the fields are not under cultivation. The choice of energy crops should also consider the preservation of the sewage fields' biodiversity as well as their possible use as a recreation area.

Under conditions of practice, the financial aspect has to be considered including expenses for the adsorbents which are considerable at the present time. Since biochar addition to soils also offers the possibility of carbon sequestration (Lehmann, 2007), the financial benefits will depend on the development of the carbon trading scheme and the costs for large-scale production in the future.

5.4 Transferability to other biochars

Although different feedstocks were used, element composition, pH and specific surface area of the maize-derived and the miscanthus-derived pyrochar used were similar and typical (Amonette & Joseph, 2009; Downie et al., 2009). Both showed a similar heavy metal reduction behaviour in the presented studies and it seems likely that alkaline pyrochars with a high pH buffer capacity are suitable for immobilization of Zn and Cd. However, the chemical and physical properties may differ widely according to feedstock and charring conditions thus affecting their metal-immobilizing ability (Kinney et al., 2012; Borchard et al., 2012). Post-treatment of pyrochar will determine the quality of DOC and the quantity of DOC release (Lin et al., 2012) and may influence its suitability for Cu- and Pb-contaminated sites. Thus, no general statement on a specific type of pyrochar for metal immobilization can be made.

Even for the hydrochars which did not seem to be suitable for soil remediation in this study, it cannot be ruled out that alteration of process parameters or post-treatment may result in hydrochars capable of immobilizing metals without exhibiting negative effects on plant growth.

5.5 Future research

In this thesis, only the effects of pyrochar addition on the main contaminants Cu, Zn, Cd and Pb present on the former sewage fields of Großbeeren were investigated. Therefore, future research should include other contaminants such as Arsenic (As), Mercury (Hg), Chromium (Cr), PCBs or PAHs. The soil chosen for the pot experiments was taken from a former wastewater inlet area and the four plots of the field experiments were located at the

same site. Therefore, the obtained results are hardly representative of the whole area of the former sewage fields and further experiments should also include the effects of biochar addition on sites with lower or higher contamination levels and organic matter contents.

Moreover, long-term effects of biochar addition should be studied under field conditions. Degradation of pyrochar may alter its chemical properties and affect its immobilizing properties. The experiments conducted suggest the precipitation of Zn and Pb mineral phases, however this remains to be further proven. Further investigations of the heavy metal-binding forms by sequential extraction methods should be performed to estimate long-term effects. Also, near edge x-ray absorption fine structure spectroscopy (NEXAFS) studies are a promising method to determine mineral phases in contaminated soils by comparison with defined mineral phases (Siebers et al., 2013). The detection of mineral species formed and the local distribution (biochar particle, rhizosphere, bulk soil) would be of interest for the elucidation of the immobilizing mechanisms.

Even if the release of DOC, and the concurrent mobilization of Cu and Pb, is a transient effect it would be desirable, especially in areas with high groundwater recharge rates, to study the conditions of DOC release. The fact that Pb is more effectively mobilized than Cu leads to the assumption that the additional DOC is biochar-derived and of high molecular weight. However, further investigations should be conducted to confirm this assumption and/or provide more information on the quality and structure of DOC so that the risk of mobilization of organic contaminants can be elucidated and possible post-treatment procedures to minimize DOC leaching can be taken.

The suction plates installed for the sampling of soil solution in the field experiments were not suitable to determine the translocation of metal precipitates since they are not permeable for colloids (Ilg et al., 2007) and no information is available on the suitability of SIAs to retain colloids of different nature. Further studies should therefore focus on the translocation of metal precipitates. NEXAFS studies may be helpful to identify the composition of colloidal material trapped in the porous suction plates. In addition, studies are required which address the determination of the quantitative export of colloid-bound heavy metals.

With respect to hydrochar, further investigations should concentrate on the question whether toxic effects or N immobilization are responsible for the reduced plant biomass production. If N limitation is responsible for the negative effects, an additional supply of N fertilizer may solve the problem of reduced yields and metal-binding should be studied

under optimal conditions for plant growth. If toxic effects are responsible, it should be clarified whether they can be eliminated by changes in the processing conditions or treatment of the hydrochars produced.

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