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Addition of biochar and compost to remediate soils contaminated with metals and PAHs

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Abstract

In the process of soil remediation, primarily areas with high concentrations of pollutants are treated, while the surrounding soil maintains low to moderately contaminated. By reducing the accessible share of soil pollutants the in-situ application of soil amendments provides a sustainable and cost efficient risk management measure for soils that exhibit mixed contamination comprising organic and inorganic pollutants. The reduction of accessibility of pollutants decreases the bioavailability for organisms and by that the risk of environmental harm [1].

The general objectives of this study comprise (i) the investigation of the influence of soil amendments on the mobility of selected metals and polycyclic aromatic hydrocarbons (PAHs) and (ii) the elucidation of the extent to which the translocation of pollutants towards groundwater can be prevented by the introduction of organic and mineralic auxiliaries. Soil amendments such as biochar or lime help to reduce the mobility of contaminants due to adsorption mechanisms, which immobilize contaminants such as metals and PAHs and increase the soil pH, which again causes a reduction of the metal mobility. The application of compost provides nutrients, improves the microbial activity and stabilizes soil pH which supports the degradation of organic soil contaminants such as PAHs.

Two different soils were tested. One not contaminated arable soil from Eschenau, which was spiked with 1000 ppm zinc, 10 ppm cadmium, 100 ppm phenanthrene and 100 ppm pyrene. This first soil was tested with single amendments as well as a combination of 5 % biochar (or aged biochar) and 10 % compost. Treatment with lime was also tested for the Eschenau soil. The second soil represents a PAH field-contaminated soil from Treffling and which was only tested with the combination of 5 % biochar and 10 % compost. The biochar used in this study (type MSP550) was produced by pyrolysis from *miscanthus* straw pellets, it exhibits a mean pH of 9.77. The compost originated from a composting plant in Pixendorf, it showed a mean pH of 7.5.

The Eschenau soil was tested in incubation studies using soil microcosms to monitor the dissipation and immobilization of PAHs and the immobilization of metals in the presence of various soil amendments over 151 days. In addition, soil lysimeters were used to monitor the mobility change of contaminants such as metals and PAHs in the Eschenau soil upon addition of soil amendments over 156 days. The Treffling soil was investigated in incubation studies with the focus being put on monitoring the dissipation of PAHs. The leaching studies with Treffling soil focused on the influence of biochar and compost on the mobility of PAHs.

The Eschenau soil incubation experiment showed that the highest reduction of extractable zinc and cadmium concentrations was reached in the treatments with lime, compost and the combined treatments with compost and biochar after a period of 151 days. The extractable zinc and cadmium concentrations were reduced in the treatment with lime by 18.5 and 5 times, in the treatment with compost by 72 and 132 times, respectively, when compared to the control treatment. The treatment with biochar and compost showed extractable zinc and cadmium concentrations that were 48 and 46 times lower, respectively, when compared to the control treatment.

Leaching studies confirmed that treatments with lime, compost and combined additives provided the highest reduction of metal mobility after 156 days. The treatment with lime resulted in extractable zinc and cadmium concentrations 15 and 5 times lower, the treatment with compost 20 and 10 times lower and the treatment with biochar and compost 13 and 5 times lower, respectively, when compared to the control.

The incubation experiment of the Eschenau soil showed that the highest reduction of extractable pyrene and phenanthrene was reached in the treatment with lime and the treatment with biochar and compost after 151 days of incubation. The treatment with lime showed extractable pyrene and phenanthrene concentrations 2 and 7 times lower, respectively, when compared to the control and the treatment with biochar and compost reached concentrations 2 and 3 times lower, respectively, when compared to the control treatment. The leaching studies of the Eschenau soil showed no difference in the mobilisation of PAHs between the treatments with soil amendments and the control treatment after 156 days.

The Treffling soil incubation study and the leaching study showed no reduction of the PAH concentration in the treatment with compost and biochar when compared to the control.

This work shows that the in-situ application of soil amendments such as lime or biochar and compost can help to reduce the mobility as well as the bioavailability of metals and organic pollutants in low to medium contaminated soils and so can help to prevent the translocation of metals into groundwater. The application is less suitable for the immobilization of PAHs but partly supports their degradation. The use of organic and mineralic soil amendments for soil remediation apparently holds some promise to provide a new sustainable, green and cost effective method for soil remediation.

Zusammenfassung

Mit konventionellen Bodensanierungsverfahren werden vorwiegend Kontaminationsherde oder Bereiche mit hohen Konzentrationen von Schadstoffen behandelt, während der umliegende Boden geringe bis mäßige Verunreinigungen beibehält. Die kombinierte in-situ-Anwendung von Bodenzusatzstoffen könnte dazu beitragen, geringe bis mäßige kontaminierte Böden durch die Verringerung des zugänglichen Anteils an Schadstoffen zu sanieren. Die Verringerung der Zugänglichkeit von Schadstoffen verringert die Bioverfügbarkeit für Organismen und damit das Risiko von Umweltschäden [1].

Die allgemeinen Ziele dieser Studie umfassen (i) die Untersuchung des Einflusses von Bodenzusatzstoffen auf die Mobilität von ausgewählter Metalle und polyzyklischer aromatischer Kohlenwasserstoffe (PAK) und (ii) inwieweit die Bewegung der Schadstoffe in Richtung Grundwasser durch die Einbringung von organischen und mineralischen Hilfsstoffen verhindert werden kann. Bodenzusatzstoffe wie Biokohle oder Kalk können durch entsprechende Adsorptionsmechanismen die Verfügbarkeit von Verunreinigungen reduzieren, durch eine gleichzeitige Erhöhung des Boden-pH-Wertes Verringerung sich die Mobilität von Metallen. Die Anwendung von Kompost erhöht die Anzahl der Bodenorganismen und verbessert die Voraussetzungen für mikrobielles Wachstum, wodurch organische Bodenverunreinigungen wie PAKs verstärkt abgebaut werden können.

Es wurden zwei verschiedene Böden getestet. Ein nicht verunreinigter Ackerboden aus Eschenau, der mit 1000 ppm Zink, 10 ppm Cadmium, 100 ppm Phenanthren und 100 ppm Pyren versetzt wurde. Dieser erste Boden wurde unter Zugabe einzelner Additive oder einer Kombination von 5% Biokohle und 10% Kompost getestet. Eine Behandlung des Eschenau-Bodens mit Kalk wurde ebenfalls getestet. Der zweite Boden stammt von einem PAK-kontaminierten Standort in Treffling und wurde nur mit der Kombination von 5% Biokohle und 10% Kompost getestet. Die verwendete Biokohle war vom Typ MSP550, sie wurde mittels Pyrolyseverfahren aus *Miscanthus*-Strohpellets hergestellt und zeigte einen mittleren pH-Wert von 9,8. Der Kompost wurde in einer Kompostieranlage in Pixendorf hergestellt, der mittlere pH-Wert lag bei 7,5.

Um die Dissipation und Immobilisierung von PAK und die Immobilisierung von Metallen in Gegenwart verschiedener Bodenzusatzstoffen zu prüfen, wurde der Boden Eschenau über 151 Tage in Bodenmikrokosmen inkubiert. Um die Veränderung der Mobilität der Schadstoffe in Gegenwart von Bodenadditiven zu erfassen, wurde Boden Eschenau über 156 Tage in Bodenlysimetern getestet. Der Boden Treffling wurde ebenfalls einer Inkubationsstudie unterzogen, wobei in diesem Fall nur die Dissipation der bereits im Boden vorhandenen PAKs untersucht wurde. Ebenso fokussierte die Sickerwasserstudie des Bodens Treffling auf den Einfluss von Biokohle und Kompost auf die Mobilität von PAKs. Die Ergebnisse des Inkubationsexperiments mit Boden Eschenau zeigten, dass die höchste Reduktion der extrahierbaren Zink- und Cadmiumkonzentrationen durch Behandlung entweder mit Kalk, Kompost oder mit einem Kompost-Biokohle Gemisch erzielt wurden. Die extrahierbaren Zink- und Cadmium-Konzentrationen waren bei der Behandlung mit Kalk 18,5 bzw. 5 mal, bei der Behandlung mit Kompost 72 bzw. 132 mal niedriger im Vergleich zur Kontrolle. Die gleichzeitige Behandlung mit Biokohle und Kompost zeigte im Vergleich zur

Kontrollbehandlung eine 48 bzw. 46 mal niedrigere extrahierbare Zink- und Cadmiumkonzentrationen.

Die Ergebnisse der Sickerwasserstudien bestätigen die gute Wirkung der Behandlung mit Kalk, Kompost und kombinierten Additiven. Die Zugabe resultierte in extrahierbare Zink- und Cadmium-Konzentrationen, die 15 bzw. 5 mal (Kalk), 20 bzw. 10 mal (Kompost) und 13 bzw. 5 mal (Biokohle und Kompost) niedriger waren im Vergleich zur Kontrollbehandlung.

Das Inkubationsexperiment des Eschenauer Bodens zeigte, dass die höchste Reduktion von extrahierbarem Pyren und Phenanthren durch Behandlung mit Kalk bzw. Behandlung mit Biokohle und Kompost erzielt wird. Die Zugabe resultierte in extrahierbare Pyren- und Phenanthren-Konzentrationen, die 2 bzw. 7 mal (Kalk) sowie 2 bzw. 3 mal (Biokohle und Kompost) niedriger waren im Vergleich zur Kontrollbehandlung. Die Sickerwasserstudien des Bodens Eschenau zeigten keinen Unterschied in der Abnahme von PAKs zwischen den Behandlungen mit Bodenzusatzstoffen und der Kontrollbehandlung im Versuchszeitraum von 156 Tagen.

Die Inkubationsstudie sowie die Sickerwasserstudie mit Boden Treffling zeigten keine Verringerung der PAK-Konzentration in der Behandlung mit Kompost und Biokohle im Vergleich zur Kontrollbehandlung.

Die vorliegende Studie zeigt, dass eine in-situ Anwendung von Bodenzusatzstoffen wie Kalk oder Biokohle und Kompost die Mobilität sowie die Bioverfügbarkeit von Metallen und organischen Schadstoffen in gering bis moderat kontaminierten Böden reduzieren und die Verfrachtung von Metallen ins Grundwasser vermindern kann. Die Anwendung ist weniger gut geeignet für eine Immobilisierung von PAKs, unterstützt aber teilweise deren Abbau. Generell kann gesagt werden, das die Verwendung von organischen und mineralischen Bodenzusatzstoffen offenbar eine neue, nachhaltige, grüne und kostengünstige Möglichkeit zur Risikoreduktion von kontaminierten Böden darstellt.

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List of Abbreviations

ANOVA	Analysis Of Variance
AIT	Austrian Institute Of Technology
AEC	Anion Exchange Capacity
CAKE	Computer Assisted Kinetic Evaluation Application
CEC	Cation Exchange Capacity
DM	Dry Mass
DOC	Dissolved Organic Carbon
DT_{50}	Dissipation Time 50 %
EPA	Environmental Protection Agency
HPLC	High Performance Liquid Chromatography
HSD	Honestly Significant Difference
LDPE	Low-Density Polyethylene
LOQ	Limit Of Quantitation
PAH	Polycyclic Aromatic Hydrocarbon
PTFE	Poly Tetra Fluoro Ethylene
PVC	Poly Vinyl Chloride

1 Introduction

Soils are the skin of the planet earth, which serve as growing medium for the world's vegetation. They are the essential basis of forests, meadows, food crops, grazing land for animals that produce meat and other products for human use. Soils are also very important as water storing medium and for water purification. Soil contaminants such as metals or organic pollutants can cause harm to the environment. The application of biochar, compost and lime as amendments for soil remediation could help to reduce the mobility of soil contaminants and therefore the bioavailability for plants and microorganisms [2].

Soils consist of a solid mixture of minerals and organic matter. Between solid particles there are spaces, which can hold gases or pore water. In these pore water, many different chemicals and minerals can be dissolved. Soils function as a vital living system, are biologically active and are habitat to a huge number of types of microorganism and invertebrates such as worms and insects. By the addition of soil amendments the soil constitution could be improved and by that the soil quality.

Food, feed, fibre and fuel production are the main functions of agricultural soils. Crop production and crop quality depend on the soil quality, determined by nutrient and water supply. In addition, the suitability as a microorganism habitat and growth medium for roots is important, determined by biophysical, chemical and environmental factors. The supply of soil with nutrients depends on decomposition and mineralization of soil organic matter and soil amendments like compost and crop residues by soil microbes, and fertilization, which means synthetic supply of essential plant nutrients. Nutrient supply also depends on soils buffering capacity of nutrients, the ability to retain and release nutrients, based on the property that both, soil particles and nutrients possess a weak electrical charge. Cation exchange capacity (CEC) is determined by the degree to which a soil can reversibly bind positively charged nutrients. The degree to which it can bind negatively charged nutrients is defined as anion exchange capacity (AEC). When soil pH drops, CEC decreases and AEC increases. On the opposite, when soil pH rises, CEC increases and AEC decreases. Soil amendments such as biochar and compost show a high CEC, which helps to reduce postivley charged soil pollutants [3] [4].

Due to the importance of soil quality for our personal and environmental health, it is necessary to provide measures, which improve soil quality in a long term, sustainable manner. Industrial activities, agricultural chemicals, commercial services, waste treatment and disposal are the main reasons for contaminated soils. The European Energy Agency identified about 250.000 sites in Europe, which require remediation. Three classes of contaminants are listed by the European Energy Agency. These are heavy metals (35%), mineral oils (24 %) and polycyclic aromatic hydrocarbons (21%). If the present contamination rate does not decrease, it is expected that the number of contaminated sites will rise by about 50% by 2025 [5]. In Austria, 35 % of registered contaminated sites are polluted with polycyclic aromatic hydrocarbons (PAHs), which can appear together with a heavy metal contamination [6]. The combination of those two pollutants causes a risk for environment and human health. In practice, it is common that in the process of soil remediation, areas with high concentrations of pollution are treated, but the surrounding soil with low diffuse

to moderate contaminations is not in remediation process included. The treatment and remediation of such low diffuse to moderate, mixed contaminated sites turns out to be very expensive. High amounts of contaminated soil needs to be moved and treated, which rises the costs disproportionately.

Gentle remediation processes, which gain more and more importance, could be a suitable alternative for treating such low diffuse to moderate, mixed contaminated sites. Organic additives, like compost or biochar, turned out to have a high potential regarding gentle remediation. Organic pollutants and heavy metals are sorbed on biochar, which prevents the movement to the groundwater, while compost accelerates the microbial degradation of organic harmful substances. This combined in-situ remediation process would offer an environmental friendly, economical strategy with a small ecological footprint. Additional, the use of organic amendments also supports renaturation processes of contaminated soils.

1.1 Soil contamination

Soil acts as the basis for food and feed production, a growth medium for roots and acts as a microorganism habitat. Further, it functions as a natural filter for contaminants and regulates important ecological cycles. To maintain that functions in a sustainable way, a good soil quality is important. Soil contamination occurs as a result of industrial activities, agricultural chemicals, commercial services, waste treatment and disposal. Soil contamination implies that a certain substance, like a nutrient, pesticide, organic chemical or metal is present in a higher concentration than it would naturally occur. The term, soil pollution, implies that a certain substance is causing harm to the environment. One can also differentiate between local soil contamination, the so-called “hot spots”, and diffuse soil contamination. Diffuse soil contaminations often cover large areas and in contrast to “hot spots”, these large surrounding areas are not always remediated, because high amounts of contaminated soil need to be moved and treated, which rises the costs disproportionately [3][5]. In the end, environmental authorities decide if a diffuse contaminated area needs to be remediated or not.

In Europe there are about 250.000 contaminated sites, which would be in the need of remediation, summarized by the European Energy Agency. An overview of the European Environment Agency (2014) listed the three biggest classes of pollutants. The class with the highest percentage are heavy metals with 35%, followed by mineral oils with 24 % and aromatic and polycyclic aromatic hydrocarbons with 21% [5]. This study focuses on two heavy metals, zinc (Zn) and cadmium (Cd) and 16 polycyclic aromatic hydrocarbons as soil contaminants, especially on pyrene and phenanthrene.

1.1.1 Heavy metals

Heavy metals are a group of naturally occurring metallic elements with a high atomic weight and a density at least five times greater than that of water. These metals are industrially and biologically important. Point and diffuse contaminations of urban and rural environment with metals are the result of geological weathering and anthropogenic activities, like mining, waste disposal and industrial production. Heavy metals are also considered as trace elements because of their presence in trace concentrations (ppb range to less than 10 ppm) in soils. Plant metabolism is dependent of several of these trace elements, especially the so-

called transition metals like copper (Cu) and zinc (Zn). Those transition metals are essential nutrients, which are required for many biochemical and physiological functions. Other metals such as aluminium (Al), arsenic (As), cadmium (Cd), gold (Au), lead (Pb), lithium (Li), or mercury (Hg) have no biological functions [7].

The behaviour, mobility, and toxicity of heavy metals are complex. Main mechanisms of metals in soils and sediments can be divided into different binding classes. They can be: packed into the solid phase, bound to surface of the solid phase, bound to ligands in solution or as free ions in solution. In general, only free metal ions are bioavailable and can be taken up by organisms. The concentration of metal ions dissolved in soil solution stays in an equilibrium with the metal ions bound to surfaces and complexes. If the concentration of metal ions dissolved in soil solution decreases by e.g. plant uptake, then desorption of metals from complexes and surfaces takes place to increase to concentration of ions dissolved in soil solution. In the same way, if a metal binding surface area increases, dissolved metal ions are removed from soil solution and get sorbed onto surface. To cause harm to an organism, metals need to be dissolved in solution and be taken up by an organism. Then, metal ions are transported to cells where toxicity may occur. In order to reduce the risks of toxic effects to organisms, it is essential to reduce the bioavailability of heavy metals to a receptor organism. This can be performed by: removing all or just parts of the source of the pollution, to eliminate the pathway of the metal from the source to the receptor, or by the modification of the exposure to the receptor.

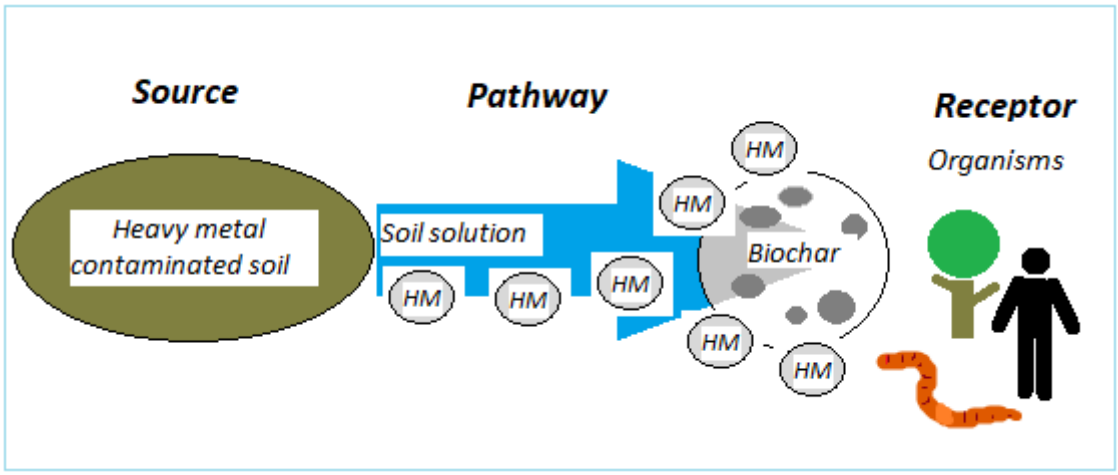

Figure 1: Schematic illustration of biochar disrupting the pathway of metals from their source to the receptor organisms [Source: own illustration2017].

Unlike organic pollutants, heavy metals cannot be degraded or broken down, which makes elimination of the pathway from source to receptor to the best option, to avoid and reduce the probability of toxic effects to organism (see *Figure 1*). Biochar could be a suitable tool to achieve less bioavailability of pollutants to an organism. The effect of pollutants to an organism is more important than the concentration of any pollutant in soils, which underlines that pathway breakdown with the support of biochar figures out as a smart and logical way [8].

1.1.2 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons are a large group of compounds, which consist of two up to six aromatic rings and are some of the most toxic compounds known. PAHs are important and dangerous pollutants, which are found in several environmental matrices all over the world, occurring in complex mixtures. Above certain concentrations, carcinogenic, mutagenic and teratogenic properties may occur to organisms [9].

PAHs are formed during many different processes, occurring naturally like forest fires or volcanic eruptions or anthropogenic activities like energy production or industry. They originate mostly from incomplete combustion, pyrolysis or gasification of organic materials [10]. According to the number of condensed rings, PAHs can be classified as light fraction with two up to three aromatic rings and the heavy fraction with at least four aromatic rings. The heavy fraction of PAHs are more stable and more toxic than the light ones [11].

There are different pathways how humans can be exposed to PAHs. The transport and distribution of PAHs in the environment depends on their relative solubility in water and organic solvents. The relative solubility determines the capacity for transport and distribution between environmental compartments. The distribution and transport of PAHs in the atmosphere is influenced by their volatility. According to their lipophilic character and the generally poor aqueous solubility, PAHs tend to accumulate in the lipid tissue of animals and plants. In plants with higher water contents, PAHs will tend to accumulate less, but the transfer rate varies and is influenced by soil characteristics and the presence of co-pollutants. The organic fraction of soils adsorbs PAHs very strongly, so they do not penetrate deep into the soils. The leaching into groundwater and also the bioavailability for plant uptake is limited by that. The toxicity depends on the structure of the PAH. Many isomers can be formed, which vary from being nontoxic to very toxic and their half-lives depend on various parameters, e.g. molecular mass. The half-lives of PAHs in soils vary from some month to years and in the atmosphere from hours to days. Cooking on barbecue or cigarette smoke may lead to human exposure but they are also present in food and feed. Food can be contaminated by PAHs which are present in the air, soil and water. The highest intake of PAHs for humans has turned out to come from cereals, oils and fats [12].

In order to reduce human health risks, it is necessary to decrease the amount of contaminated sites by sorption, degradation and mineralization. Because of their hydrophobic and apolar nature, PAHs are sorbed to particulate organic matter in soils, which decreases the availability for biological uptake by plants and microorganisms. The biological degradation of PAHs ends after several steps of hydroxylation, ring cleavage and oxidation in the complete mineralization as CO_2. This needs optimal microbial conditions, regarding nutrient, oxygen and water supply. There is a huge range of PAH degrading microbial communities. Bacteria, filamentous fungi and even algae are capable to metabolize PAHs. The remediation of contaminated sites could be supported by enriching polluted soils with PAH degrading bacteria [5]. The US Environmental Protection Agency (EPA) has listed 16 priority PAHs which this study focuses on.

1.2 Organic and inorganic amendments for soil remediation

The application of gentle or green soil remediation treatments gained more importance over the last years because of their advantages concerning sustainability, ecological footprint and financial benefits. Soil amendments include all organic and inorganic substances added to soil for a better soil constitution. Organic substances like compost or biochar are derived from living things, whereas inorganic amendments like lime are mined or man-made. One reason for the use of soil amendments is to provide a better soil environment for plant growth by improving the soil structure and texture, increasing the water holding capacity and the availability of nutrients, and improving the living conditions for soil organisms [2]. Another reason is the fact that soil amendments are capable to decrease the mobility of soil pollutants and therefore the bioavailability for plants and microorganisms.

1.2.1 Biochar

Biochar is a black, porous and carbon-rich material, which is produced by heating biomass in zero or very low oxygen conditions, called pyrolysis [13]. The pyrolysis process gives three products: liquid (bio-oil); solid (biochar); and gas (syngas) [14]. The solid material is storing carbon in a stable form over many hundred years, and has many important benefits for soil and plant growth. Biochar improves soil water retention capacity and soil structure, adds nutrients and provides a more efficient use of soil nutrients, increases cation exchange capacity and rises the soil pH, immobilizes pollutants, acts as habitat for soil organism and stores carbon in soil for more than 1000 years. Biochar and charcoal are made by the same process and are indistinguishable in physical and chemical properties. The difference between biochar and charcoal is based on the intension. While charcoal is intended to be burnt, biochar is produced to be added to soil as an amendment.

Plant residues, solid animal excrements and other organic wastes act as biomass source for biochar production. Heating biomass under oxygen – limited atmospheres to temperature between 300°C und 1000°C, results in a loss of hydrogen, nitrogen and oxygen relative to carbon, which leads to the carbon atoms being bound strongly to each other. Especially oxygen, nitrogen and hydrogen form compounds and are emitted as vapor. As a result, the chemical structure is very stable and hard for microorganism to be broken down, while biomass, which is not converted, can be broken down rapidly, releasing carbon as carbon dioxide to the atmosphere. Carbon in plant biomass comes from carbon dioxide in the atmosphere via the photosynthesis process, because of that, there is no effect on the atmospheric carbon concentration, called “carbon neutral”.

To understand the effect of biochar, it is useful to separate between short and long-term carbon cycle. The short-term carbon cycle includes carbon, which is moved through organism and occurs on timescales of minutes to some hundred years. The enormous emissions of carbon-30 billion tons of carbon dioxide every year-from fossil fuels to the atmosphere creates a big change in the short-term carbon cycle. The long-term carbon cycle occurs on timescales of thousands to million years and involves carbon which is stored in rocks and fossils [4]. Over a long time, huge amounts of carbon have been sucked out of the atmosphere and locked up in coal, oil and gas. By burning the carbon storing materials, carbon dioxide is released back to the atmosphere rapidly, which disrupts the balance of the short-term carbon dioxide cycle. By storing atmospheric carbon in a stable form for

hundreds up to thousands of years, the atmospheric concentration of carbon dioxide is reduced. This reverses the trend of adding carbon dioxide from the long-term cycle to the short-term cycle and offers a good opportunity to support the efforts against global warming and climate change.

Due to many years of cultivation with low or without return of plant residues, many soils suffer under low amounts of organic carbon. Plant based biochar consists of 70-80 % carbon, which is added as inorganic and organic matter to soil. Organic matter improves the soil quality in many different ways. The soil density is reduced, which allows a better development of plant roots. The ashes, which are concentrated in the biochar are alkaline, which is another important property. Also several nutrients, like potassium (K) or iron (Fe) concentrate during the pyrolysis process in the biochar [4]. Alkaline soils show a high concentration of so called "base cations" like sodium (Na), calcium (Ca), magnesium (Mg) and potassium. These base cations are vital for healthy plant growth. The ideal soil pH- value for arable crops ranges between 6.5- 7.0. Over the time, agricultural soils tend to become acidic, because the so called "base cations" - which counter the H^+ - are removed with the crop. Because most of biochars are alkaline and have a high pH themselves, soil pH increases after the application of biochar. Caused by the negative charged functional surface groups (carboxylic, phenolic etc.), biochar tends to remove protons, which cause acidity, and increases the pH by that. Over weeks and months a slow saturation of biochar's functional surface groups occurs, which causes a reduction of biochar pH over the time [15].

The negative charge of the surface area attracts positively charged cations such as sodium or calcium, as well as charged molecules like ammonium (NH_4^+). Because the chemical bond between surface and ion is relatively weak, organisms can easily take them up and use them for their metabolism. The loss of ions through leaching is reduced by that. That negative charged surface also functions to immobilize pollutants such as heavy metals or polycyclic aromatic hydrocarbons. The ability to sorb cations is called cation exchange capacity [10]. The ability to sorb anions is called anion exchange capacity. Both, AEC and CEC are linked to soil pH. CEC decreases when soil pH drops and increases when the soil pH rises. The opposite is the case for AEC. Soils with a high CEC have a high buffering capacity for positive charged nutrients and pollutants. Generally sandy soils show a low CEC compared to soils with high clay content [3]. The CEC of biochar is not as high as that of humus with a range from several cmol per kg to a few tens cmol per kg. Aged, oxidized biochars may have higher values up to a few hundred cmol per kg because with the oxidation process carboxyl groups return and as a result CEC and surface reactivity increase.

One of the most important qualities of biochar is its high porous structure with the resulting high specific surface area. The specific surface area varies from some cm^2 per g to some hundred m^2 per g, compared to industrial filters, which have surface areas from 1000 up to 2500 m^2 per g. That porosity and high specific surface area improves the soil-moisture holding capacity. Water and nutrients, which are dissolved in that water, are stored in biochar [9]. The diameter of the biochar pores vary from <0.9 nm in nanopores to >50 µm in macropores [14]. Microorganisms are typically 0.5 to 5 micrometre in length, therefore, it has been hypothesized since the early days of biochar research that the macro- and micropores may serve as a habitat for microorganisms where they are protected from e.g.

desiccation. The application of biochar creates new habitats and causes positive changes in environment for soil organism [5].

The chemical and physical properties vary according to the feedstock and pyrolysis conditions. Biochars, which are produced at higher temperatures (>550°C) have a higher surface area (>400 m^2 per g), an increased aromatic composition and good adsorption properties. In contrast, lower temperature (250-400C°) biochars have higher yield recoveries and more ion exchange functional groups that can serve as nutrient exchange sites after oxidation [13]. While the pyrolysis process as biomass is heated, functional groups decrease because of decarboxylation. Water and carbon dioxide are eliminated and the carbon concentration of biochar increases while oxygen and hydrogen decrease. The surface chemistry changes and becomes less reactive.

It is also important to consider possible negative impacts on the environment by the application of biochar to soil, for instance the presence of heavy metals, dioxins or polycyclic aromatic hydrocarbons. While the presence of heavy metals is caused by the feedstock, PAHs and dioxins may be formed during biochar production. These are by products of incomplete combustion process. To avoid high heavy metal concentrations, it requires feedstocks, which are low in heavy metal concentrations. The PAH concentration of biochars is influenced by the pyrolysis conditions such as temperature, time, production process and feedstock. Therefore, it is important to find ideal conditions for biochar production. The highest PAH concentrations have been observed in biochar produced at lower temperatures and shorter pyrolysis time. In order to avoid any risk, heavy metal and PAH concentration should always be carefully measured and quality tested before use as a soil amendment [4].

In many cases, the simplest and most cost effective method for contaminated soil remediation is to remove the source of contaminant by different ways like excavation or by immobilization of the soil pollutant. This study focuses on the immobilization of pollutants such as heavy metals or polycyclic aromatic hydrocarbons with biochar. The negative charge over the surface of biochar attracts positively charged metals and organic compounds, such as PAHs, to the internal biochar surface from the soil solution. The concentration of pollutants in the soil solution is reduced and, by that, the availability for organism uptake decreases.

There are different adsorption mechanisms between biochar and heavy metals including electrostatic attraction, ion exchange, surface mineral adsorption, cation-π interactions and precipitation of surface functional groups. Negatively charged biochar surface and the positively charged heavy metals cause electrostatic attraction. Biochars produced at lower pyrolysis temperatures show stronger electrostatic attraction because of the higher amount of functional groups compared to those produced at higher temperatures. Ion exchange depends on the cation exchange capacity and was found to be one of the main mechanisms involved in the adsorption process. Biochar feedstocks contain mineral compounds including calcium (Ca), silicon (Si), and manganese (Mn), which accumulate in the form of ash on biochar surface during pyrolysis process. That mineral component on the biochar surface has a high adsorption capacity and high affinity for heavy metals. Cation-π interaction is a complex combination of electrostatic adsorption and π-π conjugation and depends on the

aromaticity (which can be defined as the total proportion of aromatic carbon) of the biochar's surface [16].

With increasing pyrolysis temperature and increasing pyrolysis time, the structure becomes more aromatic and the adsorption capacity becomes higher. Surface functional groups are another important factor in metal adsorption. Hydroxyl, carboxyl and phenolic groups can form complexes easily with heavy metals. Precipitation of heavy metals at biochar is caused by two aspects. First, the addition of biochar increases the soil pH, which leads to a decreased mobilization of metals and metal-hydroxide precipitates are formed. Second, various phosphate and carbonate precipitates are formed under different conditions [16]. Organic pollutants, including PAHs, adsorb to biochar by three main mechanisms. The first mechanism is the interaction of π-electrons from the PAH aromatic ring and those of biochar surfaces. Second, are the biochar nanopores, which are important sorption sites for PAHs. Third and least mechanism is phase partitioning, which may play a role. During the use of biochar for heavy metal and PAH immobilization, all those mechanisms act together to immobilize pollutants in soil and soil solution and decrease the availability for organism uptake [5].

1.2.2 Compost

Composting is a controlled biodegradation process of a substrate mixture, carried out by microorganisms under aerobic conditions and in the solid state. It is an exothermic process, producing energy in form of heat, which results in an increase of the biomass temperature. At the end, the composting process leads to the production of carbon dioxide, water, minerals and stabilized organic matter, which is named compost. During the composting process, fresh organic matter undergoes three phases. First phase is called decomposition, where easily degradable organic matter is oxidized. In the second phase, the stabilization phase, slowly degradable organic matter is stabilized through mineralization and other, more complex processes, like humification of ligno-cellulosic compounds, are included. The last step is the incomplete process of humification. The composting process is stopped at a phase where organic matter is still present in a large quantity. Otherwise the composting process would continue, until all of the organic compounds are completely mineralized. The transformation process of fresh organic matter into compost is carried out for three main reasons. First, to reduce the presence of organisms, which are pathogenic to humans, animals and plants. Second, to overcome the phytotoxicity of non-stabilized fresh organic matter. The third reason is to produce an organic fertilizer and soil conditioner, recycling organic wastes and biomass.

The major compounds found in compost substrates are lignin, cellulose, hemicellulose, murein and chitin. Lignin is the major structural component of plants, and is degraded the slowest. The content of lignin in wood varies from 18-30 %. Cellulose is found in almost every type of organic waste and is the most abundant component of plants. The most important hemicelluloses are xylan, pectin and starch. Xylan is the most important of them and found in straw, wood and bagasse. Murein is the main component of the cell wall of most bacteria. Chitin is the most important compound in the cell walls of fungi and the main component, which makes up the exoskeleton of insects and crustaceans. During composting process, about 50 % of the biodegradable organic matter is converted into H_20 and CO_2,

mineral salts and energy. About 20 % the organic matter undergoes complex metabolic processes which results in the production of humic-like substances. The degradation of the remaining 30 % of organic matter by aerobic and anaerobic processes results in the production of less complex organic molecules. The loss of organic matter during the composting process varies between 30-60 %, depending on the composting parameters including length of the process, quality of the fresh organic matter, system of composting, aeration system, temperature, moisture content, hydrogen ion level (pH), particle size and carbon to nitrogen ratio [17].

The application of compost as soil amendment has many physical, chemical and biological benefits. Physical benefits include the improved soil structure, density and porosity, which increases the gas and water permeability and supports the plant root environment. The soil binding properties of compost is based on the humus content, which is very stable and acts as a soil glue. As a result, the soil particles hold together, which makes them more resistant to erosion and give soil a higher ability of holding moisture. Chemical properties are improved by different factors. Compost contains different macro- and micronutrients, essential for plant growth. Plants are supplied with nutrients over a longer period of time in a slow released form, since the sources of organic matter in compost are relatively stable. The cation exchange capacity and the pH are also improved by using compost as soil amendment. A higher CEC allows soils to retain nutrients longer and provides a higher bioavailability for plant uptake. Nutrients are also more protected from leaching off the soil by a higher CEC. The addition of compost may also modify and stabilize the soil pH, depending on the compost pH and on the native soil [18]. This influences the heavy metal mobility, in both ways, positively and negatively. A higher pH decreases the metal mobility, while a lower pH increases the mobility [19]. Among biological benefits is the improved soil biota. The use of compost as soil amendment affects both, diversity of soil microorganisms and the size of the microbial communities [20]. The activity of soil organisms is essential for productive soils and for plant growth. By the addition of fresh compost, energy sources are brought into soil, which provide the microbial population and by that, the soil biota and the activity of soil organisms can be improved [18].

There are several positive effects on contaminated soils by addition of fresh compost. The organic materials enhance biodegradation of pollutants by improving soil texture and oxygen transfer. Specific soil microorganisms, which are capable to degrade natural humic substances, are responsible for the co-metabolic degradation of pollutants such as polycyclic aromatic hydrocarbons [21]. Some studies by Sayara et al. showed, that a large range of PAHs can be degraded by different composts up to 90% in a time range of 30 days [22] [23]. All that properties justify the use of compost as sustainable soil amendment, which improves the health of microbial soil populations and supplies the reduction of soil pollutants such as PAHs.

1.2.3 Lime

Agricultural lime is a soil additive, based on calcium or magnesium oxide, carbonates and hydroxides. The main component of naturally occurring limestone is calcium carbonate ($CaCO_3$). Lime is added to soil in order to neutralize soil acidity caused by hydrogen and aluminium ions. That increases activity of soil bacteria and immobilizes heavy metals in soil

solution. Lime also supplies the soil with plant growth supporting nutrients such as magnesium or calcium [24]. The addition of lime and the resulting increased soil pH causes heavy metals to precipitate as metal carbonates, hydroxides or oxides, which decreases heavy metal solubility [25].

1.2.4 Combined amendments

The use of combined additives for in-situ application figured out as a suitable and relatively low cost soil remediation measure to reduce the bioavailability of pollutants. Various amendments including phosphate compounds, liming materials, metal oxides and organic materials have been examined to immobilize pollutants such as heavy metals in contaminated soils [26]. This study focuses on biochar and compost as organic amendments. Organic pollutants and metals are sorbed to biochar, which decreases transfer to deeper soil and to groundwater, while compost improves soil quality and increases the microbial activity, and by that, supports the degradation of organic pollutants such as polycyclic aromatic hydrocarbons. Biochar increases soil moisture and prevents soil nutrients and pollutants of leaching into the groundwater. Furthermore, the use of biochar for soil remediation stores carbon over at least some hundred years, which constitutes another benefit concerning the reduction of greenhouse gases and the risk of global warming. In order to ensure a safe application, it is necessary to control the quality of the soil amendments to predict health risks for environment and humans. [8] [22].

1.3 Aims of the study

1.3.1 Objectives

The general objectives comprise

- the investigation of the influence of soil amendments such as biochar, compost and lime on the mobility of selected metals and polycyclic aromatic hydrocarbons
- and to reveal the extent to which the movement of the pollutants towards groundwater is prevented by the introduction of those organic and mineralic auxiliaries.

1.3.2 Experimental approach

The experimental approach comprises

- incubation studies using soil microcosms to monitor the dissipation and immobilization of PAHs and the immobilization of metals in the presence of various soil amendments
- and leaching studies using soil lysimeters for testing the mobility change of contaminants such as metals and PAHs upon addition of soil amendments.

1.3.3 Working hypothesis

Soil amendments as biochar or lime will reduce the mobility of contaminants due to

- adsorption mechanisms, which immobilize contaminants such as metals and PAHs
- the capacity to increase the soil pH, which causes a reduction of the metal mobility.

The application of compost will reduce the mobility of contaminants due to

- a stabilized soil pH and an improved microbial activity as a result of the addition of nutrients and the increased number of soil organisms, which help to degrade organic soil contaminants such as PAHs.

The combined in-situ application of biochar, lime and compost will help to reduce pollutants such as metals and PAHs in low to moderately contaminated soils.

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2 Methods

2.1 Experimental set-up

2.1.1 Lysimeter set up for soil pore water sampling

The lysimeter set up for soil pore water sampling was performed in the greenhouse at the AIT Tulln. The set-up, shown in *Figure 2*, consisted of 10 different treatments with four replicates. For the lysimeter construction, polyvinylchloride (PVC) columns with a diameter of 20 cm and a length of 80 cm were used. The PVC columns were lined with Teflon, to avoid sorption of the PAHs. A two-meter PVC bar was fixed on one column, with two one-liter water collection bottles fixed on it at a height of 130 cm, to supply two lysimeter with fresh water at the same time. From the bottom side of the water collection bottle, a tube led to the upper side of the lysimeter in order to wet the surface of the soil. To control the water flow, a clamp was fixed on the tube.

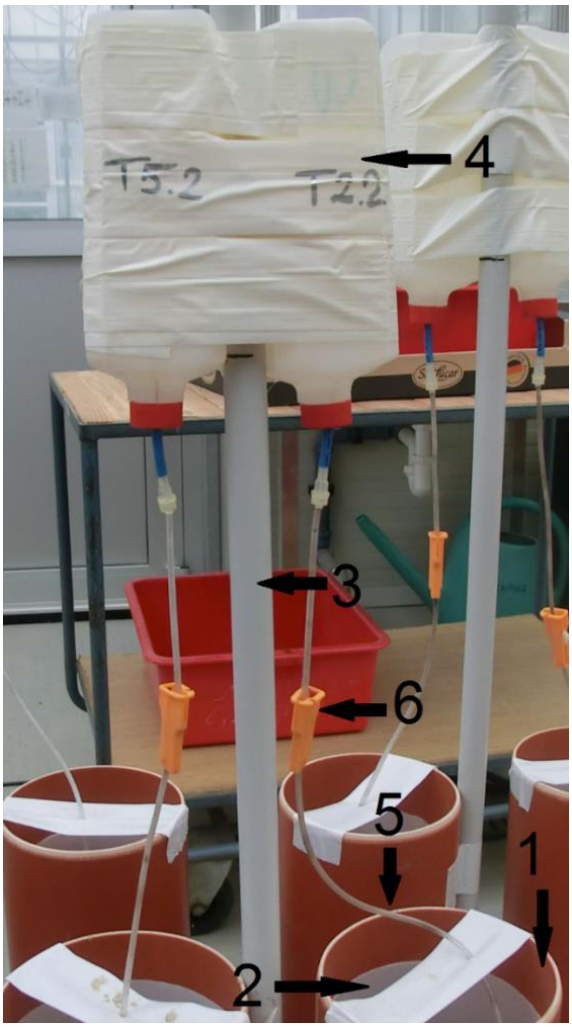

Figure 2: For the lysimeter construction, polyvinylchloride (PVC) columns (1) were lined with Teflon (2), to avoid sorption of the PAHs. A two-meter PVC bar (3) was fixed on one column in order to hold the two one litre water collection bottles (4) and a tube (5), which leads to the upper side of the lysimeter in order to wet the soil surface. A clamp (6) was fixed on the tube, to control the water flow.

The soil surface was covered with a water permeable fleece, to homogenize the water distribution over the soil surface, illustrated in *Figure 3*.

Figure 3: Water permeable fleece (7) to homogenize the water distribution over the soil surface.

At the bottom side there was a perforated plate, connected with a tube to a one liter leachate collection bottle. The bottom opening was closed with a PVC cap, with a hole in it for the tube coming from the suction plate. Five collection bottles were connected with a buffer bottle to a cluster, illustrated in *Figure 4*. Four of these clusters were connected together with a tube in a row. The tube led to a vacuum pump, which generated a negative pressure about 200 hPa.

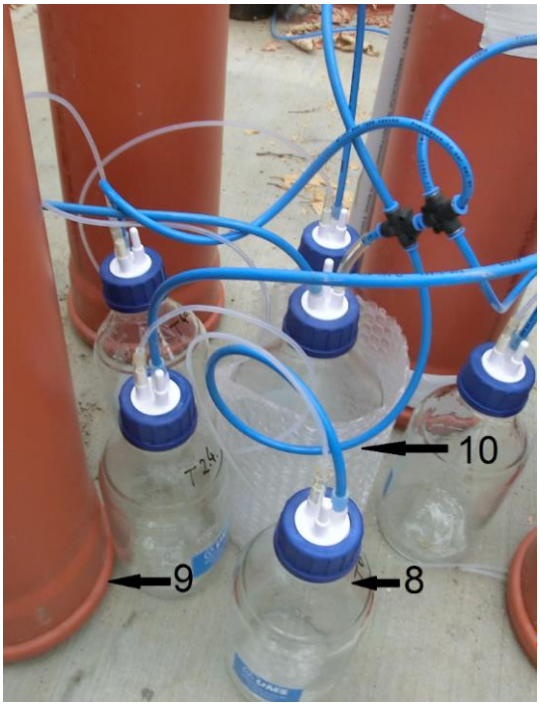

Figure 4: The bottom opening was closed with a PVC cap (9). Five collection bottles (8) were connected with a buffer bottle (10) to a cluster.

There were two rows with 20 lysimeter in each row, illustrated in *Figure 5*. Each of the four columns of one treatment was filled with soil, which had been mixed before in a defined composition.

Figure 5: Two rows with 20 lysimeter each, which resulted in 40 randomly placed lysimeters.

2.1.2 Soil incubation experiment with amendments in Erlenmeyer flasks

The experimental set up for soil sampling was also performed in the greenhouse at the AIT Tulln. Each of the four Erlenmayer flasks was filled with about 1 kg of soil. The flasks were covered with aluminium foil, to protect the sample from light and was closed with a cotton plug, illustrated in *Figure 6*.

Figure 6: Soil incubation experiment with amendments in Erlenmeyer flasks 1.0 l Erlenmeyer flasks were covered with aluminium foil and closed with cotton plug.

2.2 Soils and amendments

Two different soils, Eschenau and Treffling, were used for the set-up. The soil from Eschenau, which is in Lower Austria, is a not contaminated arable soil from a farmland. It is a sandy soil with a pH about 5.4 see *Table 2*. The soil was mixed with biochar, aged (oxidized) biochar and compost in a certain composition, which is shown in the *Table 1* below. The Eschenau soil was spiked with zinc, cadmium, pyrene and phenanthrene. The initial concentrations of the PAHs were set to 100-ppm pyrene and 100-ppm phenanthrene. The

initial concentrations of heavy metals were 1000-ppm zinc and 10-ppm cadmium. The heavy metals, zinc and cadmium were added as nitrates. Additionally, treatment two was mixed with 1 % lime in form of calcium carbonate to puffer the soil. There was also one control treatment.

Table 1: Soil composition of the 10 different treatments. Treatment 2 contained 1 % lime. The initial concentrations of heavy metals were 1000-ppm zinc and 10-ppm cadmium. The concentrations of additional PAHs were 100-ppm pyrene and 100-ppm phenanthren.

Treatment	Soil	Amendments			Zn, Cd added	PAHs added
		Lime	Biochar [%]	Compost [%]		
1	Eschenau (Control)	no	0	0	yes	yes
2	Eschenau	yes	0	0	yes	yes
3	Eschenau	no	0	10	yes	yes
4	Eschenau	no	5	0	yes	yes
4a	Eschenau	no	5 (aged)	0	yes	yes
5	Eschenau	no	5	10	yes	yes
5a	Eschenau	no	5 (aged)	10	yes	yes
6	Eschenau	no	5	10	no	yes
7	Treffling	no	5	10	no	no
8	Treffling (Control)	no	0	0	no	no

The Treffling soil origins from a mixed contaminated site next to Linz, from a former clay target shooting range. The soil is field contaminated with zinc, cadmium and PAHs and was not spiked. The use of clay targets caused a contamination with polycyclic aromatic hydrocarbons (PAHs). The dominant soil type is pseudogley, a clayey soil mostly free from lime with a high content of humus and a pH <4.6 see *Table 2*. The low pH increases the mobility of heavy metals, which enables the movement of metals deeper into soil and into the ground water [27]. This soil was mixed with biochar and compost, which is shown in the *Table 1* below. There was also one control treatment.

Table 2: Characteristics of the two different soil.

Soil	Soil type	pH	Humus content
Eschenau	Sandy	5.4	Low
Treffling	Pseudoclay	<4.6	High

The biochar type MSP550, produced under pyrolysis process with *miscanthus* straw pellets as feedstock, was used. The peak temperature of the pyrolysis process was about 550°C and the mean pH of the produced biochar about 9.77. This type of biochar is well characterized, readily available and good reproducible. The compost was produced at a composting plant in Pixendorf, with a mean pH about 7.5 [28].

For the evaluation of the concentration of a soil pollutant, different tables with limit values, test values and threshold values exist. *Table 3* illustrates the different preventive threshold values for heavy metals and organic pollutants in different soil types [29].

Table 3: Preventive threshold values for heavy metals (aqua regia digestion) and PAHs in soil in mg/kg DM [29].

Type of soil	Zinc [mg/kg] DM	Cadmium [mg/kg] DM	16 EPA PAHs [mg/kg] DM
Sandy soil	60	0,4	-
Loamy/ silty soil	150	1	-
Clayey soil	200	1,5	-
Humus content > 8%	-	-	10
Humus content ≤ 8%	-	-	3

Table 4 illustrates Austrian orientation values concerning metal concentrations in the topsoil (0-20 cm) for agricultural or horticultural use. Additionally the metal limit values for permanent grassland soil are in that table [30].

Table 4: Orientation and limit values for heavy metal concentrations in soils [30].

Soil	Zinc [mg/kg] DM	Cadmium [mg/kg] DM
Soil for agricultural or horticultural use	300	1
Permanent grassland soil	150	1

2.3 Sampling

The samples were taken after about 0, 0.5, 1, 2, 4 months. The temperature in the greenhouse was between 15°C and 25°C with a relatively constant humidity. The soil moisture content was held between 65-75 % of field capacity. The soil sampling was performed one week before the soil pore water sampling. The actual sampling timeline is illustrated in *Figure 7.*

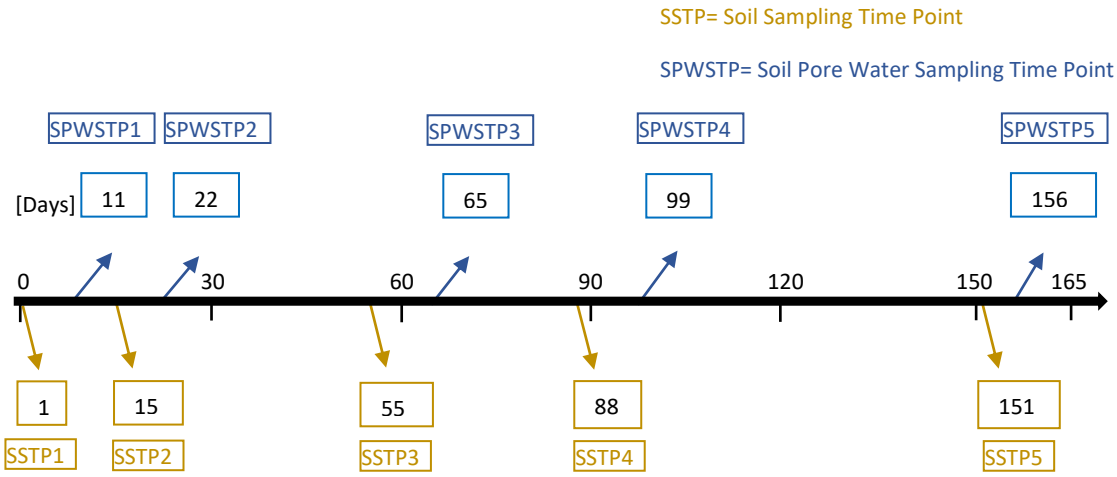

Figure 7: Timeline of the soil and soil pore water sampling time points.

2.3.1 Soil pore water sampling

For the soil pore water sampling, about 1200 ml of fresh water were filled in the water collection bottles and the water flow was adjusted to about one droplet per second. The vacuum pump was turned on to generate a negative pressure of about 200 hPa in order to draw the fresh water through the contaminated soil and into the collection bottles. About 1000 ml of leachate were collected and stored at 4°C in the cooling room.

2.3.2 Soil sampling

The soil was homogenized with a long spoon in the Erlenmayer flask and about 100 g soil sample was collected in a 100 ml LDPE vessel. The samples were stored in the freezer at -20 °C.

Figure 8: Air dried soil was sieved with a 2.00 mm soil sieve.

Before analysis, the soil was dried at 60 °C for 24 hours and sieved with a 2.0 mm soil sieve to obtain homogenous soil particles and to sort out plastic residues and wood (see *Figure 8*).

2.4 Methods in the analysis of soil

2.4.1 Determination of acidity

Acidity or pH- value was determined with 20 g of dried, sieved soil sample, which was transferred into a 100.0 ml LPDE vessel and suspended with 50 ml of a 0.01 M calcium-chloride solution. The suspension was homogenized on an Edmund Bühler GmbH SM30 shaking plate for 2 hours at 230 rpm. After the homogenization, the pH was measured with a WTW inoLab pH-meter. The calibration of the pH- meter had to be controlled with calibration fluids at pH 4 and pH 7. The calibration fluids had to warm up to room temperature before the control of the pH-meter was started. While measuring, the sample was mixed with a magnetic stirrer to guarantee homogenization [31].

2.4.2 Determination of electric conductivity

10.0 g of sieved soil sample was transferred into 100 ml LPDE vessel and 100 ml deionized water was added. The suspension was homogenized on an Edmund Bühler GmbH SM30 shaking plate for 1 hour at 230 rpm. Then, the electric conductivity was determined with a WTW inoLab conductivity meter. While measuring, the suspension was homogenized with a magnetic stirrer. The unit of the results is µS/cm [32].

2.4.3 Determination of polycyclic aromatic hydrocarbons in soil

For the determination of the dry mass of the sieved soil sample, 5 g were dried at 105°C for 24 hours. The dried sample was weighted again and the difference used to calculate the dry mass. For determination of polycyclic aromatic hydrocarbons in soil, 10 g of sieved soil sample was transferred into an extraction thimble. Some glass wool was used, to keep the soil in the thimble during the extraction process. The Soxhlet apparatus, which is illustrated in *Figure 9*, was assembled, the thimble was transferred into the upper reservoir of the return tube and 120 ml of ethyl acetate were added.

Figure 9: Soxhlet apparatus for the extraction of polycyclic aromatic hydrocarbons from soil.

Water for cooling and heating mantles were turned on at level 7-8. The samples were heated for 6 hours. After cooling to room temperature, the samples were transferred into

100.0 ml volumetric flasks and filled up with ethyl acetate to the mark. 1.0 ml was transferred into a vial for analysis with an Agilent 1100 Series HPLC. A hydrophobic C-18 column for separation was used. The detection was performed with a fluorescence detector and a diode array detector. For the calibration standard calibration solutions with different concentrations were used. The samples were stored at 4 °C in the cooling room. The unit of the results is mg/kg DM (Dry Mass) [33].

2.4.4 Soil extraction of mobile metals

For the determination of the mobile zinc and cadmium concentration, 20 g of dried and sieved soil were extracted for 1 hour with 20.0 ml of 1 M ammonium nitrate solution. After the extraction, the solution was filtered through a Whatmann GE Healthcare Life Sciences 589/2 white ribbon filter and collected in a 50 ml LPDE vessel. The first five droplets were disposed because of particles, which could affect the analysis. 500 µl of 65 % nitric acid for stabilization were added. The samples were measured with a Perkin Elmer Analyst Atomic Absorption spectrometer. For the dilution and the blank, high quality water was used. For the calibration, calibration standard solutions from 0.5 ppm to 2 ppm were used. The unit of the results is mg/kg DM [34].

2.4.5 Aqua regia digestion for total heavy metal determination

For the total metal determination, 2 g of dried and sieved soil sample was transferred into a 100.0 ml volumetric flask. 15 ml of 12 M hydrochloric acid and 10 ml of 15.8 M nitric acid were added. The samples were heated for 30 minutes at 60 °C on an Electrothermal heating plate, 2-3 droplets octanol were added, to avoid the generation of foam. The sample was then cooked at 135 °C for 2 hours, till all nitrous gases were driven out. The sample was cooled down to about 40 °C and filled up with deionized water to 100.0 ml mark. 1 ml of the sample was transferred into a 1.0 ml sample vial and the analysis of heavy metal concentration was performed with a Perkin Elmer AAnalyst Atomic Absorption spectrometer. If necessary, the leachate samples were diluted with high quality water. For the calibration, standard solutions from 0.5 ppm to 2 ppm were used. The unit of the results is mg/kg DM [35].

2.4.6 Sequential extraction for the fractionation of heavy metals

To assess the chemical form of heavy metals in soils, sequential extraction was applied. For step one, 2 g of sieved soil sample was transferred into a 100 ml LDPE vessel and 80 ml of a 0.11 M acetic acid were added. The sample was shaken for 16 hours over night. The solution was filtered through a Sartorius 0.45 µm filter, transferred into a 100 ml LPDE vessel and stored at 4°C in the cooling room. The remaining soil sample was dried at 60 °C over night for 12 hours and the remaining soil weighted in again into a fresh 100.0 ml vessel. In step two, the residues of step one were suspended with 80 ml of freshly prepared 0.5 M hydroxylamine hydrochloride solution. The extraction procedure was performed as described in step one. In the third step, the residues of step two were mixed with 20 ml of 8.8 M hydrogen peroxide. Small aliquots were carefully added. The vessel was covered with a clock glass and the sample was digested at room temperature for 1 hour. Then, the vessel was heated with a HERA-US oven at 85 °C for 1 hour. The volume was reduced to less than 3 ml by further heating without clock glass. Again, 20 ml hydrogen peroxide were added and

the digestion procedure was repeated. Next, 100 ml of 1 M ammonium acetate were added and shaken as in step 1. The residues were digested with aqua regia. 15 ml of 12 M hydrochloric acid and 10 ml of 15.8 M nitric acid were added.

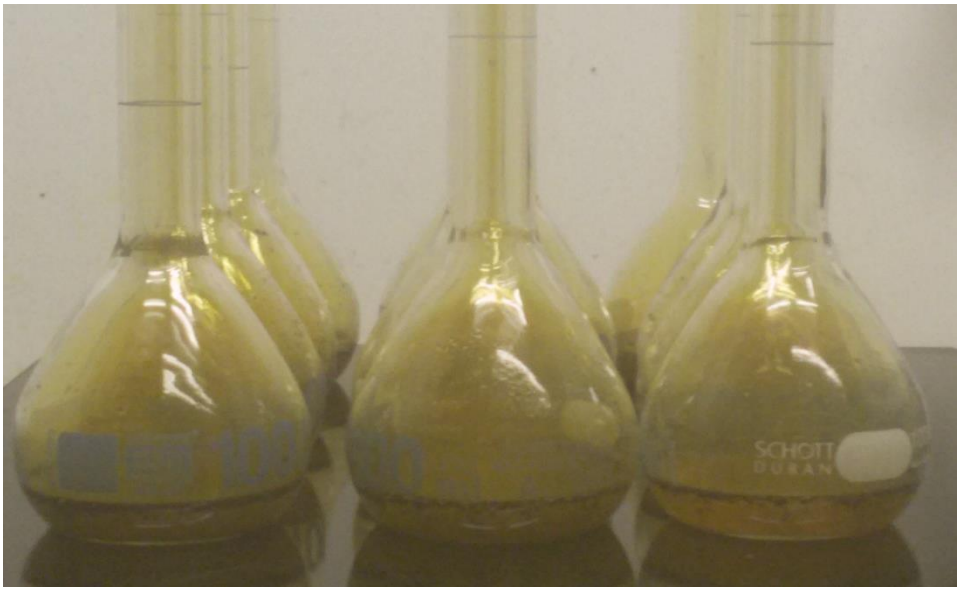

Figure 10: Last step of sequential extraction- aqua regia digestion of soil samples on the heating plate. The yellow vapour origins from nitrous gases, which were driven out.

The samples were heated for 30 minutes at 60 °C, 2-3 droplets octanol were added, to avoid the generation of foam. The sample was then cooked at 135 °C for 2 hours, till all nitrous gases were driven out (see *Figure 10*). The sample was cooled down to about 40 °C and filled up with distilled water to 100.0 ml mark. For the calculation of the extraction efficiency, another aqua regia digestion was performed without the other step described before. The analysis of heavy metal concentration was performed with a Perkin Elmer AAnalyst Atomic Absorption spectrometer. If necessary, the pore water samples were diluted with high quality water. For the calibration, standard solutions from 0.5 ppm to 2 ppm were used. The unit of the results is mg/kg DM [36].

2.5 Methods in the analysis of soil pore water

2.5.1 Fluid-fluid extraction of polycyclic aromatic hydrocarbons in soil pore water

500 ml of leachate sample were mixed with 12.5 ml n-hexane and extracted for one hour. Next, the aqueous and the organic phase, which should contain the extracted PAHs, were separated with a separating funnel. About 2 g of sodium sulphate were used to dry the sample 30 minutes from water. The extract was transferred into a 25.0 ml reducing flask and then concentrated with a Heidolph ind. Laborota 4000- efficient rotary evaporator to less than 2.0 ml at 30 °C and 200 hPa. After that, 250 µl N,N- dimethylformamid and 500.0 µl acetone for homogenization were added. Hexane and acetone wereremoved with a Techne sample concentrator under a low nitrogen stream to 200-250 µl. The concentrated extract was transferred into a 1.0 ml volumetric flask and filled up to 1 ml with ethyl acetate. The extracted leachate samples were stored in a HPLC vials at 4 °C. The analysis of 16 PAHs was performed with an Agilent 1100 Series HPLC equipment. A hydrophobic C-18 column was

used for that chromatography. The detection was performed with a fluorescence detector and a diode array detector. For the calibration, standard solutions with different concentrations were used. The units of the results are mg/l or µg/l [37].

The samples 6.1-8.4 of the time points T3 and T4 were analysed by the MAPAG company in Gumpoldskirchen because the values of PAHs were under the limit of detection at the AIT. The limit of detection with the Agilent 1100 Series HPLC equipment is 13.33 µg/l for pyrene and 10.0 µg/l for phenanthrene.

The samples 1.1-5a.4 were extracted as described above with n-hexane and dried with 2 g of sodium sulphate. 20.0 µl of a marker for pyrene and phenanthrene determination was added. The analysis was performed by Gabriel Sigmund at the Faculty of Earth sciences, Geography and Astronomy on University of Vienna.

2.5.2 Analysis of heavy metals in soil pore water

For the analysis of heavy metals in soil pore water, 50 ml sample solution was transferred into a 50 LPDE vessel and 500 µl of a 65 % nitric acid was added. Cations are more stable at an acid pH. 1 ml of the sample was transferred into a 1.0 ml sample vial and the absorption was measured with a Perkin Elmer AAnalyst Atomic Absorption spectrometer. If necessary, the leachate samples were diluted with high quality water. For the calibration, standard solutions from 0.5 ppm to 2 ppm were used. The unit of the results are mg/l [34].

2.5.3 Determination of soil pore water acidity

For the determination of the acidity, 10 ml of soil pore water was transferred from the soil pore water collection bottle into a 22 ml Supelco PTFE vessel and measured at room temperature with the WTW inoLab pH- meter. The calibration of the pH- meter had to be controlled with calibration fluids at pH 4 and pH 7. The calibration fluids had to warm up to room temperature before the control of the pH-meter was started.

2.5.4 Determination of dissolved organic carbon in soil pore water

About 10 ml of soil pore water from the collection bottle was filtered through a Sartorius 0.45 µm filter to clean it and make it free of particles. The blank was measured with deionised water before measuring the samples. For the determination of dissolved organic carbon, 1 ml of the cleaned sample was transferred into a quartz cuvette and measured with a Varian Cary 3C UV- Visible spectrophotometer at 254 nm. For dilution, deionised water was used. The unit of the results is mg/l. For the calculation of the dissolved organic carbon concentration, the following formula was used by Brandstetter is used:

DOC [mg/l] = 0.46 *Absorbance + 1 (for 1 meter cuvette length) [38]

2.5.5 Determination of electric conductivity of soil pore water

For the determination of electric conductivity, 10 ml of soil pore water sample was transferred from the collection bottle into a 22 ml Supelco PTFE vessel and measured at room temperature with WTW inoLab conductivity meter. The unit of the results is µS/cm.

2.6 Statistical assessment

First, statistical outliers of the analyses datasets were eliminated with the Dixon's Q test for outlier identification after the following formula:

$$Q = \frac{[x_2 - x_1]}{[x_n - x_1]}$$

x_1= is the smallest value

x_2= is the second smallest value

x_n= is the largest value

Q= rejection quotient

If Q value had been higher than the critical value (for a level of significance α=0.1 and a number of values n=4) 0.679, then the tested outlier was eliminated. Next, the remaining data were statistical analysed with the program *STATISTICA 2013* (StatSoft Inc., Tulsa, Oklahoma). The mean value and standard deviation were calculated for each treatment. Next, every dataset was tested for normality with the Kolmogorow-Smirnow test, with a level of significance α=0.05. If the dataset was not normally distributed, a log linearization was performed to linearize the dataset for the ANOVA. After that, an ANOVA was performed and the homogenous subsets were defined with the Tukey's HSD (Honestly Significant Difference) test, with a level of significance α=0.05.

Finally, the results were arranged in diagrams with the help of the program *SigmaPlot* (Systat Software Inc., San Jose, California). The rate of dissipation of a pollutant is often expressed as a first order half-life or DT_{50}, the time required for 50 % of the initial dose of a pollutant to disappear [39]. For the calculation another program named *CAKE* (Tessella company, Oxfordshire, England) was used. The intension was to perform data processing for all treatments in the same way.

2.7 Materials

2.7.1 Materials for soil analysis

All materials used for soil analysis are listed in *Table 5*.

Table 5: List with materials for soil analysis.

Method	Material
Determination of acidity	VWR international 100 ml LPDE vessel 0.01 M $CaCl_2$ Solution Edmund Bühler GmbH SM30 shaking plate WTW inoLab pH- meter
Determination of electric conductivity	VWR international 100 ml LPDE vessel Deionized water WTW inoLab conductivity meter
Analysis of polycyclic aromatic hydrocarbons in soil	Soxhlet aperture 100.0 ml volumetric flask Glass wool Ethyl acetate Agilent 1100 Series HPLC
Soil extraction of heavy metals	VWR international 50 ml LPDE vessel 1 M ammonium nitrate Whatmann GE Healthcare Life Sciences 589/2 white ribbon filter 65% nitric acid High quality water Perkin Elmer AAnalyst Atomic Absorption spectrometer
Aqua regia digestion for total heavy metal determination	100.0 ml volumetric flask Electrothermal heating plate 12 M hydrochloric acid 15.8 M nitric acid Octanol 1.0 ml Sample vial High quality water Perkin Elmer AAnalyst Atomic Absorption spectrometer
Sequential extraction for the fractionation of heavy metals	0.11 M acetic acid 0.5 M hydroxylamine hydrochloride solution 8.8 M hydrogen peroxide HERA US oven 1 M ammonium acetate 12 M hydrochloric acid 15.8 M nitric acid Octanol High quality water AAnalyst Atomic Absorption spectrometer

2.7.2 Materials for soil pore water analysis

All materials used for soil pore water analyses are listed in *Table 6.*

Table 6: List with materials for soil pore water analyses.

Method	Material
Fluid-fluid extraction of polycyclic aromatic hydrocarbons in soil pore water	N-hexane Magnetic stirrer Separating funnel Sodium sulphate 25.0 ml reducing flask N,N- dimethylformamid Acetone Techne sample concentrator 1.0 ml volumetric flask Ethyl acetate HPLC vials Agilent 1100 Series HPLC equipment Heidolph ind. Laborota 4000- efficient rotary evaporator
Analysis of heavy metals in soil pore water	VWR international 50 ml LPDE vessel 65 % nitric 1.0 ml sample vial High quality water Perkin Elmer AAnalyst Atomic Absorption spectrometer
Determination of acidity	22 ml Supelco PTFE vessel WTW inoLab pH- meter
Determination of dissolved organic carbon	Sartorius 0.45 µm filter Deionized water Varian Cary 3C UV- Visible spectrophotometer
Determination of electric conductivity	22 ml Supelco PTFE vessel WTW inoLab conductivity meter

3 Results

3.1 Results of soil analysis

3.1.1 Polycyclic aromatic hydrocarbons extractable from soil

3.1.1.1 Sum of 16 PAHs

The sum of 16 PAHs was only determined in the treatments 7 (Treffling- biochar + compost) and 8 (Treffling- control), because only the soil Treffling was field contaminated with a broad range of PAHs.

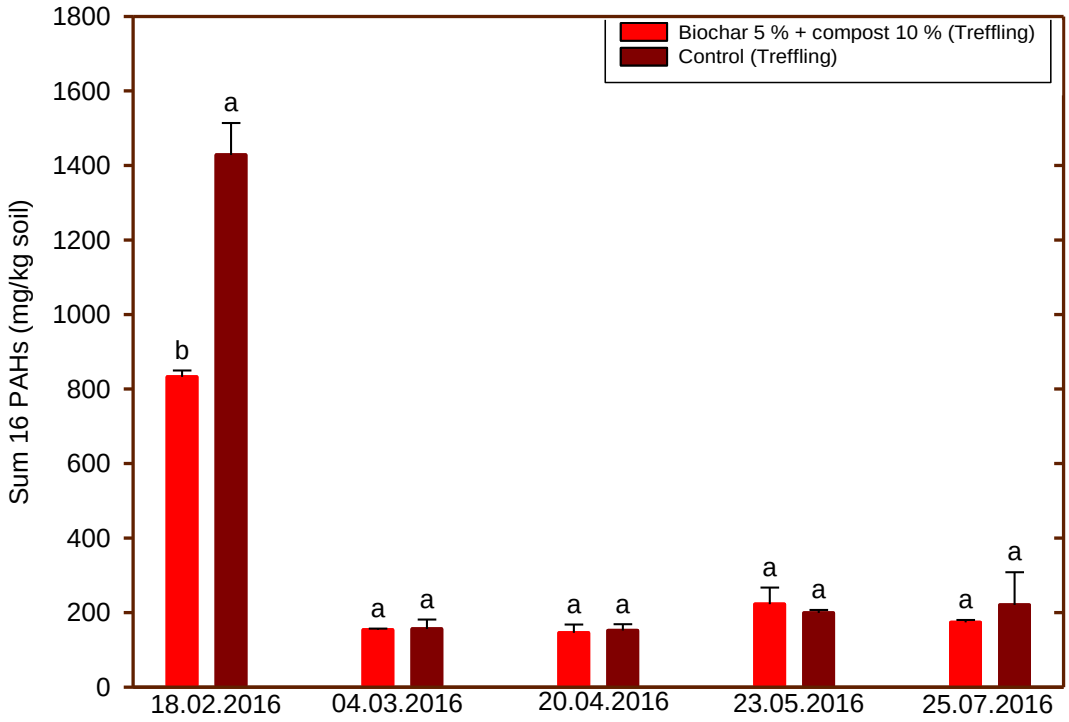

Figure 11: The diagram illustrates the sum of 16 PAHs extracted with ethyl acetate from soil samples over 151 days.

The concentrations of the sum of all 16 PAHs is illustrated in *Figure 11*. After one day, at the first sampling time point, one can see a statistically significant influence between treatment 7 and 8. The concentration of 16 PAHs of the Treffling control treatment 8 was about 1428 mg/kg soil dry mass (DM) at the first sampling time point, which is about 42 % higher compared to treatment 7 (Treffling soil- biochar + compost, without metals) (see *Table 9*). From the second sampling time point, the concentrations stayed almost constant for the next four sampling time points, without significant differences between the two different treatments.

3.1.1.2 Pyrene

Figure 12 shows the extractable pyrene concentration of soil samples over five sampling time points. The treatment 8 (Treffling- control) had with 144 mg/kg soil dry mass an about 30 % higher concentration of extractable pyrene, compared to treatment 7 (Treffling- biochar + compost, without metals), what matches with the results of the sum of 16 PAHs (see *Figure 11*).

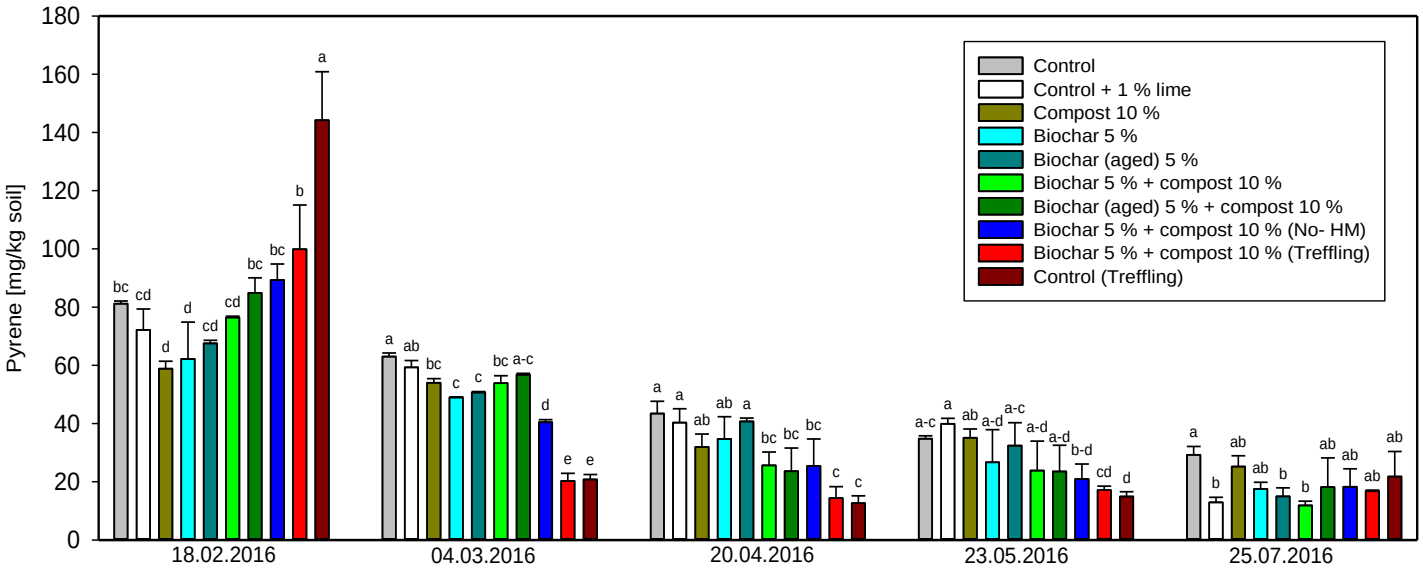

Figure 12:The diagram illustrates the pyrene concentration extracted with ethyl acetate from soil samples over 151 days.

The concentrations of extractable pyrene in the Eschenau soil treatments were under the initial concentration of 100 ppm pyrene.

After one day, at the first sampling time point the concentration of treatment 3 (Eschenau-compost) was about 59 % of the starting concentration. The treatments 3 (Eschenau-compost) and 4 (Eschenau- biochar) reduced the highest amount of pyrene by degradation and immobilization after one day of incubation. The treatments 4.a (Eschenau- aged biochar) and 5.a (Eschenau- aged biochar + compost) showed a 10 % higher content of extractable pyrene compared to the treatments with non-aged biochar (see *Table 10*).

At sampling time point five, after 151 days, the treatments 2 (Eschenau- lime), 4a (Eschenau-aged biochar) and 5 (Eschenau- biochar + compost) showed the lowest extractable pyrene concentrations with about 12-15 mg/kg DM, which is 12-15 % of the starting concentrations. The treatment 1 (Eschenau- control) had the highest extractable pyrene concentration with 29.2 mg/kg soil DM, which is about 29 % of the starting concentration. The treatment 6 (Eschenau- biochar + compost; without metals) showed no significance difference compared to treatments with added heavy metals. The other treatments 3, 4, 5.a, 6, 7 and 8 showed no significant differences with similar results between 18-25 % of the starting concentration at sampling time point five. Between the two treatments with biochar and aged biochar were no significant differences at the last four sampling time points.

3.1.1.3 Phenanthrene

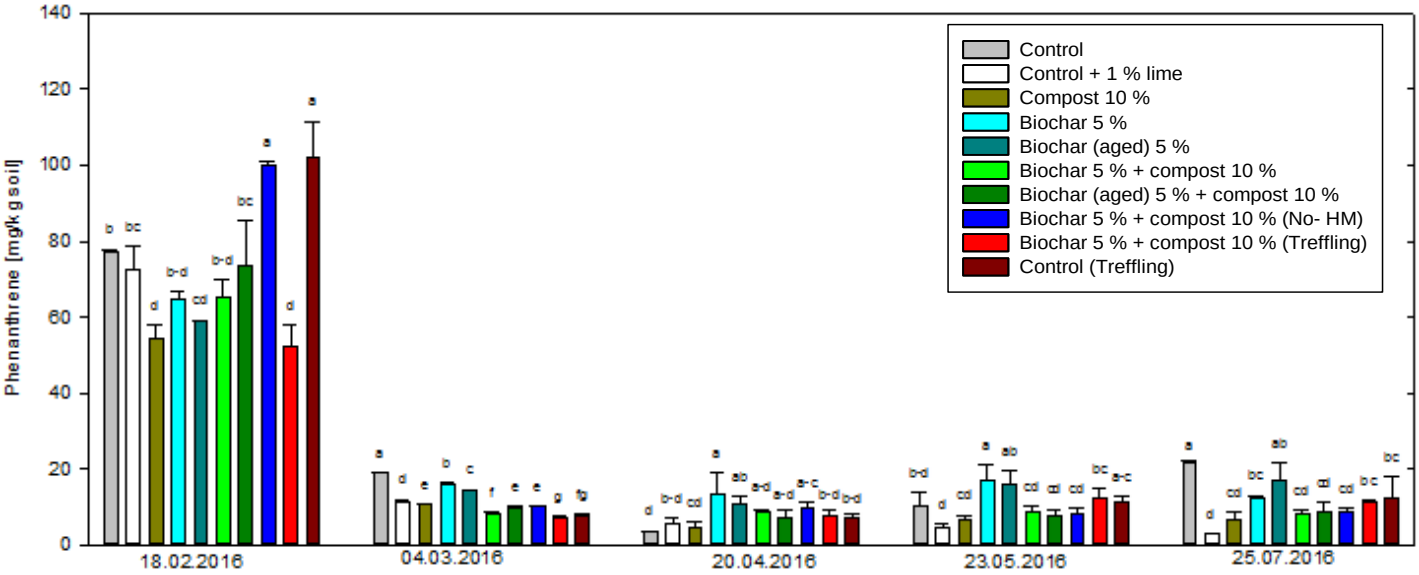

Figure 13: The diagram illustrates the phenanthrene concentration extracted with ethyl acetate from soil samples over 151 days.

Figure 13 shows the extractable phenanthrene concentrations of soil samples over five sampling time points. Treatment 8 (Treffling- control) had with 102.8 mg/kg soil dry mass an about 47 % higher concentration of extractable phenanthrene, compared to treatment 7 (Treffling- biochar + compost, without metals), what matches with the results of the sum of 16 PAHs (see *Figure 11*). The concentrations of extractable phenanthrene in the Eschenau soil treatments were under the initial concentration of 100 ppm, except treatment 6 (Eschenau- biochar + compost; without metals), which maintained the original concentration of 100 mg/kg soil DM.

Among the Eschenau soil treatments, the treatment 3 with compost degraded the highest amount of phenanthrene at the first sampling time point, which is similar to the results of pyrene. After about two weeks, at the second sampling time point, the extractable phenanthrene concentration decreased in all treatments to 7-19 % of the starting concentration (see *Table 11*).

At sampling time point five, treatment 2 (Eschenau- lime) showed the lowest phenanthrene concentration with about 3 mg/kg DM, which presents 3 % of the initial concentration. Treatments 3 (Eschenau- compost) and 5 (Eschenau- biochar + compost), 5.a (Eschenau- aged biochar + compost) and 6 (Eschenau- biochar + compost, without metals) also showed low extractable phenanthrene concentrations with 7-9 mg/kg soil DM. The treatment 6 without added metals showed no significance difference to treatments with added heavy metals. The treatment 1 (Eschenau- control) had the highest extractable phenanthrene concentration with 21.6 mg/kg soil DM. The treatment 4.a (Eschenau- aged biochar) showed a higher concentration, with 17 % of the initial concentration, than the treatment 4 (Eschenau- biochar) with 13 % of the initial concentration.

3.1.2 Soil extractable metals

3.1.2.1 Cadmium

Figure 14 shows the total cadmium content in soil samples at the first sampling time point. The initial concentration was 10 ppm. The results show that the aqua regia digestion had a very high recovery rate between 89 % and 97 % (see *Table 12*). The treatments 6, 7 and 8 were not analysed on cadmium because no cadmium was added (see *Table 1*).

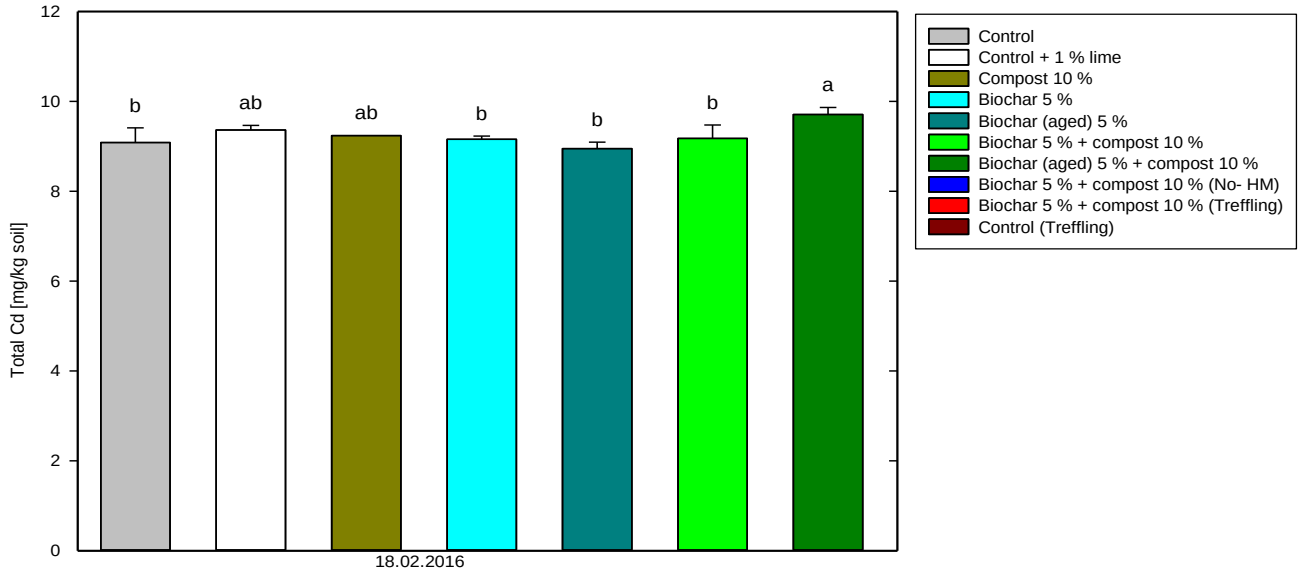

Figure 14: The diagram illustrates the total cadmium content after aqua regia digestion of the treatments 1-5.a.

Figure 15 illustrates the concentration of the mobile fraction of cadmium in soil samples over five sampling time points. Only the treatments with added heavy metals were analysed. Over all sampling time points, there were significant differences of the extractable cadmium concentrations between the different treatments.

At the first sampling time point the Eschenau control treatment had the highest extractable cadmium content with 3.1 mg/kg DM, which is 31 % of the initial concentration (see *Table 13*). The treatments 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) showed lower extractable cadmium concentrations with 2.4-2.6 mg/kg DM. The cadmium concentration of treatment 2 (Eschenau- lime) was 1.0 mg/kg DM. The treatments with compost number 3, 5, and 5.a, showed the lowest extractable cadmium concentrations with 0.5 mg/kg DM, which is about 5 % of the initial concentration.

At sampling time point five, there were no significant differences between the treatment 1 (Eschenau- control) and the treatments 2 (Eschenau- lime), 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) with extractable cadmium concentrations between 3-15% of the initial cadmium concentration. Treatments with compost 3 (Eschenau- compost), 5 (Eschenau- biochar + compost) and 5.a (Eschenau- aged biochar + compost) showed significantly lower extractable cadmium concentrations with 3-15 % of the initial cadmium concentration. The pH values of the different treatments match with the extractable cadmium concentration *(*see *Figure 20*).

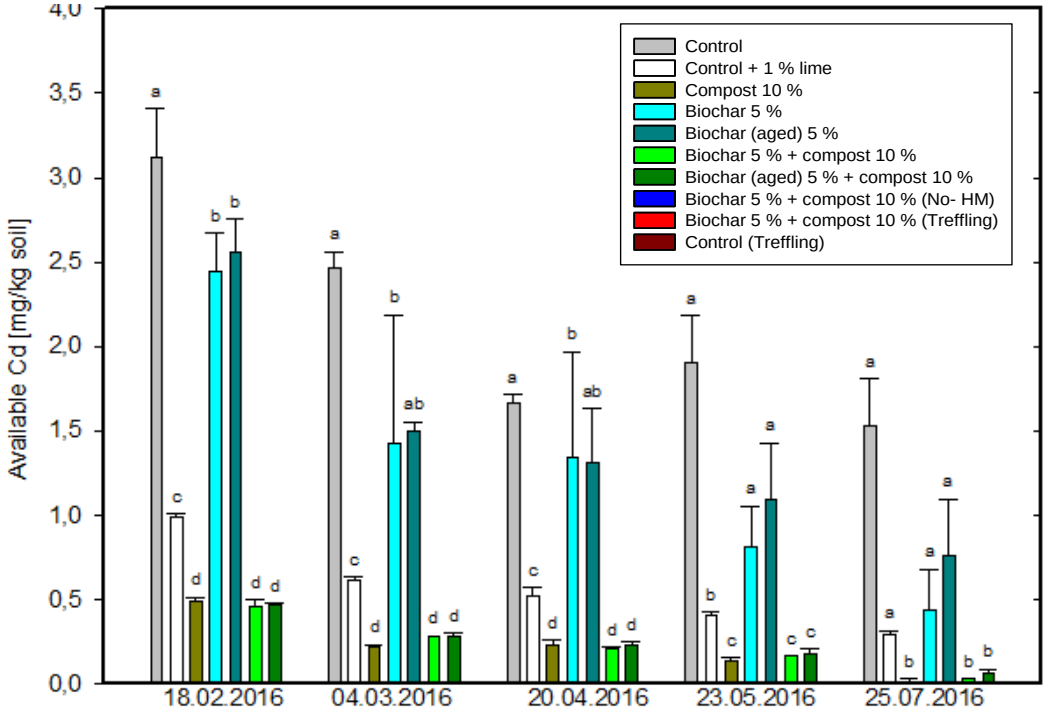

Figure 15: The diagram illustrates the extractable cadmium content after extraction with 1M ammonium nitrate solution.

Figure 16 presents the results of the sequential extraction of cadmium of soil samples. The sum of the cadmium concentration of all steps of the sequential extraction was about 10 mg/kg DM.

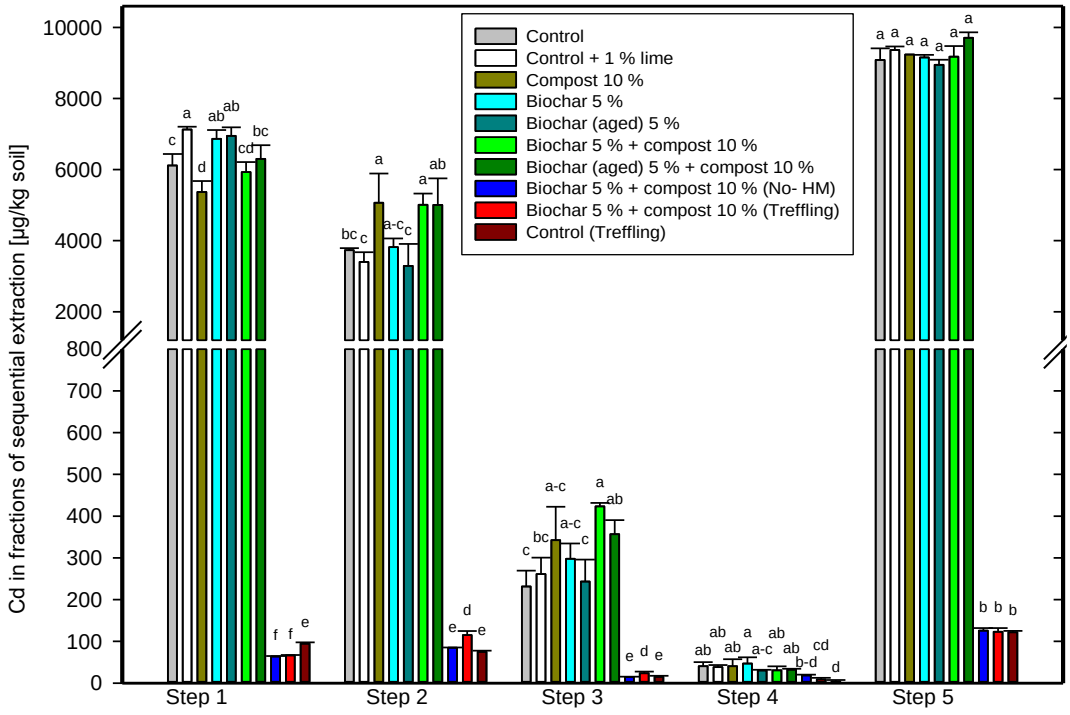

Figure 16: Cadmium fractions after sequential extraction in µg/kg soil DM.

For the calculation of the extraction efficiency, an additional total metal extraction with aqua regia was performed (Step 5). The extraction efficiency was calculated as follows:

Extraction efficiency = [(Step 1 + Step 2 + Step 3 + Step 4)/Step 5] x 100

The extraction efficiency of the sequential cadmium extraction varied between 109-175 % (see *Table 7*). The high recovery values with up to 175 % resulted from the inhomogeneous nature of soil samples. The first step with 0.11 M acetic acid was the extraction of the with carbonates associated and exchangeable fraction. The exchangeable fraction contains extractable metals, which are sorbed on the surface of particles and are mobilized at an acidic pH level.

Table 7: Distribution of the percentage of cadmium between the different fractions after sequential extraction.

Treatment	Step 1 [%] Acetic acid (0.11 M)	Step 2 [%] Hydroxylamine hydrochloride (0.5 M)	Step 3 [%] Hydrogen peroxide (8.8 M)	Step 4 [%] Hydrochloric acid (12 M) + Nitric acid (15.8 M)	Extraction efficiency [%]
T1	67,3	38,7	2,5	0,4	109,1
T2	74,2	36,3	2,8	0,4	113,7
T3	57,5	54,3	3,7	0,4	115,9
T4	74,1	36,3	3,2	0,5	114,1
T4.a	79,3	41,0	3,0	0,3	123,7
T5	64,6	54,6	4,1	0,3	123,6
T5.a	64,9	51,6	3,7	0,3	120,5
T6	52,5	68,0	13,7	12,8	147,0
T7	55,1	93,7	19,4	7,0	175,3
T8	69,3	55,1	11,2	2,9	138,4

The carbonates associated fraction was dissolved with acetic acid and bound metals were mobilized. The treatments 2 (Eschenau- lime), 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) showed higher exchangeable cadmium concentrations with 74-79 % of the total cadmium compared to the treatment 1 (Eschenau- control), 5 (Eschenau biochar + compost) and 5.a (Eschenau- aged biochar + compost) with 65-67 % of the total cadmium. The treatment 3 (Eschenau- compost) showed the lowest cadmium concentration with 58 % of the total cadmium. The treatments without added metals number 6, 7 and 8 showed low exchangeable cadmium concentrations with 64-96 µg/kg DM.

Step two, the extraction with 0.5 M hydroxylamin hydrochlorid, to extract fractions associated with easily and moderately reducible iron and manganese oxyhydroxides, showed opposite results. Heavy metals are bound by adsorption and precipitation to iron, and manganese oxyhydroxides in neutral soil conditions. Under reducing conditions, the oxyhydroxide precipitate dissolves and the bound metal gets as ion into solution.

The Eschenau treatments with compost number 3, 5, and 5.a, with values between 52-55 %, showed a higher content of oxyhydroxides bound cadmium compared to the control treatment 1 with 39 % of the total cadmium concentration. The treatments 2 (Eschenau-

lime), 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) showed no difference to the control treatment with values between 36-41 %. The treatments without added metals number 6, 7 and 8 showed low oxyhydroxides bound cadmium concentrations with 75-115 µg/kg DM.

Step three, which is associated with organic matter and sulfide bound fraction and step four, the aqua regia extractable residual fraction with non-silicate bound metals, showed minor amounts of cadmium.

At step 3, the Eschenau treatments showed organic matter and sulfide bound cadmium values between 3-4 % of the total cadmium concentration. The treatments without added metals number 6, 7 and 8 showed low cadmium concentrations with 15-24 µg/kg DM.

At step four, the concentrations of the remaining cadmium were between 0.3-0.5 % of the total cadmium content in the Eschenau soil treatments. The treatments without added metals number 6, 7, and 8 showed low cadmium concentrations with 4-19 µg/kg DM.

3.1.2.2 Zinc

Figure 17 shows the total zinc content at the first sampling time point. The initial concentration was 100 ppm. The results show that the zinc content in the treatments 2-5.a was higher than the initial concentration, which was caused by the natural zinc content of biochar and compost. The analysis of the Pixendorf compost showed a total zinc content of 184 mg/kg DM [28]. The biochar MSP550 showed a total zinc content of 63.4 mg/kg DM [40]. Treatment 6 (Eschenau- biochar + compost, without metals) showed a zinc concentration of 23 mg/kg DM (see *Table 14*). The Treffling soil treatments without added zinc showed a zinc content between 17-20 mg/kg soil DM, which is under the preventive threshold value (60 mg/kg soil DM for sandy soils; 200 mg/kg soil DM for clayey soils, see *Table 2*).

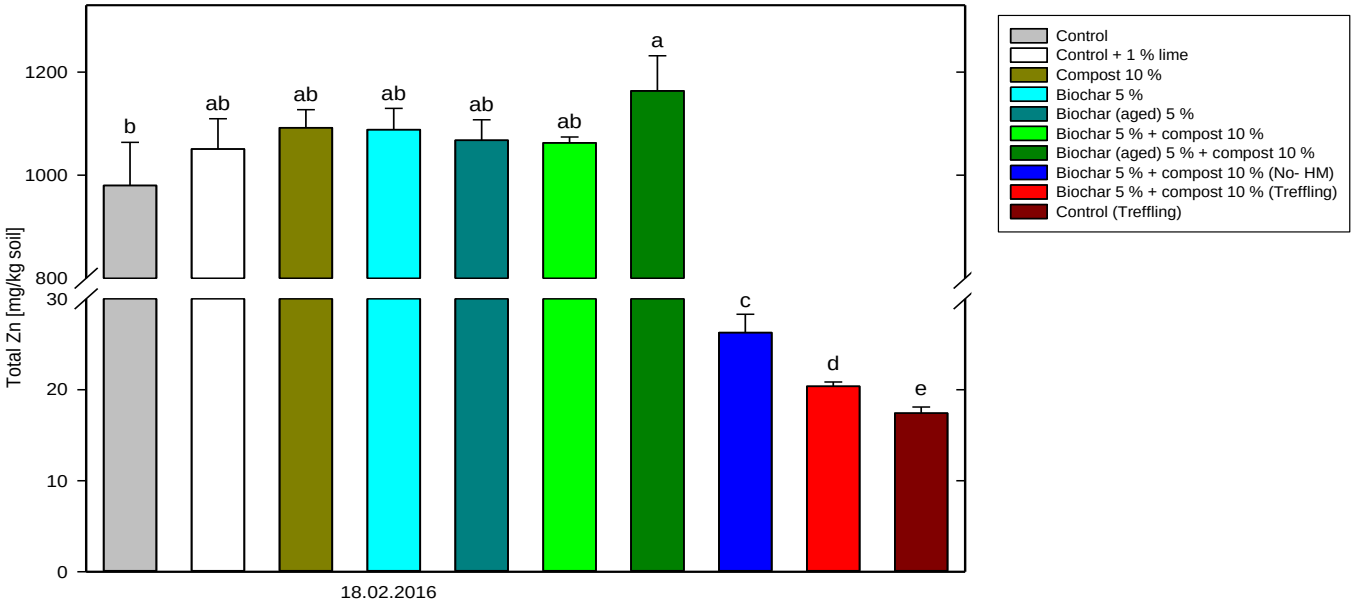

Figure 17: The diagram illustrates the total zinc content after aqua regia digestion of the treatments 1-8.

The zinc content was higher in the treatments with combined amendments, which indicates, that compost and biochar increased the zinc content.

Figure 18 illustrates the concentration of the mobile fraction of zinc in soil samples over five sampling time points. Only the treatments with added heavy metals were analysed. Over all sampling time points, there were significant differences of the extractable zinc concentrations between the treatments, similar to the results of extractable cadmium (see *Figure 16*).

At the first sampling time point, the control treatment 1 had the highest extractable zinc content with 389 mg/kg DM, which is 39 % of the initial concentration (see *Table 16*). The treatments 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) showed extractable zinc concentrations between 302-328 mg/kg DM. The zinc concentration of treatment 2 (Eschenau- lime) was at 16 mg/kg DM. The treatments with compost number 3 (Eschenau- compost), 5 (Eschenau- biochar + compost), and 5.a (Eschenau- aged biochar + compost), showed the lowest extractable zinc concentrations between 11-15 mg/kg DM, which is about 1-2 % of the initial concentration.

At sampling time point five, the treatment 1 (Eschenau- control) showed significantly higher extractable zinc concentrations (115 mg/kg DM), compared to the other treatments. There was no significance difference between the two treatments 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar). The content of extractable zinc was between 1.7-3.4 % of the initial concentration.

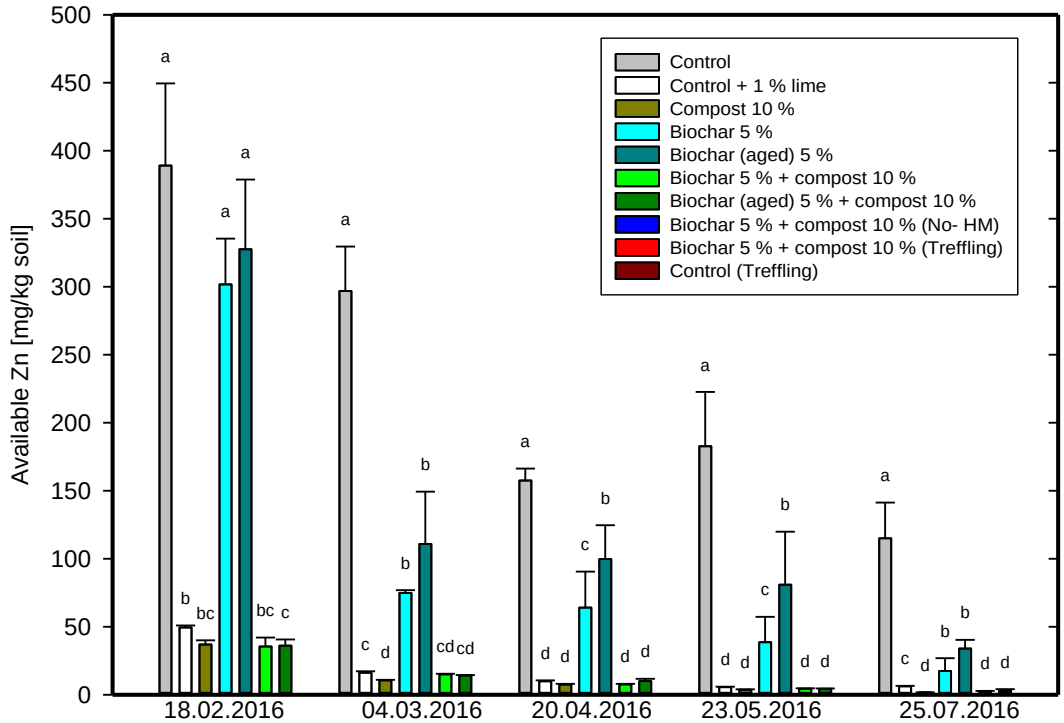

Figure 18: The diagram illustrates the extractable zinc content in soil samples after extraction with 1M ammonium nitrate solution.

Treatment 2 (Eschenau- lime) showed an extractable zinc concentration of 0.6 % of the starting concentration. Treatments with compost number 3 (Eschenau- compost), 5 (Eschenau- biochar + compost) and 5.a (Eschenau- aged biochar + compost) showed significantly lower extractable zinc concentrations with 0.2-0.3 % of the initial zinc concentration. The pH values of the different treatments almost match with the amount of extractable zinc (see *Figure 20*).

Figure 19 presents the results of the sequential extraction of zinc from soil samples. The sum of the zinc concentration of all fractions after the sequential extraction was about 100 mg/kg DM. The extraction efficiency of the sequential zinc extraction varied between 89-120 % (see *Table 8*).

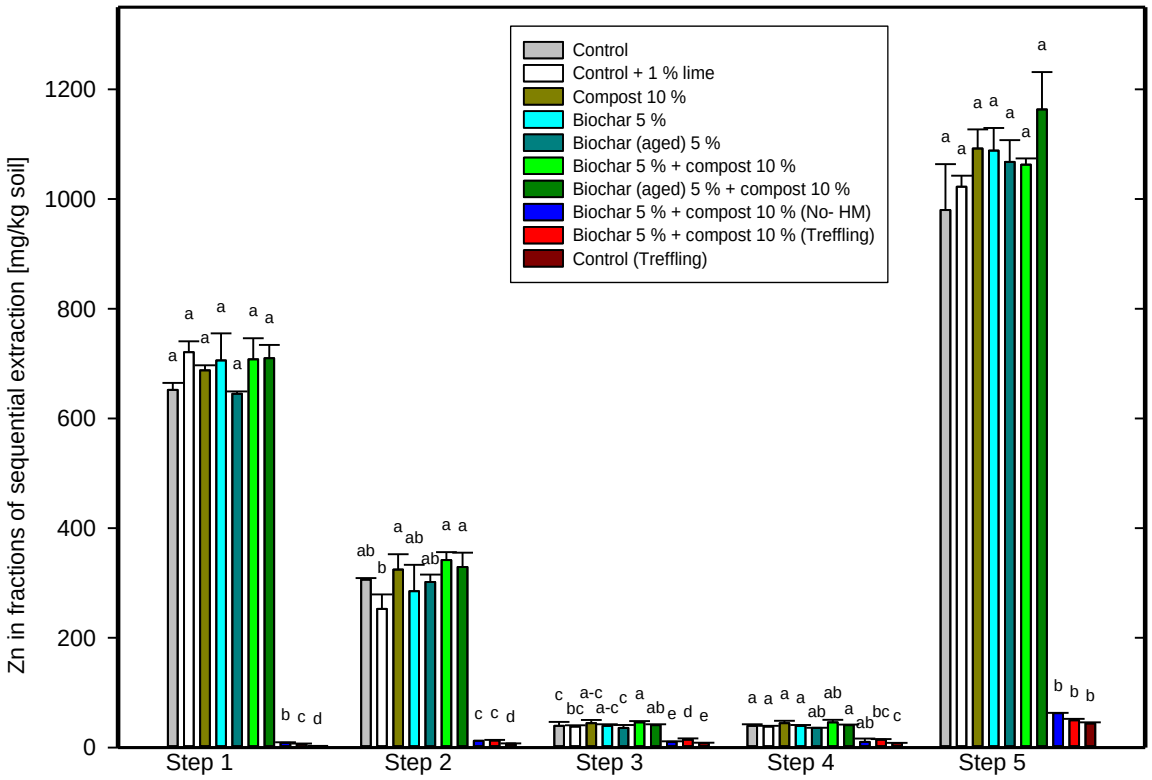

Figure 19: Zinc fractions after sequential extraction in µg/kg soil DM.

The treatments with added zinc, number 1, 2, 3, 4, 4a, 5, and 5. a showed no significant differences of exchangeable zinc concentrations with values between 66-76 %. The treatments with no added metals showed minor exchangeable zinc concentrations between 3-9 mg/kg soil DM.

Step two, the extraction with 0.5 M hydroxylamine hydrochloride solution, to extract fractions associated with easily and moderately reducible iron and manganese oxyhydroxides, showed that there significant differences between the treatments with added zinc. Heavy metals are bound by adsorption to iron and manganese oxyhydroxides under neutral soil conditions. Under reducing conditions, the oxyhydroxide precipitates dissolve and the bound metal gets as ion into solution. The treatments with compost number 3 (Eschenau- compost), 5 (Eschenau biochar + compost) and 5.a (Eschenau- aged

biochar + compost) had higher zinc concentrations with 32-37 % compared to the treatments 1 (Eschenau- control), 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) with 30-31 % of the total zinc content. The treatment 2 (Eschenau- lime) had the lowest zinc content with 27 % of the total zinc concentration. The treatments without added metals number 6 (Eschenau- biochar + compost, without metals), 7 (Treffling- biochar + compost, without metals) and 8 (Treffling- control) showed low oxyhydroxides bound zinc concentrations between 7-13 mg/kg DM.

Table 8: Distribution of the percentage of zinc between the different fractions after sequential extraction.

Treatment	Step 1 [%] Acetic acid (0.11 M)	Step 2 [%] Hydroxylamine hydrochloride (0.5 M)	Step 3 [%] Hydrogen peroxide (8.8 M)	Step 4 [%] Hydrochloric acid (12 M) + Nitric acid (15.8 M)	Extraction efficiency [%]
T1	70,4	30,8	4,3	3,2	108,8
T2	76,0	26,6	4,0	3,2	110,0
T3	67,1	31,6	4,3	3,3	106,4
T4	72,6	30,1	4,6	3,7	111,1
T4.a	65,7	31,0	4,0	3,3	104,3
T5	75,6	36,5	4,5	3,4	120,0
T5.a	75,3	34,9	4,3	3,6	118,4
T6	13,4	18,7	15,9	40,5	88,7
T7	13,1	26,1	28,7	38,6	106,2
T8	8,8	17,2	20,2	41,5	87,9

Step three, which is associated with organic matter and sulfides bound fraction and step four, which is the aqua regia extractable residual fraction with non-silicate bound metals, showed only minor amounts of zinc. At step three, the Eschenau treatments showed zinc values between 3.2-3.7 % of the initial zinc concentration. The treatments without added metals number 6, 7 and 8 showed low zinc concentrations with 8-14 mg/kg DM.

At step four, the concentrations of the remained zinc were between 3.2-3.7 % of the total zinc content in the Eschenau soil treatments. The treatments without added metals number 6, 7, and 8 showed zinc concentrations between 18-26 mg/kg DM.

3.1.3 Soil pH and electric conductivity of soil samples

Figure 20 illustrates the pH values of the ten different soil treatments. The ideal soil pH-value for arable crops ranges between 6.5- 7.0. The Eschenau control treatment showed a low pH compared to the Treffling control treatment. The pH value of both control treatments stayed almost constant over the time with pH values of Eschenau control treatment between 5.4 and 5.6 and the Treffling control treatment between 6.3-6.9 (see *Table 18*).

At the first sampling time point, the treatments with compost number 3 (Eschenau- compost), 5 (Eschenau- biochar + compost) and 5.a (Eschenau- aged biochar + compost) showed significantly higher pH values between 6.5-7.0 compared to the treatments 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) with pH values between 5.6-5.8. The treatment 4.a (Eschenau- aged biochar) had a significantly lower pH value compared to the treatment 4 (Eschenau- biochar). The treatment 2 with lime, showed a significantly higher pH value with 6.4 compared to the control treatment 1. The pH value of the treatment with lime stayed almost constant over the five sampling time points. The treatment 6 (Eschenau- biochar + compost) had higher pH values compared to the treatments with added heavy metals 5 (Eschenau- biochar + compost) and 5.a (Eschenau- aged biochar + compost). The pH value of treatment 7 (Treffling- biochar + compost, without metals) was significantly higher compared to the Treffling control treatment. At sampling time point five, the pH values of the treatments with compost number 3, 5, 5.a, 6 and 7 increased up to values between 7.3-7.6 without significant differences. The pH level of the treatments 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) increased to values between 6.2-6.3 and exhibited no significant differences.

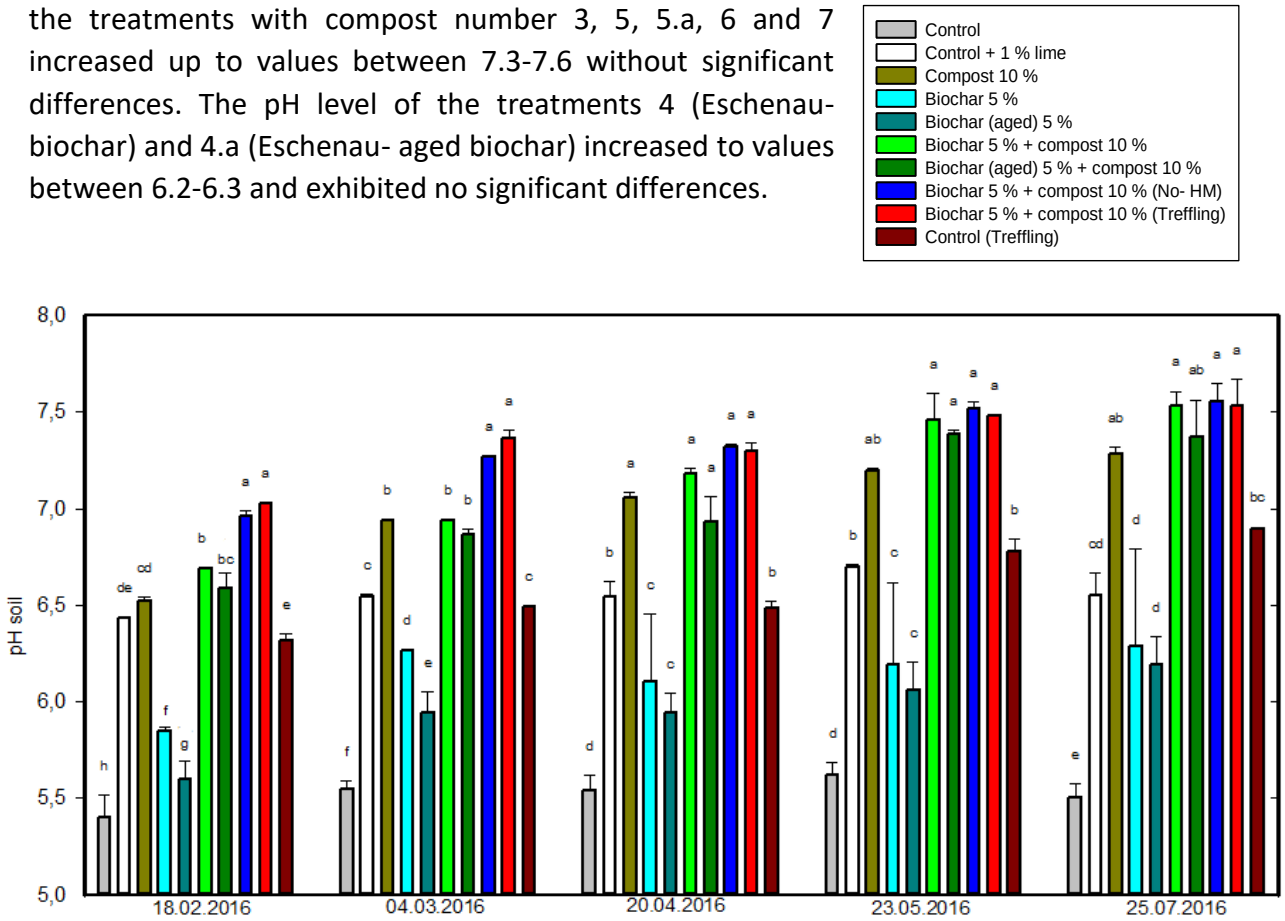

Figure 20: pH values of ten different soil treatments.

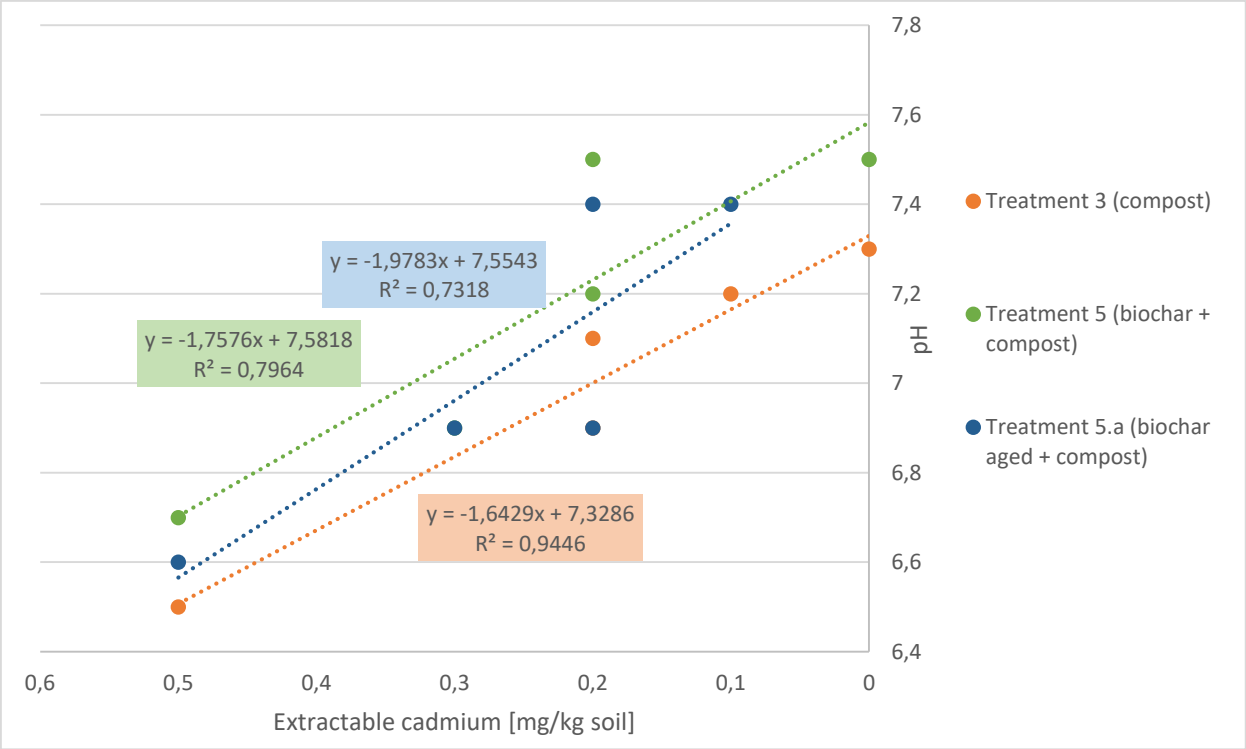

Figure 21: The diagram illustrates the concentration of extractable cadmium (1M ammonium nitrate solution) versus the pH over five sampling time points.

Figure 21 and *Figure 22* illustrate the concentration of with 1M ammonium nitrate solution extractable cadmium and zinc versus the pH. The diagrams confirm that there is a connection between the high reduction of mobile cadmium and zinc in the Eschenau soil treatments with compost and the pH values, which means that compost part could be responsible for that increased reduction.

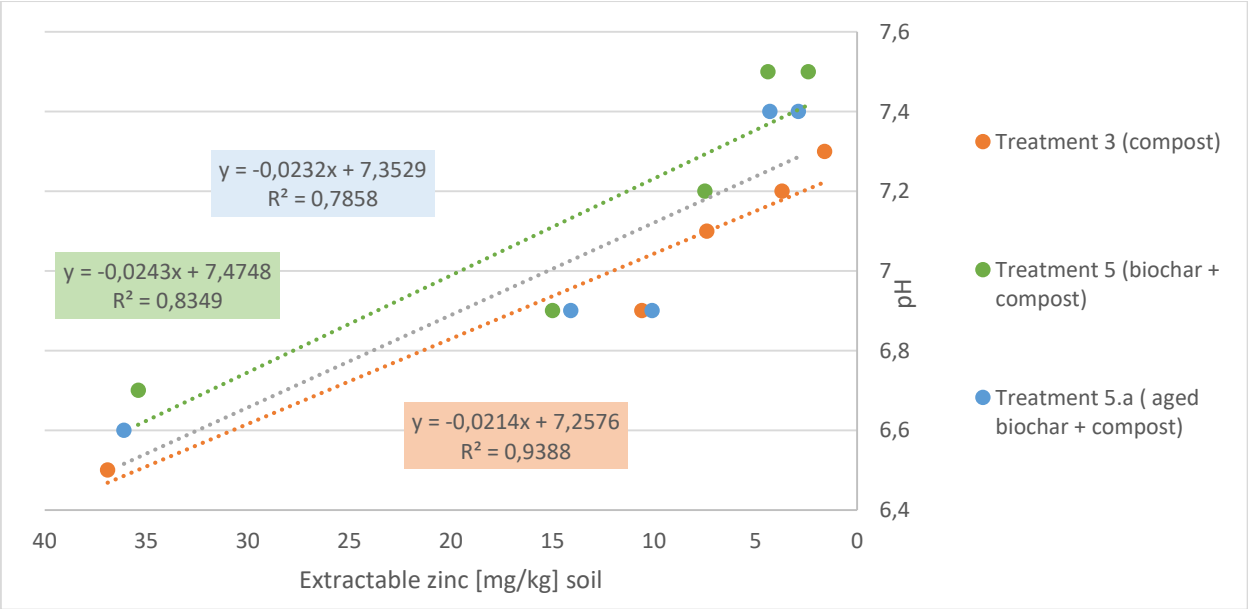

Figure 22: The diagram illustrates the concentration of extractable zinc (1M ammonium nitrate solution) versus the pH over five sampling time points.

Figure 23 shows the electric conductivity measured at three different sampling time points. At the first sampling time point, the treatments 3 (Eschenau- compost), 5 (Eschenau- biochar + compost), 5.a (Eschenau- aged biochar + compost) and 7 (Treffling- biochar + compost, without metals) showed higher electric conductivity values compared to the control treatments 1 (Eschenau- control) and 8 (Treffling- control) (see *Table 19*).

The treatments 2 (Eschenau- lime), 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) had lower EC values compared to the treatments 3, 5, 5.a and 7. The EC values of the Treffling control treatment stayed almost constant between 70-115 µS/cm. The values of the Treffling control treatment 8 were lower compared to the Eschenau control treatment. Treatment 6 (Eschenau- biochar + compost) showed lower EC values than the treatments 5 (Eschenau- biochar + compost) and 5.a (Eschenau- aged biochar + compost) with metals at the first and fourth sampling time point.

At sampling time point four, the treatments 5 (Eschenau- biochar + compost), 5.a (Eschenau- aged biochar + compost) and 7 (Treffling- biochar + compost, without metals) had the highest EC values between 277-333 µS/cm. The treatments 2 (Eschenau- lime), 3 (Eschenau- compost), 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) showed similar EC values with 215-228 µS/cm as the Eschenau control treatment with 173 µS/cm.

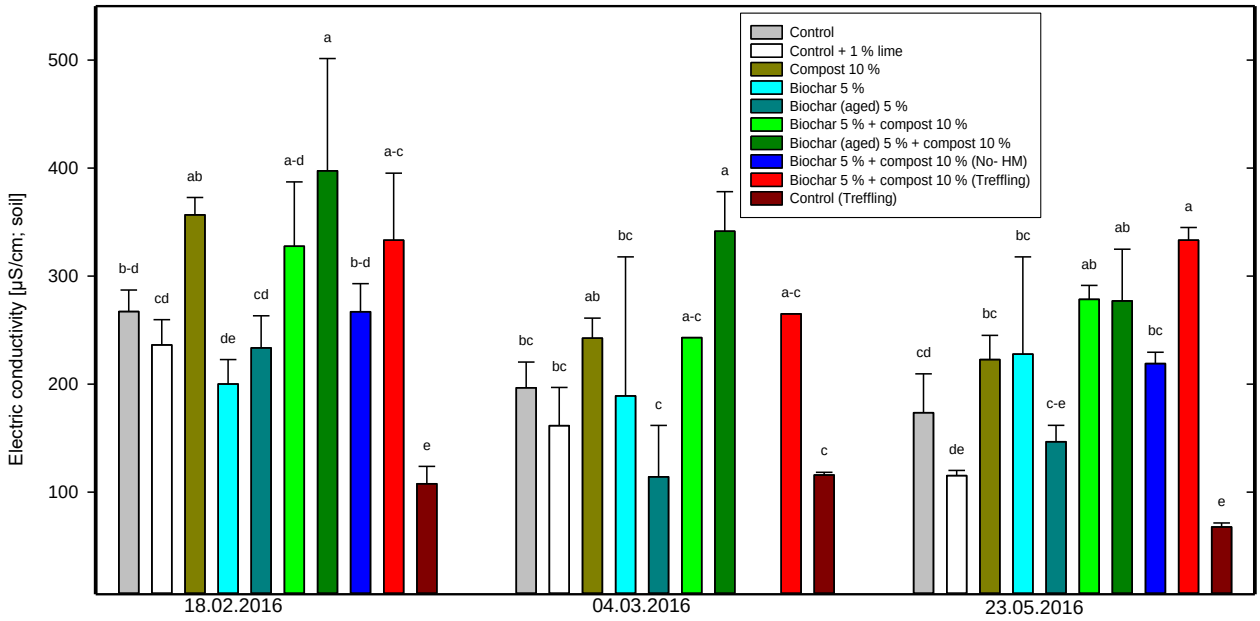

Figure 23: Electric conductivity of ten different soil treatments.

3.1.4 Dissipation time 50 of pollutants

Figure 24 illustrates the dissipation time 50 (DT_{50}), the time after which 50 % of a soil pollutant was dissipated. The DT_{50} value shows the reduction of the concentration of a pollutant over the time and provides information if a soil amendment is suitable or not. For the determination of the DT_{50} of pyrene and phenanthrene, an additional sampling time point with the starting concentration of 100 ppm was added, two days before the first sampling time point.

The control treatment had a longer dissipation time of zinc (75 days) compared to treatments with soil amendments (see *Table 20*). The treatments with soil amendments showed no significance difference with DT_{50} values between 9-26 days.

The DT_{50} value of cadmium in the treatment 1 (Eschenau- control) was significantly higher with 149 days compared to the treatments with soil amendments, with values between 44-87 days.

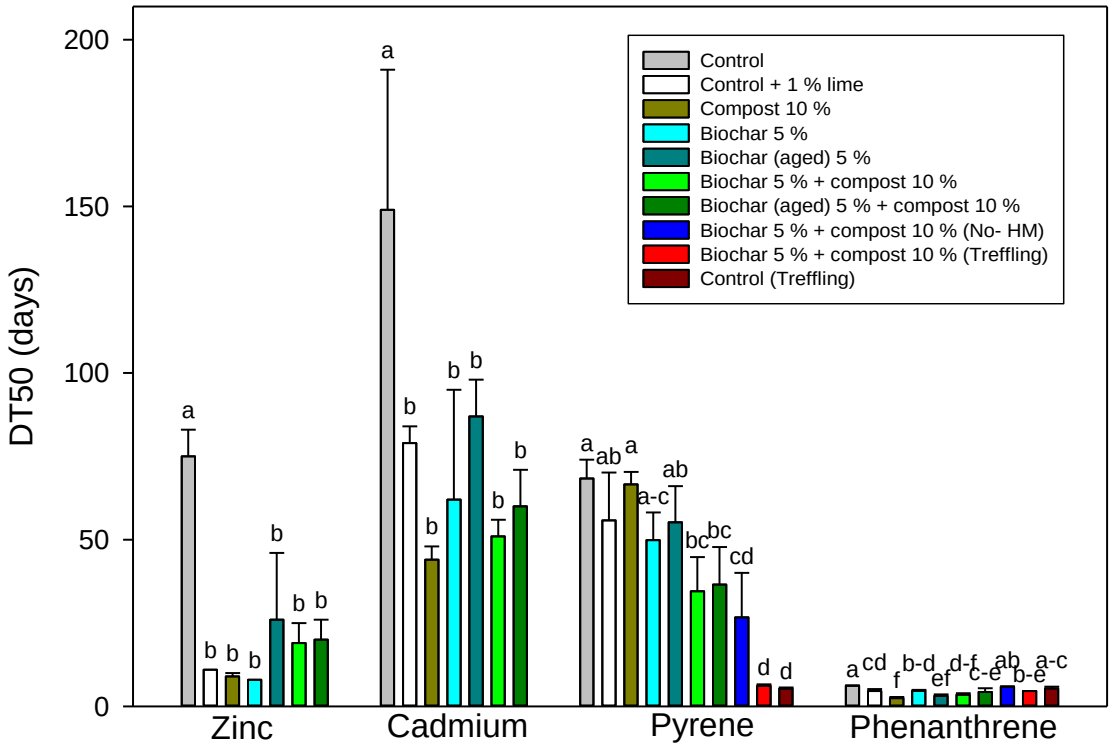

Figure 24: Dissipation time 50 (DT50) values of pollutants in different soil samples.

The Treffling soils showed very low DT_{50} values with 5 to 6 days compared to the Eschenau soil with DT_{50} values between 27 and 68 days. The Eschenau treatments with combined soil amendments showed significantly lower values with 35-37 days compared to the Eschenau control treatment. The treatments with a single amendment number 2 (Eschenau- lime), 3 (Eschenau- compost), 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) had values between 50-68 days.

Phenanthrene decreased in all treatments very fast, which caused a very low dissipation time between2-6 days. The treatment 3 (Eschenau- compost) had the lowest DT_{50} value with 2 days.

3.2 Results of soil pore water analysis

3.2.1 Polycyclic aromatic hydrocarbons extracted from soil pore water

3.2.1.1 Sum of 16 PAHs

The sum of all 16 PAHs was determined only of the treatments 7 (Treffling- biochar + compost, without metals) and 8 (Treffling- control). The low concentrations of the sum of 16 PAHs at the sampling time points two to five had the consequence that only data for the first sampling time point of soil pore water were measurable (see *Table 21*). The concentration of the sum of 16 PAHs at sampling time point one is illustrated in *Figure 25*. Treatment 7 (Treffling- biochar + compost, without metals) had significantly lower concentrations of 16 PAHs with 142 mg/kg DM compared to the control treatment with 244 mg/kg DM.

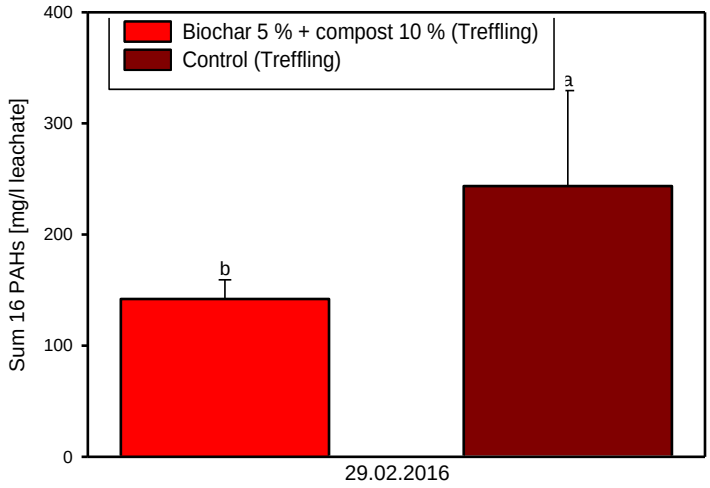

Figure 25: The diagram illustrates the sum of 16 PAHs extracted with n-hexane from pore water samples.

3.2.1.2 Pyrene

Figure 26 illustrates the concentration of extractable pyrene in soil pore water. At the first sampling time point, the pyrene concentration of the Eschenau treatments was about 100 mg/l (see *Table 22*).

At the second sampling time point, the extractable pyrene concentrations of the Eschenau treatments with soil amendments showed no significant difference to the Eschenau control treatment. The pyrene concentration was reduced to about 2-6 mg/l soil pore water. The extractable pyrene concentration in treatment 6 (Eschenau- biochar + compost, without metals), 7 (Treffling- biochar + compost, without metals) and 8 (Treffling- control) were lower than the limit of quantitation (LOQ) (<13.33 µg/l soil pore water). That indicates, that major part pyrene had leached out with soil pore water at the first sampling time point or had been degraded by microorganisms.

At the third sampling time point, the pyrene concentrations of all treatments were lower than the LOQ (<13.33 µg/l soil pore water).

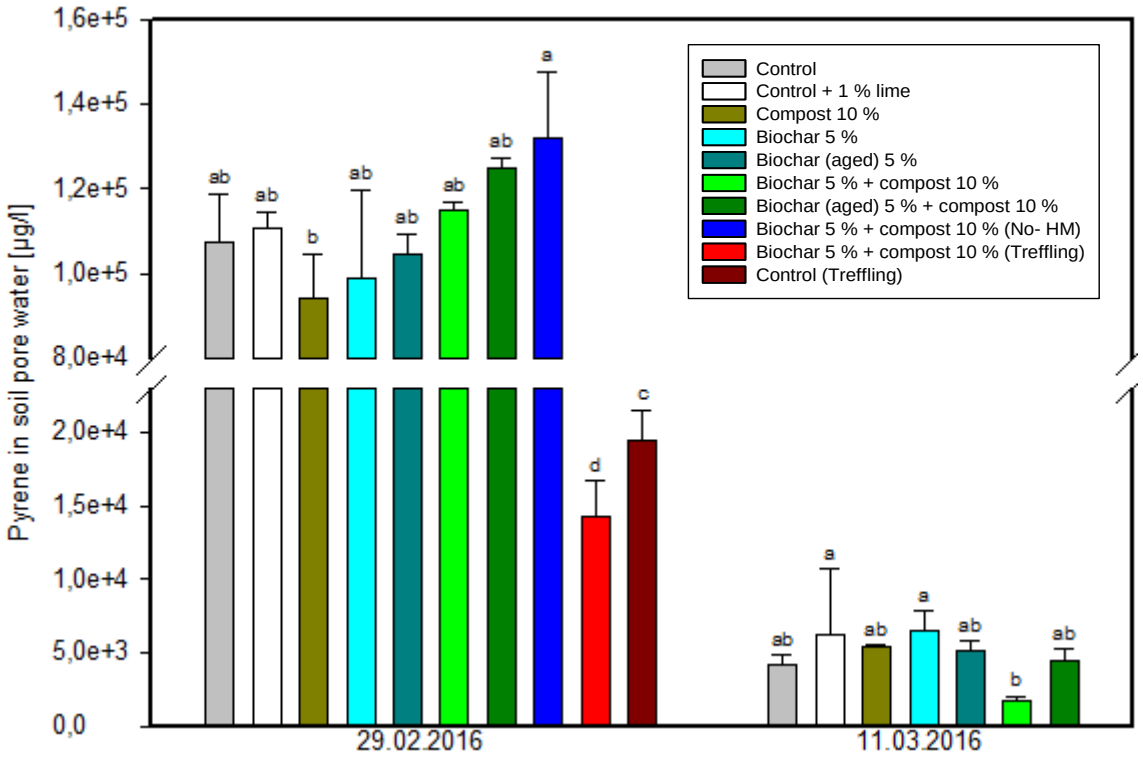

Figure 26: Concentrations of pyrene extracted with n-hexane from soil pore water samples.

3.2.1.3 Phenanthrene

Figure 27 illustrates the concentration of extractable phenanthrene in soil pore water. The results of the phenanthrene concentration in soil pore water were similar to the results of pyrene. At the first sampling time point, the extractable phenanthrene concentration of the Eschenau treatments was about 100 mg/l (see *Table 23*).

At sampling time point one, there was no significant difference between the two Treffling treatments. The Eschenau treatment 3 (Eschenau- compost) and 4 (Eschenau- biochar) had lower extractable phenanthrene concentrations compared to treatment 6 (Eschenau- biochar + compost, without metals), which indicates that presence of metals influence the degradation of phenanthrene.

At the second sampling time point, the extractable phenanthrene concentrations of all treatments were lower than the LOQ (<10 µg/l soil pore water), which indicates, that the major part of the phenanthrene had leached out of the Eschenau soil treatments with soil pore water at sampling time point one or had been degraded by microorganisms.

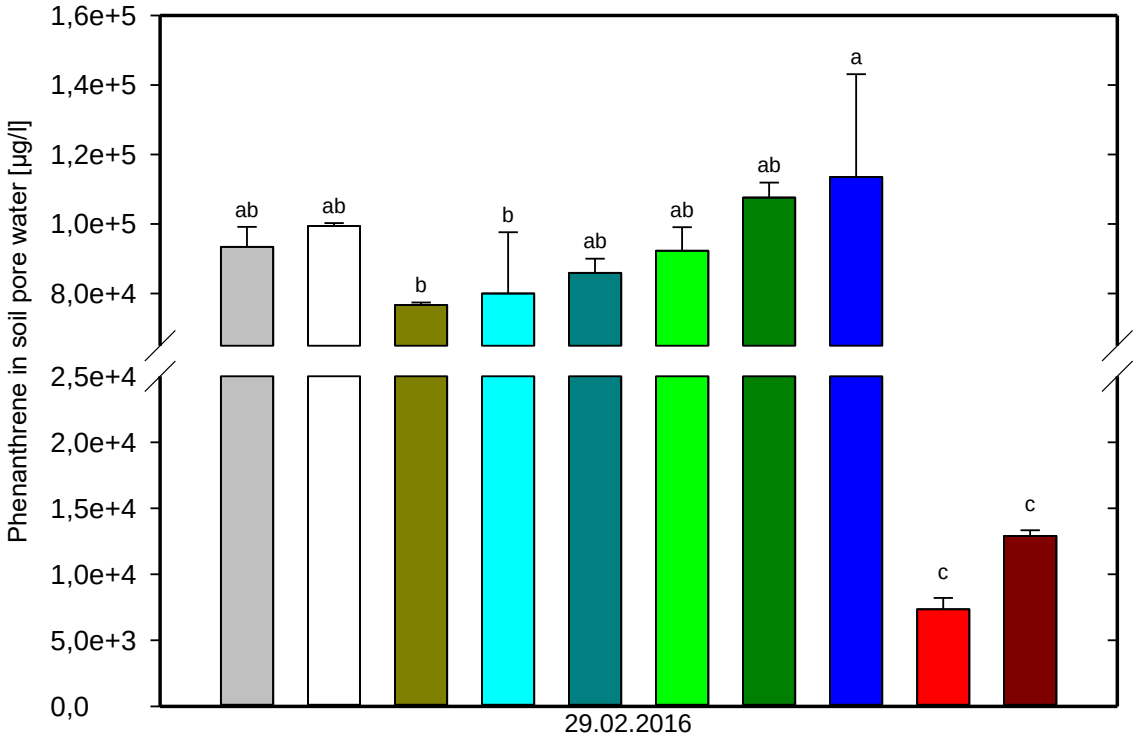

Figure 27: Concentrations of phenanthrene extracted with n-hexane from soil pore water samples. For legend, see Figure 26.

3.2.2 Metals extracted from soil pore water

3.2.2.1 Cadmium

The concentration of cadmium extracted from soil pore water is illustrated in ***Figure 28.***

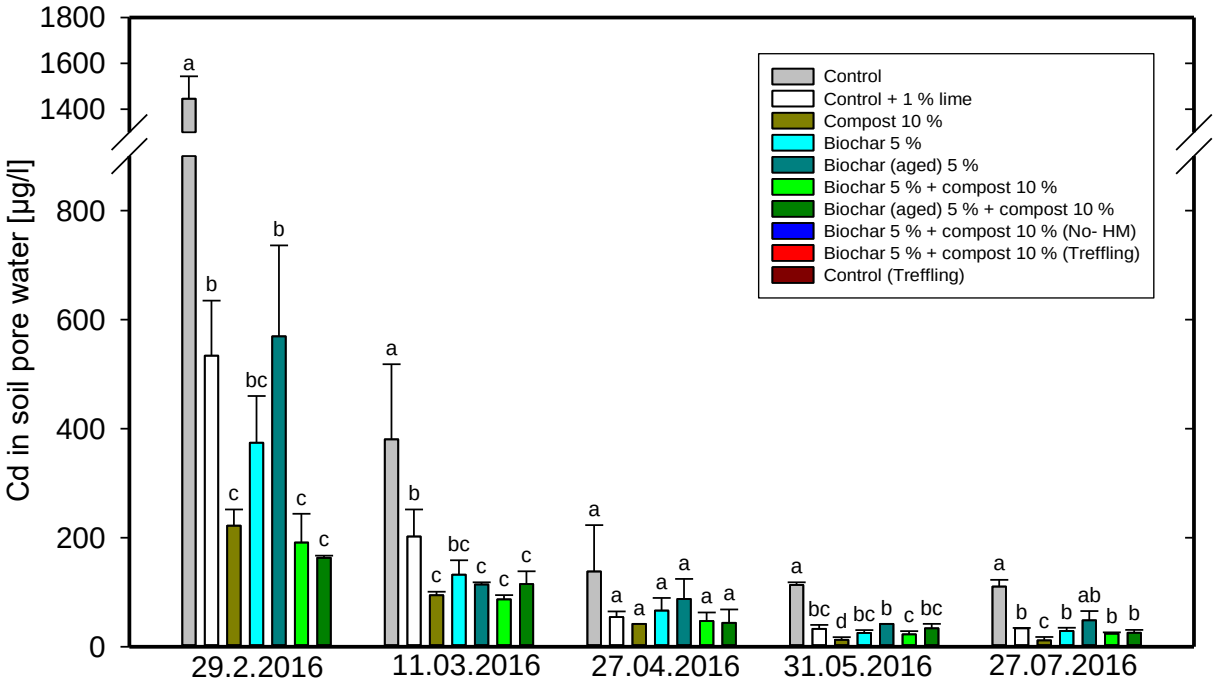

Figure 28: The diagram illustrates the concentration of cadmium extracted with 65 % nitric acid from soil pore water.

The extractable cadmium concentration of the treatments 6 (Eschenau- biochar + compost, without metals), 7 (Treffling- biochar + compost, without metals) and 8 (Treffling- control) were lower than the LOQ (<34.4 µg/l soil pore water) at all sampling time points (see *Table 24*). Over all sampling time points, there were significant differences of the extractable cadmium concentrations between the different treatments.

At the first sampling time point, the Eschenau control treatment had a significantly higher extractable cadmium concentration in soil pore water, with about 1446 µg/l soil pore water, compared to the Eschenau treatments with soil amendments. The treatments 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) showed lower extractable cadmium concentrations with 374-569 µg/l soil pore water. The extractable cadmium concentration of treatment 2 (Eschenau- lime) was also in the same range with 534 µg/l soil pore water. The treatments with compost number 3 (Eschenau- compost), 5 (Eschenau- biochar + compost) and 5.a (Eschenau- aged biochar + compost) showed the lowest extractable cadmium concentrations between 163-222 µg/l soil pore water.

At sampling time point five, the extractable cadmium concentration in the Eschenau control treatment was reduced to 110 µg/l soil pore water. Treatment 4.a (Eschenau- aged biochar) had a concentration of 48 µg/l soil pore water. The treatments 2 (Eschenau- lime), 4 (Eschenau- biochar), 5 (Eschenau- biochar + compost) and 5.a (Eschenau- aged biochar + compost) showed significantly lower extractable cadmium concentrations with values between 24-34 µg/l soil pore water, compared to the treatment 1 (Eschenau- control). The treatment 3 (Eschenau- compost) showed the lowest extractable cadmium concentration with 11 µg/l soil pore water. The pH values of the different treatments match with the extractable cadmium concentrations *(*see *Figure 31*).

3.2.2.2 Zinc

The concentration of zinc extracted from soil pore water is illustrated in *Figure 29*. The extractable zinc concentration of the treatments 6 (Eschenau- biochar + compost, without metals), 7 (Treffling- biochar + compost, without metals) and 8 (Treffling- control) were lower than the LOQ (<0.034 mg/l soil pore water) (see *Table 25*). Over all sampling time points, there were significant differences of the extractable zinc concentrations between the different treatments. The results of the extractable zinc were similar to the results of extractable cadmium.

At the first sampling time point, the Eschenau control treatment had a significantly higher zinc concentration in soil pore water, with about 240 mg/l soil pore water, compared to the Eschenau treatments with soil amendments. The treatments 2 (Eschenau- lime) and 4.a (Eschenau- aged biochar) showed lower extractable zinc concentrations with 58-75 mg/l soil pore water. Treatment 4 (Eschenau- biochar) had an extractable zinc concentration of 33 mg/l soil pore water. The treatments with compost number 3 (Eschenau- compost), 5 (Eschenau- biochar + compost) and 5.a (Eschenau- aged biochar + compost) showed the lowest extractable zinc concentrations between 12-19 mg/l soil pore water.

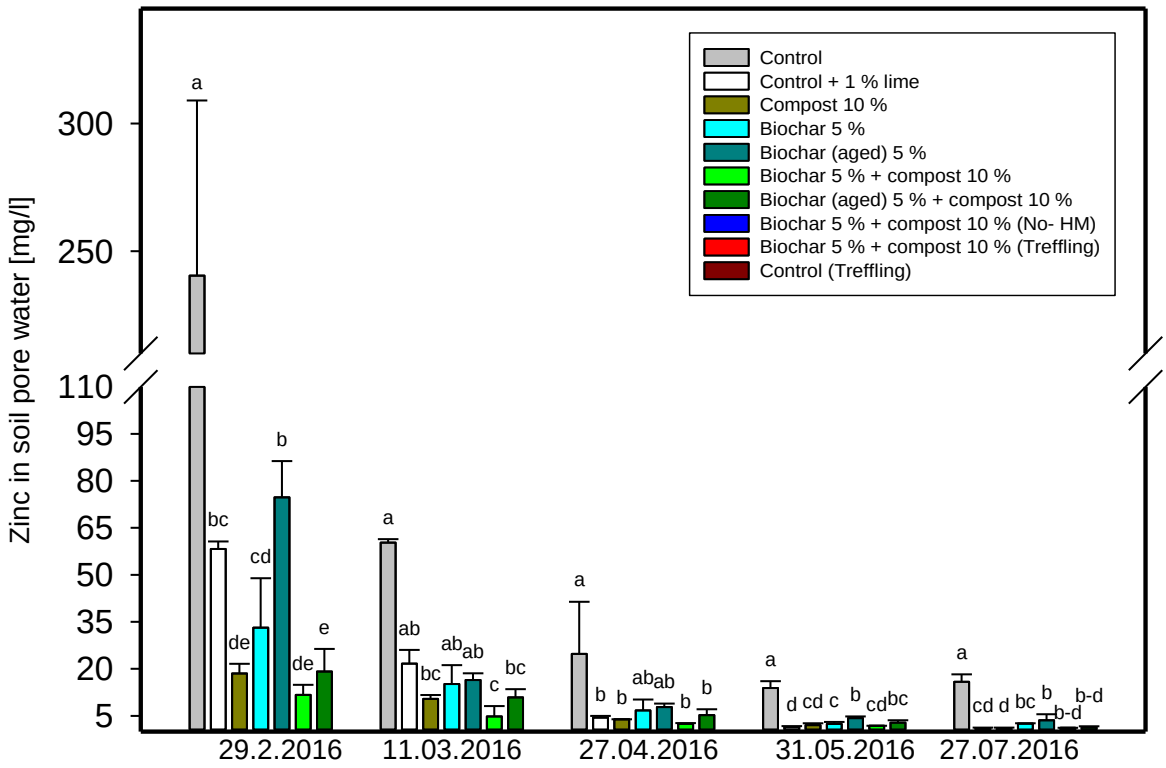

Figure 29: The diagram illustrates the zinc concentration extracted with 65 % nitric acid from soil pore water.

At sampling time point five, the extractable zinc concentration in the Eschenau control treatment was reduced to 16 mg/l soil pore water. Treatment 4.a (Eschenau- aged biochar) had a zinc concentration of 4 mg/l soil pore water. The treatments 2 (Eschenau- lime), 4 (Eschenau- biochar), 5 (Eschenau- biochar + compost) and 5.a (Eschenau- aged biochar + compost) showed significantly lower extractable zinc concentrations between 1-3 mg/l soil pore water, compared to the treatment 1 (Eschenau- control). The treatment 3 (Eschenau- compost) showed the lowest extractable zinc concentration with 0.8 mg/l soil pore water. The pH values of the different treatments match with the extractable zinc concentrations (see *Figure 31*).

3.2.3 Dissolved organic carbon, pH and electric conductivity from soil pore water

Figure 30 illustrates the content of dissolved organic carbon (DOC) in mg/l soil pore water. At the first sampling time point were significant differences between the treatments with compost number 3 (Eschenau- compost), 5 (Eschenau- biochar + compost), 5.a (Eschenau- aged biochar + compost), 6 (Eschenau- biochar + compost, without metals) and 7 (Treffling- biochar + compost) with DOC values between 222-325 mg/l soil pore water. After 11 days, at the first sampling time point, the two treatments without added metals number 6 (Eschenau- biochar + compost, without metals) and 7 (Treffling- biochar + compost, without metals) had with 278-325 mg/l soil pore water significantly higher DOC values compared to the treatments with metals number 3 (Eschenau- compost), 5 (Eschenau- biochar + compost) and 5.a (Eschenau- aged biochar + compost) with DOC values between 22-244 mg/l soil pore

water. Between treatment 1 (Eschenau- control) and the treatments 2 (Eschenau- lime), 4 (Eschenau- biochar), 4.a (Eschenau- aged biochar) and 8 (Treffling- control) there were no significant differences with DOC values between 24-30 mg/l soil pore water (see *Table 26*).

After 151 days, at sampling time point five, the DOC values of the treatments with compost number 3 (Eschenau- compost), 5 (Eschenau- biochar + compost), 5.a (Eschenau- aged biochar + compost), 6 (Eschenau- biochar + compost, without metals) and 7 (Treffling- biochar + compost) decreased to values between 71-100 mg/l soil pore water. The DOC values of the treatments 1 (Eschenau- control), 2 (Eschenau- lime), 4.a (Eschenau- aged biochar) and 8 (Treffling- control) stayed almost constant between 29-51 mg/l soil pore water. The treatment 4 (Eschenau- biochar) had an increased DOC value with 75 mg/l soil pore water compared to the first sampling time point.

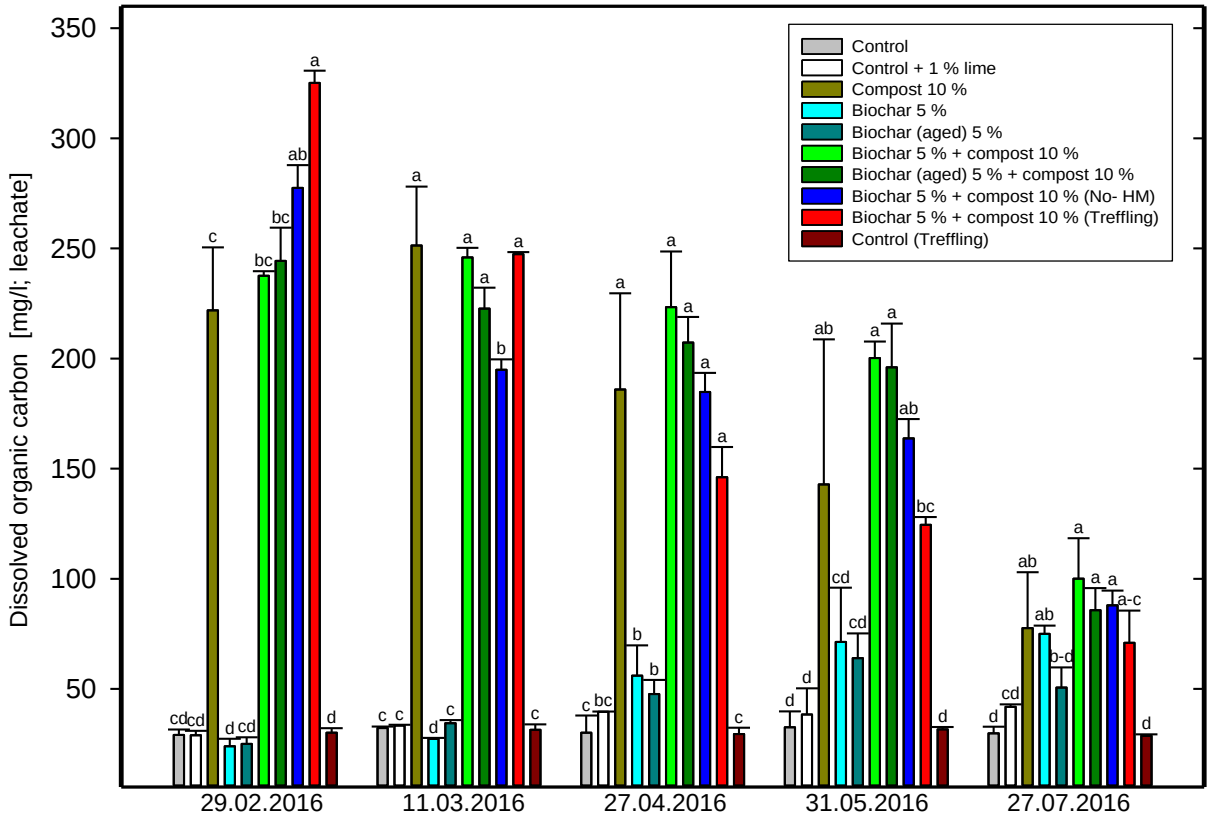

Figure 30: Concentration of dissolved organic carbon of soil pore water samples.

Figure 31 illustrates the pH values of the ten different soil pore water samples. The ideal soil pH- value for arable crops ranges between 6.5- 7.0. The pH values of the Eschenau control treatment ranged between 6.5- 7.0 over the five sampling time point (see *Table 27*). The Eschenau control treatment showed a lower pH compared to the Treffling control treatment, what matches with the pH results of soil analysis.

At the first sampling time point, the pH of treatment 8 (Treffling- control) showed no significance difference to the treatment 7 (Treffling- biochar + compost, without metals) with pH values about 7.5-7.6. Treatment 1 (Eschenau- control) had the lowest pH with 6.5.

The treatments 2 (Eschenau- lime) and 4.a (Eschenau- aged biochar) had pH values about 6.8. The treatment 3 (Eschenau- compost), 4 (Eschenau- biochar) and 5.a (Eschenau- aged biochar + compost) had pH values between 7.2-.7.3. The highest pH values showed the treatments 5 (Eschenau- biochar + compost) and 6 (Eschenau- biochar + compost, without metals) with values about 7.7.

At sampling time point five, treatment 1 (Eschenau- control) had with 6.9 the lowest pH value. The treatments 2 (Eschenau- lime), 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) showed increased values between 7.4-7.6. The remaining treatments 3 (Eschenau- compost), 5 (Eschenau- biochar + compost), 5.a (Eschenau- aged biochar + compost), 6 (Eschenau- biochar + compost, without metals), 7 (Treffling- biochar + compost, without metals) and 8 (Treffling control) reached the highest pH values between 7.9-8.2.

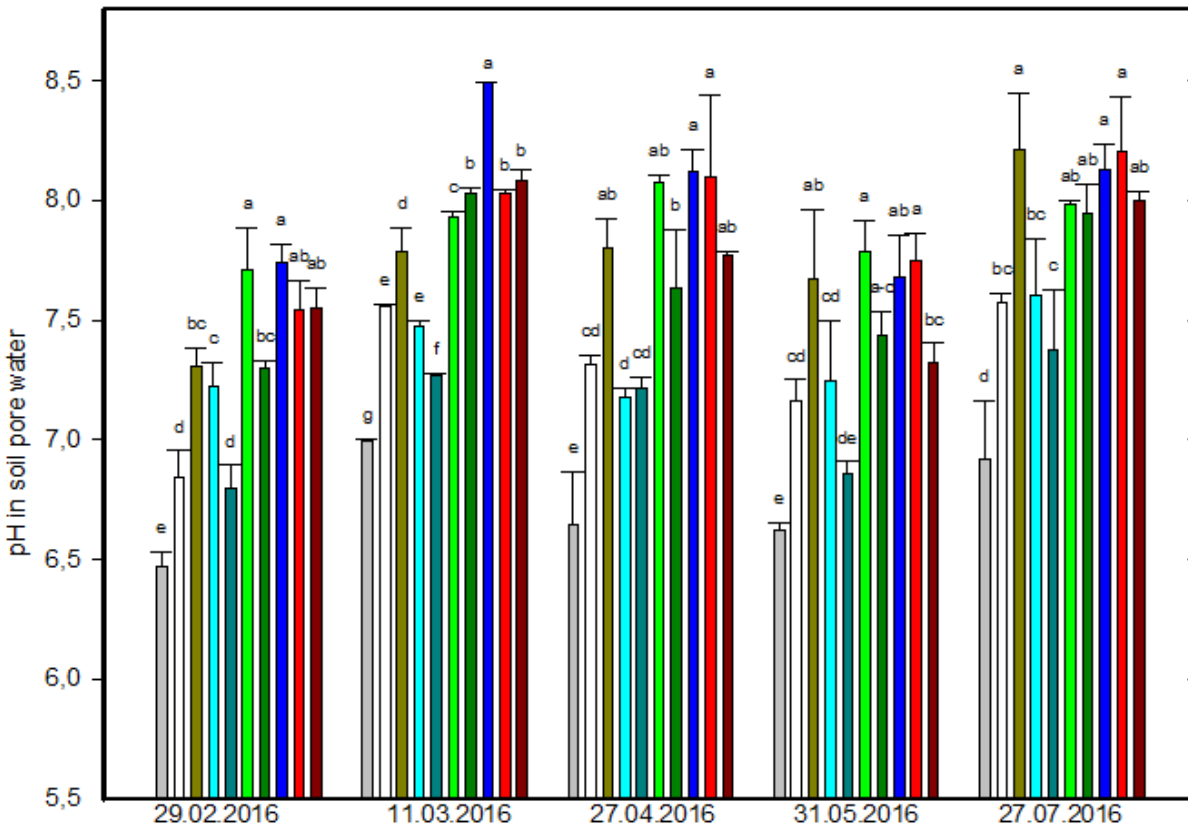

Figure 31: pH values of ten different soil pore water samples.

Figure 32 illustrates the electric conductivity measured at five sampling time points. At sampling time point one, the treatments 3 (Eschenau- compost), 5 (Eschenau- biochar + compost), 5.a (Eschenau- aged biochar + compost), 6 (Eschenau- biochar + compost, without metals), 7 (Treffling- biochar+ compost, without metals) showed the highest EC values between 8710-9475 µS/cm (see *Table 28*). The treatment 1 (Eschenau- control) had a EC

value of 7507 µS/cm and the treatments 2 (Eschenau- lime), 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) values between 5750-7033 µS/cm. The Treffling control treatment 1 had the lowest EC value with 3625 µS/cm at sampling time point one.

At sampling time point five, the EC values of all treatments decreased. Treatment 7 (Treffling- biochar + compost, without metals) had the highest EC values with 2209 µS/cm. The treatments with compost number 3 (Eschenau- compost), 5,(Eschenau- biochar + compost), 5.a (Eschenau- aged biochar + compost) and 6 (Eschenau- biochar + compost, without metals) had EC values between 1403-1781 µS/cm. The Treffling control treatment 8 had a EC value of 1129 µS/cm and the treatments 1 (Eschenau- control), 2 (Eschenau- lime) 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) EC values between 652-836 µS/cm at sampling time point five.

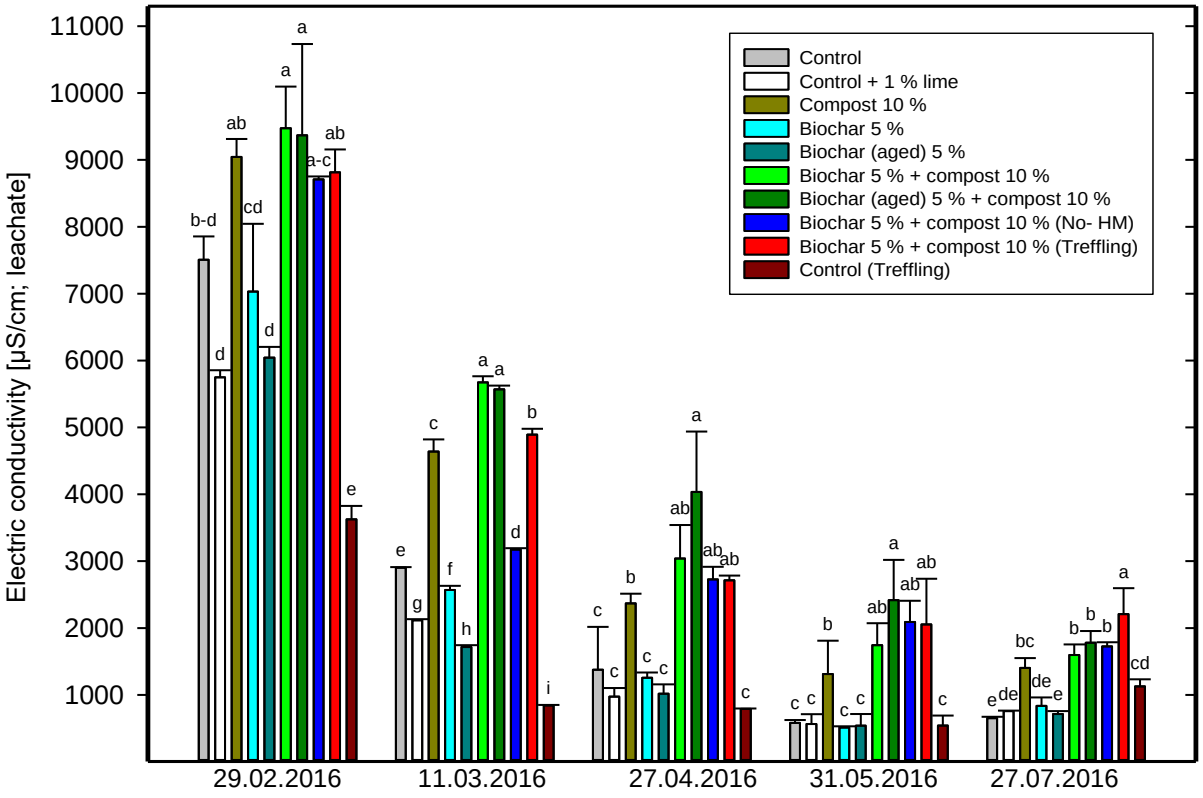

Figure 32: Electric conductivity of ten different soil pore water samples.

3.2.4 Dissipation time 50 of pollutants in soil pore water

Figure 33 illustrates the dissipation time 50 (DT_{50}), the time after which 50 % of a soil pollutant was dissipated. For the DT_{50} of heavy metals for the treatments 6-8 were not available because they had not been spiked and analysed. The values of phenanthrene were only available for the first sampling time point. At least, it would take the datasets of two sampling time points to determine the DT_{50} value and because of that, DT_{50} determination was not possible

The dissipation time of zinc showed no significant difference between the treatments with DT_{50} values between 5-28 days.

The DT_{50} values of cadmium were between 20-35 days in the treatments with compost number 5 (Eschenau- biochar + compost) and 5.a (Eschenau- aged biochar + compost) and higher compared to the treatments 1 (Eschenau- control), 2 (Eschenau- lime), 3 (Eschenau- compost) 4 (Eschenau- biochar) and 4.a (Eschenau- aged biochar) with DT_{50} values between 6-10 days (see *Table 29*).

The DT_{50} determination of pyrene showed no significant difference with values between 2-3 days.

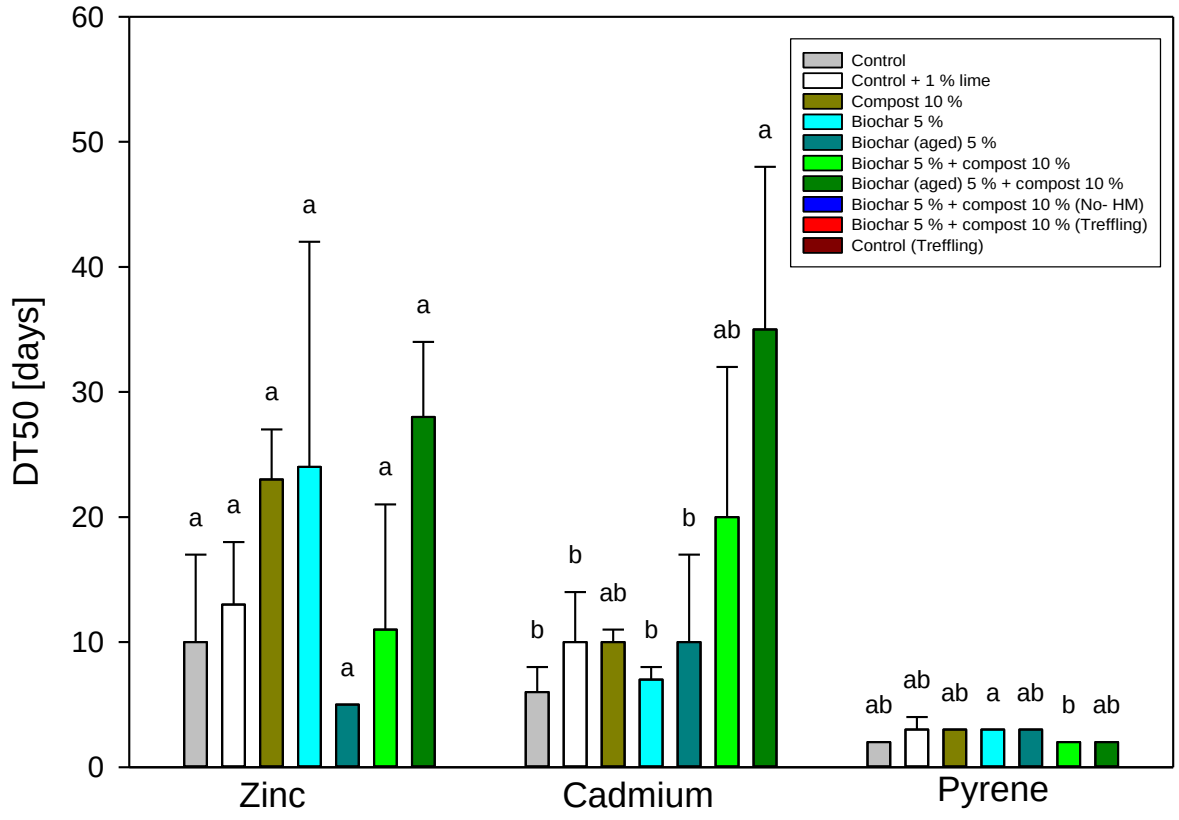

Figure 33: Dissipation time 50 (DT50) values of pollutants of the ten different soil pore water samples.

4 Discussion

4.1 Influence of the soil additives on the mobility of polycyclic aromatic hydrocarbons

151 days after start of the experiment, at sampling time point five, there were significant differences between the extractable pyrene and phenanthrene concentrations of the Eschenau soil treatments with soil amendments and the Eschenau control treatment. Between the Treffling control treatment and the Treffling treatment with soil amendments there were no significant differences of the concentration of extractable pyrene and phenanthrene after 151 days.

At the first sampling time point, the concentrations of extractable pyrene and phenanthrene were under the initial concentration of 100 ppm in treatments with Eschenau soil because a part of pyrene and phenanthrene had already dissipated between the time point of experimental installation and the first sampling time point, which was one day.

After 151 days, at the fifth sampling time point, the concentration of extractable pyrene in the Eschenau soil control treatment was reduced to 29 % of the initial pyrene concentration (see *Table 10)*. The extractable phenanthrene was reduced to about 22 % of the initial phenanthrene concentration in the Eschenau soil control treatment (see *Table 11*).

After 151, there was a significant reduction of extractable pyrene reached among the Eschenau soil treatments in the treatment with lime, the treatment with aged biochar and the treatment with biochar and compost. The extractable pyrene concentrations were between 13-15 % of the initial pyrene concentration. The other treatments reached extractable pyrene concentrations between 18-25 % of the initial pyrene concentration, which indicates that all soil amendments had helped to reduce the extractable pyrene concentration compared to the control treatment without soil amendments.

The highest reduction of extractable phenanthrene among the Eschenau soil treatments was reached in the treatment with lime with 3 % of the initial phenanthrene concentration extracted after 151 days. The significant reduction of both, the extractable pyrene and phenanthrene concentration, partly will have been caused by immobilization promoted by the added lime [42]. Lime also caused an increased soil pH to 6.6 (see *Table 18*), which improves the microbial activity and therefore provides a better environment for the microbial degradation of PAHs [5][24]. The Eschenau soil treatment with compost and the treatments with compost and biochar or aged biochar had extractable phenanthrene concentrations between 7-9 % of the initial phenanthrene content. The Eschenau treatments with biochar or aged biochar had higher values with 13-17 % of the initial phenanthrene content. That indicates that the compost was responsible for the higher reduction of extractable phenanthrene in the treatments with compost compared to the control treatment and the treatments with biochar or aged biochar. The biological degradation was enhanced by compost. Saraya et al. (2010, 2011) reached a reduction of 90 % of several PAHs in soils with added compost after 30 days [22][23]. Wu et al.(2013) also reached PAH degradation rates between 60-70 % in different soils with composts as soil amendment [43]. That indicates that compost or lime are more suitable for the reduction of PAHs as biochar or aged biochar.

Between the Treffling control treatment and the Treffling treatment with combined soil amendments there were no significant differences of the extractable pyrene and phenanthrene concentrations after 151 days. The DT_{50} values showed that the Treffling soil had the fastest reduction of extractable pyrene with values between 5-6 days (see *Table 20*). The DT_{50} values of extractable phenanthrene in all ten different soil samples were between 2-6 days. The lowest DT_{50} value had the Eschenau treatment with compost with 2 days. Caused by the fact that phenanthrene is a relatively "low molecular weight" PAH with three aromatic rings and pyrene, a so called "high molecular weight" PAH, with four aromatic rings, phenanthrene is more volatile and by that, the extractable phenanthrene concentrations decreased stronger compared to the extractable pyrene concentrations over the five sampling time points [44]. Phenanthrene is also easier to degrade biologically, which is another reason why the extractable phenanthrene DT_{50} values were lower compared to the DT_{50} values of extractable pyrene. Over all sampling time points, except for extractable pyrene at time point two, the Eschenau treatment with combined soil amendments and without added heavy metals showed no significant difference to the treatments with added metals, which indicates that the presence of heavy metals did not influence the reduction of extractable pyrene and phenanthrene.

The analyses of 16 PAHs in the two Treffling soil treatments showed that the addition of biochar and compost decreased the amount of extractable PAHs significantly compared to the Treffling control treatment at sampling time point one (see *Table 9*). Beesley et al. (2010) had also reached significant reductions of PAH concentrations using both, biochar and compost, as soil amendments. Especially the heavier and more toxicologically ones were reduced significantly [45]. At the second sampling time point, the concentration of the sum of 16 PAHs of the treatment with soil amendments showed no significant difference to the control treatment, which indicates that the addition of soil amendments had reduced the amount of PAHs fast after the application but after about two weeks the concentrations of the two treatments remained at a constant level without differences concerning the long-term effect. That indicates that after two weeks was no further effect of soil amendments on the reduction of extractable PAHs.

The analyses of extractable pyrene in soil pore water showed similar results as the analyses of extractable phenanthrene at the first sampling time point. Among the Eschenau treatments, the treatment three with compost showed the lowest extractable pyrene and phenanthrene concentrations. Treatment number six, without added heavy metals, had higher extractable pyrene and phenanthrene concentrations compared to the Eschenau control treatment.

At the first sampling time point, the extractable pyrene concentrations of the Eschenau soil treatments showed no significant difference with values between 94-132 mg/l soil pore water. The extractable phenanthrene concentrations also showed no significant difference and were between 77-114 mg/l soil pore water in the Eschenau soil treatments (see *Table 22 & 23*). At sampling time point two, the extractable pyrene concentrations had decreased to 2-6 mg/l soil pore water and the extractable phenanthrene concentrations were lower than the limit of quantitation (< 10 µg/l soil pore water), which indicates, that the part, which was not adsorbed, had leached out with soil pore water at the first sampling time point or had

been degraded. At the third, fourth and fifth sampling time point the extractable pyrene concentrations were lower than the LOQ (< 13.33 µg/l soil pore water). There were no significant differences between the DT_{50} values of extractable pyrene in the different treatments. The time until 50 % of extractable pyrene dissipated was between 2-3 days (see *Table 29*).

At the first sampling time point, the extractable pyrene concentration was about 14 mg/l soil pore water in the Treffling soil treatment with soil amendments and about 19 mg/l soil pore water in the Treffling soil control treatment. The treatment with soil amendments showed an about 26 % higher reduction of extractable pyrene compared to the Treffling control treatment. That indicates that the soil amendments had caused that significant reduction and had helped to prevent the movement into soil pore water. At sampling time point two, the extractable pyrene concentrations were lower than the LOQ (< 13.33 µg/l soil pore water) (see *Table 22*). The extractable phenanthrene concentrations were between 9-12 mg/l soil pore water in the Treffling treatments. At sampling time point two, the extractable phenanthrene concentrations were lower than the LOQ (< 10 µg/l soil pore water) (see *Table 23*). That indicates that the major part of phenanthrene and pyrene had been bound into the soil structure or had been biologically degraded and did not move out with the soil pore water.

The concentration of the sum of 16 PAHs in soil pore water samples showed similar results as the analyses of 16 PAHs in soil samples. At the first sampling time point, the Treffling treatment with soil amendments showed a significantly lower concentration of 16 PAHs than the Treffling control treatment. That indicates that biochar and compost had the amount of extractable PAHs in soil pore water significantly reduced after addition to soil. At the second, third, fourth and fifth sampling time points were the concentrations of 16 PAHs under the different LOQs (see *Table 21*).

4.2 Influence on metal mobility

The results of the extractable zinc and cadmium in soil samples showed significant differences between the treatments. The extractable zinc concentration of the Eschenau control treatment was about 11.5 % of the initial zinc content and the extractable cadmium concentration was at about 15 % of the initial cadmium concentration after 151 days. The treatments with biochar and aged biochar showed lower concentrations than the control treatment with extractable zinc values between 1.7-3.4 % of the initial zinc concentration and extractable cadmium 4-8 % of the initial cadmium content. That higher reduction of the metal mobility was apparently caused by the adsorption capacity of biochar and the increased pH value based on the alkali nature of the ash of biochar [10][15][16]. The study of Houben et al. (2013) supports the results of significantly lower extractable metal concentrations after the application of biochar, compared to the control treatment. The extractable metal concentrations decreased gradual with time. After 151 days, the extractable cadmium and zinc concentrations were 2.4 and 5.4 times lower than those measured after 1 hour of incubation [46]. The gradually reduction of extractable metals matches with the increasing pH values over the time, which could indicate that the soil pH was responsible for that reduction (see *Table 18*).

The treatments containing compost had the lowest extractable zinc and cadmium concentrations with extractable zinc values between 0.2-0.3 % of the initial zinc content and extractable cadmium concentrations between 0.1-0.6 % of the initial cadmium content. Those treatments also had shown the highest increase of the soil pH, which indicates that the compost part was notably responsible for the major reduction of extractable zinc and cadmium. The amended compost and biochar raised the soil pH, which caused a reduction in the mobility of metals and the amount of extractable zinc and cadmium decreased (see *Table 18*) [18][19]. Karami et al. also reached the highest pH values in soils amended with biochar and compost [47]. The results of the electric conductivity of the soil samples showed, that the treatments with compost had increased ionic concentration (see *Table 19*). The results of the electric conductivity of soil pore water samples confirm that (see *Table 28*).

The treatment with lime also showed low extractable zinc and cadmium concentrations with 0.6 % of the initial zinc content and 3 % of the initial cadmium content, which was also caused by the increased pH of the treatment [25]. The DT_{50} values of extractable cadmium and zinc confirmed that the treatments with soil amendments needed the fewest time for the reduction of 50 % of the initial metals (see *Table 20*). The DT_{50} value of extractable zinc of the control was 75 days and the DT_{50} value of extractable cadmium 149 days. The DT_{50} values of extractable zinc in the treatments with soil amendments were between 8-26 days and the DT_{50} values of extractable cadmium between 44-87 days.

The results of the sequential extraction of the treatments with freshly added cadmium and zinc showed that the major part of the metals were divided into the first, the exchangeable fraction and the second, the reducible fraction (see *Table 6* and *7*). The first step was the extraction of the exchangeable and with carbonates associated fraction with 0.11 M acetic acid. The exchangeable fraction contained extractable metals, which were sorbed on the surface of particles and mobilized at a neutral pH level. The treatments with metals had exchangeable zinc concentrations between 66-76 % of the total zinc content without significant differences between the treatments. The exchangeable cadmium concentration was between 58-79 % of the total cadmium content. The treatment with compost showed the highest reduction with 58 % of the initial cadmium content.

Step two, the extraction with 0.5 M hydroxylamine hydrochloride solution, to extract fractions associated with easily and moderately reducible iron and manganese oxyhydroxides, contained 27-37 % of the total zinc and 36-55 % of the total cadmium. The treatment number two with lime had the lowest extractable zinc concentration with 27 % of the initial zinc content and treatment number 4.a the lowest cadmium concentration with 36 % of the initial cadmium content. Zinc and cadmium were bound by adsorption to iron and manganese oxyhydroxides in neutral soil conditions. Under reducing conditions, the oxyhydroxide precipitates dissolved and the bound metal got as ions into solution.

The oxidizable and the mineral bound residual fraction contained only minor amounts of zinc and cadmium. The oxidizable zinc content in step three was between 4-5 % and the oxidizable cadmium content between 3-4 %. Step four, the mineral bound residual fraction, contained 3-4 % of the initial zinc content and <1 % of the initial cadmium content. That

indicates that the major amount of fresh added metals were not bound very strong and exchangeable.

The treatments without freshly added metals had a total zinc content between 44-63 mg/kg DM and a total cadmium content between 122-126 µg/kg DM. Both, the total zinc and cadmium content, were under the limit values for metals in permanent grassland soils with limit values for zinc of 150 mg/kg DM and cadmium <1 mg/kg DM (see *Table 14* and*17*) [30].

The analyses of extractable zinc and cadmium in soil pore water showed similar results as the soil analysis after 156 days. At sampling time point five, the extractable zinc and cadmium concentrations were significantly lower in the treatments with soil amendments compared to the control treatment. The control treatment had an extractable zinc concentration of 16 mg/l soil pore water and an extractable cadmium concentration of 110 µg/l soil pore water. The lowest extractable zinc concentrations showed the treatment with lime and the treatment with compost with values between 0.8-1.3 mg/l soil pore water, which presents 0.08-0.13 % of the initial zinc content. The lowest extractable cadmium concentration had the treatment with compost with 12 µg/l soil pore water. The treatments with lime, biochar or combined amendments had values between 12-34 µg/l soil pore water. As in the soil samples, the pH values of soil pore water samples were significantly higher in the treatments with soil amendments (see *Table 18* and *27*) and matches well with the results of the extractable zinc and cadmium (see *Figure 21* and *22)*, which indicates that the higher pH- values were responsible for the decreased metal concentrations. Beesley et al. (2010) had also reached significant reductions of cadmium and zinc by the application of compost, biochar or both amendments combined after 60 days. The study also observed increased pH and dissolved organic carbon values in the treatments with only one or both soil amendments but no significant influence of DOC on the mobility of zinc and cadmium, which indicates that the main reason for the reduction of extractable metals were increased pH values [45].

The DOC results indicate that there was no influence of dissolved organic carbon on the mobility of zinc and cadmium because the DOC of the treatment with lime was as low as the control treatment but the extractable metal concentrations were significantly reduced compared to the control treatment. The amount of dissolved organic carbon (DOC) was significantly higher in the treatments with compost and biochar compared to the control treatment (see *Table 26*). That higher amount of DOC in those treatments was based on the amended compost. The amount of dissolved organic carbon particles in the treatments with compost decreased over the time. That indicates that the compost provided high amounts of organic matter, which were quickly degraded to small particles of DOC after the addition to soil. The treatments with biochar showed an opposite behaviour. At sampling time point three, the DOC concentration started to increase in the treatments with biochar and aged biochar. Biochar pores are good microbial habitats, because nutrients and water are stored and by that, the higher microbial activity caused a higher degradation rate of organic matter and a generation of DOC [4][5]. A part of the generated DOC could also origin from the surface of the biochar. The increasing DOC concentration in the treatments with biochar and the high initial content of organic matter added by compost application caused the highest

DOC concentrations at sampling time point five in the treatments with combined amendments.

The dissipation times of extractable zinc and cadmium in soil pore water were lower in the treatments with soil amendments, which confirms that the immobilization of metals was higher in the treatments with soil amendments compared to the control treatment, except the dissipation time of zinc in treatment 4.a with aged biochar.

5 Summary and conclusion

The aims of this study were the investigation of the influence of biochar and compost on the mobility of selected heavy metals and polycyclic aromatic hydrocarbons (PAHs) and to reveal the extent to which the transport of the pollutants towards groundwater was prevented by the introduction of organic amendments. This study showed that the application of 5 % biochar and 10 % compost to heavy metal contaminated soil can help to reduce the extractability as well as the bioavailability of zinc and cadmium, notably because it raises the soil pH. Moreover, the translocation of metals towards groundwater can be prevented by immobilization.

The results of the Eschenau soil incubation experiment showed that the highest reduction of extractable zinc and cadmium concentrations was reached in the treatments with lime, compost and the treatments with compost and biochar mixtures after 151 days of incubation. The extractable zinc and cadmium concentrations were in the treatment with lime 18.5 and 5 times, in the treatment with compost 72 and 132 times lower, respectively, when compared to the control treatment. The treatment with biochar and compost showed extractable zinc and cadmium concentrations 48 and 46 times lower, respectively, when compared to the control treatment. The results of the leaching studies confirmed that the treatments with lime, compost and combined amendments provide the highest reduction of metal mobility after 156 days. For zinc and cadmium, the treatment with lime resulted in values 14.5 and 5 times lower, respectively, the treatment with compost in 20 and 9,6 times lower, respectively, and the treatment with biochar and compost 13 and 5 times lower, respectively, when compared to the control treatment. This indicates that the transfer of metals into groundwater was distinctly reduced by the application of lime, biochar and compost for soil remediation.

The incubation experiment of the Eschenau soil showed that the highest reduction of extractable pyrene and phenanthrene was reached in the treatments with lime and the treatment with biochar and compost after 151 days of incubation. The treatment with lime showed extractable pyrene and phenanthrene concentrations 2 and 7 times lower, respectively, when compared to the control treatment and the treatment with biochar and compost reached concentrations 2 and 3 times lower, respectively, when compared to the control treatment. The leaching studies of the Eschernau soil showed no difference in the dissipation of PAHs between the treatments with soil amendments and the control treatment after 156 days.

The Treffling soil incubation study and the leaching study showed no reduction of the PAH concentration of the treatment with compost and biochar when compared to the control treatment.

Overall, one can say, that the use of combined amendments is a promising and suitable soil remediation application concerning immobilization of heavy metals and by that, the prevention of their transport into groundwater. Moreover, the use of biochar and compost as soil amendment has many benefits for soil parameters such as soil density, water holding capacity, pH, CEC and EC but also supports the efforts against global warming. The

application is less suitable for the immobilization of PAHs but partly supports their degradation.

6 Annex

6.1 Tables with the summarized results of soil analysis

6.1.1 Sum of 16 PAHs

Table 9: Summary of the results of the concentration of the sum of 16 PAHs extracted (ethyl acetate) from soil samples over five sampling time points. Means followed by different letters are significant difference according to the Tukey's multiple range test. Letters denote significant difference p < 0.05 (means ± standard deviation; n = 4; E = Eschenau soil; T = Treffling soil; CP = compost; BC = biochar; BCa = aged biochar; nHM = no added heavy metals).

Sum 16 PAHs (mg kg^{-1})					
Treatment	**18.02.2016**	**04.03.2016**	**20.04.2016**	**23.05.2016**	**25.07.2016**
E Control	-	-	-	-	-
E/ Lime	-	-	-	-	-
E/ 10% CP	-	-	-	-	-
E/ 5% BC	-	-	-	-	-
E/ 5% BCa	-	-	-	-	-
E/ 5% BC/ 10% CP	-	-	-	-	-
E/ 5% BCa/ 10% CP	-	-	-	-	-
E/ 5% BCa/ 10% CP/ nHM	-	-	-	-	-
T/ 5% BC / 10% CP	832,4 ± 17,3 B	153,6 ± 3,3 A	145,7 ± 22,2 A	222,6 ± 44,6 A	173,9 ± 6,1 A
T/ Control	1428,0 ± 86,0 A	156,0 ± 25,2 A	152,1 ± 16,6 A	199,2 ± 7,9 A	220,6 ± 87,7 A
P of ANOVA	p < 0,001	p = 0,86	p = 0,66	p = 0,42	p = 0,41

6.1.2 Pyrene

Table 10: Summary of the results of the pyrene concentration extracted (ethyl acetate) from soil samples over five sampling time points. Legend to the table, see Table 9.

Pyrene (mg kg^{-1})					
Treatment	**18.02.2016**	**04.03.2016**	**20.04.2016**	**23.05.2016**	**25.07.2016**
E Control	81,2 ± 0,9 BC	63,0 ± 1,2 A	43,4 ± 4,2 A	34,8 ± 1,0 A-C	29,2 ± 2,9 A
E/ Lime	72,2 ± 7,2 CD	59,3 ± 2,3 AB	40,3 ± 4,8 A	39,9 ± 1,9 A	12,9 ± 1,8 B
E/ 10% CP	58,9 ± 2,6 D	54,0 ± 1,4 BC	32,0 ± 4,4 AB	35,1 ± 3,0 AB	25,2 ± 3,7 AB
E/ 5% BC	62,2 ± 12,7 D	49,0 ± 0,2 C	34,7 ± 7,7 AB	26,7 ± 11,2 A-D	17,5 ± 2,3 AB
E/ 5% BCa	67,5 ± 1,0 CD	50,7 ± 0,3 C	40,7 ± 1,2 A	32,4 ± 7,9 A-C	15,0 ± 2,9 B
E/ 5% BC/ 10% CP	76,4 ± 0,5 CD	53,9 ± 2,6 BC	25,6 ± 4,6 BC	23,8 ± 10,1 A-D	11,9 ± 1,5 B
E/ 5% BCa/ 10% CP	84,9 ± 5,2 BC	56,8 ± 0,4 A-C	23,6 ± 7,9 BC	23,5 ± 9,0 A-D	18,2 ± 10,0 AB
E/ 5% BCa/ 10% CP/ nHM	89,3 ± 5,5 BC	40,5 ± 0,9 D	25,4 ± 9,3 BC	20,9 ± 5,2 B-D	18,3 ± 6,2 AB
T/ 5% BC / 10% CP	99,9 ± 15,2 B	20,3 ± 2,6 E	14,4 ± 3,9 C	17,1 ± 1,4 CD	16,8 ± 0,4 AB
T/ Control	144,2 ± 16,7 A	20,8 ± 1,7 E	12,7 ± 2,5 C	14,9 ± 1,6 D	21,8 ± 8,6 AB
P of ANOVA	p < 0,001	p < 0,001	p < 0,001	p < 0,001	p = 0,0032

6.1.3 Phenanthrene

Table 11: Summary of the results of the phenanthrene concentration extracted (ethyl acetate) from soil samples over five sampling time points. Legend to the table, see Table 9.

Phenanthrene (mg kg^{-1})					
Treatment	**18.02.2016**	**04.03.2016**	**20.04.2016**	**23.05.2016**	**25.07.2016**
E Control	77,2 ± 0,8 B	19,0 ± 0,1 A	3,4 ± 0,4 D	10,2 ± 3,7 B-D	21,6 ± 0,7 A
E/ Lime	72,6 ± 6,1 BC	11,6 ± 0,5 D	5,6 ± 1,6 B-D	4,8 ± 1,0 D	2,9 ± 0,4 D
E/ 10% CP	54,4 ± 3,4 D	10,6 ± 0,3 E	4,7 ± 1,2 CD	6,7 ± 1,2 CD	6,8 ± 1,8 CD
E/ 5% BC	64,7 ± 2,1 B-D	16,3 ± 0,2 B	13,5 ± 5,7 A	16,9 ± 4,1 A	12,5 ± 0,6 BC
E/ 5% BCa	59,1 ± 0,2 CD	14,6 ± 0,1 C	11,0 ± 2,1 AB	15,9 ± 3,9 AB	16,8 ± 5,0 AB
E/ 5% BC/ 10% CP	65,3 ± 4,4 B-D	8,4 ± 0,1 F	8,6 ± 0,7 A-D	8,9 ± 1,6 CD	8,2 ± 0,9 CD
E/ 5% BCa/ 10% CP	73,5 ± 12,0 BC	10,0 ± 0,3 E	7,2 ± 2,0 B-D	7,6 ± 1,9 CD	8,9 ± 2,6 CD
E/ 5% BCa/ 10% CP/ nHM	100,0 ± 1,0 A	10,1 ± 0,2 E	9,8 ± 1,7 A-C	8,5 ± 1,1 CD	8,8 ± 1,1 CD
T/ 5% BC / 10% CP	52,3 ± 5,7 D	7,4 ± 0,2 G	7,5 ± 1,6 B-D	12,4 ± 2,3 BC	11,1 ± 0,7 BC
T/ Control	101,8 ± 9,8 A	7,8 ± 0,6 FG	7,2 ± 1,0 B-D	11,2 ± 1,6 A-C	12,6 ± 5,5 BC
P of ANOVA	p < 0,001	p < 0,001	p < 0,001	p < 0,001	p < 0,001

6.1.4 Cadmium

Table 12: Summary of the results of the total cadmium content (aqua regia) of soil samples after first sampling time point. Legend to the table, see Table 9.

Total Cadmium (mg kg^{-1})					
Treatment	**18.02.2016**	**04.03.2016**	**20.04.2016**	**23.05.2016**	**25.07.2016**
E Control	9,1 ± 0,3 B	-	-	-	-
E/ Lime	9,4 ± 0,1 AB	-	-	-	-
E/ 10% CP	9,2 ± 0,0 AB	-	-	-	-
E/ 5% BC	9,2 ± 0,1 B	-	-	-	-
E/ 5% BCa	8,9 ± 0,1 B	-	-	-	-
E/ 5% BC/ 10% CP	9,2 ± 0,3 B	-	-	-	-
E/ 5% BCa/ 10% CP	9,7 ± 0,2 A	-	-	-	-
E/ 5% BCa/ 10% CP/ nHM	< 0,055	-	-	-	-
T/ 5% BC / 10% CP	< 0,055	-	-	-	-
T/ Control	< 0,055	-	-	-	-
P of ANOVA	p = 0,003				

Table 13: Table 13: Summary of the extractable (1 M ammonium nitrate solution) cadmium concentration of soil samples. Legend to the table, see Table 9.

Cadmium (mg kg^{-1})					
Treatment	**18.02.2016**	**04.03.2016**	**20.04.2016**	**23.05.2016**	**25.07.2016**
E Control	3,1 ± 0,29 A	2,5 ± 0,09 A	1,7 ± 0,05 A	1,9 ± 0,28 A	1,5 ± 0,29 A
E/ Lime	1,0 ± 0,02 C	0,6 ± 0,02 C	0,5 ± 0,05 B	0,4 ± 0,02 C	0,3 ± 0,01 A
E/ 10% CP	0,5 ± 0,02 D	0,2 ± 0,01 D	0,2 ± 0,03 C	0,1 ± 0,02 D	0,0 ± 0,00 B
E/ 5% BC	2,4 ± 0,23 B	1,4 ± 0,76 B	1,3 ± 0,62 A	0,8 ± 0,24 B	0,4 ± 0,15 A
E/ 5% BCa	2,6 ± 0,20 B	1,5 ± 0,06 AB	1,3 ± 0,32 A	1,1 ± 0,33 B	0,8 ± 0,23 A
E/ 5% BC/ 10% CP	0,5 ± 0,04 D	0,3 ± 0,00 D	0,2 ± 0,01 C	0,2 ± 0,00 D	0,0 ± 0,01 B
E/ 5% BCa/ 10% CP	0,5 ± 0,02 D	0,3 ± 0,02 D	0,2 ± 0,02 C	0,2 ± 0,03 D	0,1 ± 0,06 B
E/ 5% BCa/ 10% CP/ nHM	< 0,183	< 0,183	< 0,183	< 0,183	< 0,183
T/ 5% BC / 10% CP	< 0,183	< 0,183	< 0,183	< 0,183	< 0,183
T/ Control	< 0,183	< 0,183	< 0,183	< 0,183	< 0,183
P of ANOVA	p < 0,001	p < 0,001	p < 0,001	p < 0,001	p < 0,001

Table 14: Summary of the results of the cadmium concentration after sequential extraction of soil samples. Legend to the table, see Table 9.

Sequential extraction 27.04.2016 Cadmium (µg kg^{-1})					
Treatment	**Step 1**	**Step 2**	**Step 3**	**Step 4**	**Step 5**
E Control	6116,4 ± 323,1 C	3731,8 ± 57,6 BC	231,4 ± 38,0 C	40,4 ± 9,9 AB	9082,4 ± 328,3 A
E/ Lime	7125,9 ± 82,3 A	3401,0 ± 273,9 C	261,0 ± 39,5 BC	38,2 ± 4,9 AB	9363,3 ± 101,9 A
E/ 10% CP	5368,2 ± 307,9 D	5066,3 ± 824,4 A	342,5 ± 80,0 A-C	40,6 ± 16,8 AB	9238,5 ± 0,0 A
E/ 5% BC	6864,6 ± 246,8 AB	3817,3 ± 243,5 A-C	297,9 ± 36,7 A-C	46,8 ± 15,1 A	9155,2 ± 72,1 A
E/ 5% BCa	6949,5 ± 239,2 AB	3291,0 ± 617,3 C	243,4 ± 52,5 C	30,4 ± 1,4 A-C	8947,1 ± 144,2 A
E/ 5% BC/ 10% CP	5927,3 ± 286,5 CD	5009,3 ± 317,2 A	423,3 ± 8,3 A	30,8 ± 9,3 AB	9176,0 ± 297,2 A
E/ 5% BCa/ 10% CP	6303,0 ± 381,8 BC	5007,9 ± 745,1 AB	356,7 ± 33,6 AB	32,2 ± 2,3 AB	9706,6 ± 157,1 A
E/ 5% BCa/ 10% CP/ nHM	63,8 ± 1,2 F	84,7 ± 0,6 E	14,6 ± 0,8 E	18,6 ± 1,7 B-D	125,7 ± 6,2 B
T/ 5% BC / 10% CP	66,4 ± 1,0 F	115,1 ± 9,6 D	23,8 ± 4,0 D	8,6 ± 4,0 CD	122,9 ± 9,0 B
T/ Control	94,5 ± 3,0 E	75,1 ± 2,7 E	15,2 ± 2,5 E	3,9 ± 3,7 D	121,9 ± 3,3 B
P of ANOVA	p < 0,001	p < 0,001	p < 0,001	p < 0,001	p < 0,001

6.1.5 Zinc

Table 15: Summary of the results of the total zinc content (aqua regia) of soil samples after first sampling time point. Legend to the table, see Table 9.

Total Zinc (mg kg^{-1})					
Treatment	**18.02.2016**	**04.03.2016**	**20.04.2016**	**23.05.2016**	**25.07.2016**
E Control	980,0 ± 83,8 B	-	-	-	-
E/ Lime	1050,8 ± 58,7 AB	-	-	-	-
E/ 10% CP	1092,1 ± 34,9 AB	-	-	-	-
E/ 5% BC	1088,3 ± 41,4 AB	-	-	-	-
E/ 5% BCa	1067,7 ± 39,8 AB	-	-	-	-
E/ 5% BC/ 10% CP	1062,7 ± 11,5 AB	-	-	-	-
E/ 5% BCa/ 10% CP	1163,5 ± 68,2 A	-	-	-	-
E/ 5% BCa/ 10% CP/ nHM	26,3 ± 2,0 C	-	-	-	-
T/ 5% BC / 10% CP	20,4 ± 0,5 D	-	-	-	-
T/ Control	17,4 ± 0,7 E	-	-	-	-
P of ANOVA	p < 0,001				

Table 16: Summary of the results of the extractable (1 M ammonium nitrate solution) zinc concentration of soil samples. Legend to the table, see Table 9.

Zinc (mg kg^{-1})					
Treatment	**18.02.2016**	**04.03.2016**	**20.04.2016**	**23.05.2016**	**25.07.2016**
E Control	389,2 ± 60,4 A	296,8 ± 32,8 A	157,5 ± 8,9 A	182,7 ± 39,9 A	115,0 ± 26,3 A
E/ Lime	49,4 ± 1,5 B	16,2 ± 1,0 C	9,9 ± 0,7 D	5,6 ± 0,3 D	6,2 ± 0,3 C
E/ 10% CP	36,9 ± 3,1 BC	10,6 ± 0,4 D	7,4 ± 0,6 D	3,7 ± 0,4 D	1,6 ± 0,1 D
E/ 5% BC	301,7 ± 33,7 A	74,9 ± 2,0 B	64,1 ± 26,5 C	38,6 ± 18,7 C	17,4 ± 9,5 B
E/ 5% BCa	327,6 ± 51,2 A	110,9 ± 38,4 B	99,8 ± 24,8 B	80,9 ± 39,0 B	34,0 ± 6,3 B
E/ 5% BC/ 10% CP	35,4 ± 6,6 BC	15,0 ± 0,5 CD	7,5 ± 0,5 D	4,4 ± 0,4 D	2,4 ± 0,4 D
E/ 5% BCa/ 10% CP	36,1 ± 4,5 C	14,1 ± 0,4 CD	10,1 ± 1,6 D	4,3 ± 0,3 D	2,9 ± 1,2 D
E/ 5% BCa/ 10% CP/ nHM	< 0,099	< 0,099	< 0,099	< 0,099	< 0,099
T/ 5% BC / 10% CP	< 0,099	< 0,099	< 0,099	< 0,099	< 0,099
T/ Control	< 0,099	< 0,099	< 0,099	< 0,099	< 0,099
P of ANOVA	p < 0,001	p < 0,001	p < 0,001	p < 0,001	p < 0,001

Table 17: Summary of the results of the zinc concentration after sequential extraction of soil samples. Legend to the table, see Table 9.

Sequential extraction 27.04.2016 Zinc (mg kg^{-1})					
Treatment	**Step 1**	**Step 2**	**Step 3**	**Step 4**	**Step 5**
E Control	652,2 ± 12,5 A	306,2 ± 2,8 AB	39,5 ± 7,1 C	29,6 ± 2,8 A	980,0 ± 83,8 A
E/ Lime	720,8 ± 19,9 A	252,8 ± 26,4 B	38,4 ± 2,1 BC	31,8 ± 1,1 A	1022,6 ± 19,9 A
E/ 10% CP	687,8 ± 9,2 A	324,4 ± 28,0 A	44,3 ± 5,9 A-C	33,6 ± 4,3 A	1092,1 ± 34,9 A
E/ 5% BC	705,7 ± 49,4 A	285,1 ± 47,9 AB	39,5 ± 2,8 A-C	34,7 ± 1,5 A	1088,3 ± 41,4 A
E/ 5% BCa	645,0 ± 4,4 A	301,7 ± 13,5 AB	35,7 ± 5,5 C	31,2 ± 0,2 AB	1067,7 ± 39,8 A
E/ 5% BC/ 10% CP	707,8 ± 38,5 A	341,7 ± 14,6 A	45,8 ± 2,3 A	31,4 ± 4,7 AB	1062,7 ± 11,5 A
E/ 5% BCa/ 10% CP	709,9 ± 24,2 A	329,1 ± 26,1 A	40,8 ± 1,6 AB	34,1 ± 1,1 A	1163,5 ± 68,2 A
E/ 5% BCa/ 10% CP/ nHM	8,6 ± 1,0 B	12,4 ± 0,0 C	10,2 ± 1,2 E	26,0 ± 6,2 AB	62,8 ± 0,4 B
T/ 5% BC / 10% CP	6,5 ± 0,7 C	12,9 ± 1,0 C	14,3 ± 2,3 D	20,7 ± 1,2 BC	49,7 ± 2,7 B
T/ Control	2,6 ± 0,4 D	7,0 ± 0,5 D	8,3 ± 0,4 E	17,7 ± 0,3 C	43,8 ± 2,0 B
P of ANOVA	p < 0,001	p < 0,001	p < 0,001	p < 0,001	p < 0,001

6.1.6 Soil pH value and electric conductivity of soil samples

Table 18: Summary of the results of the pH values of different soil samples. Legend to the table, see Table 9.

pH- value Soil					
Treatment	**18.02.2016**	**04.03.2016**	**20.04.2016**	**23.05.2016**	**25.07.2016**
E Control	5,4 ± 0,11 H	5,5 ± 0,05 F	5,5 ± 0,08 D	5,6 ± 0,07 D	5,5 ± 0,07 E
E/ Lime	6,4 ± 0,01 DE	6,5 ± 0,02 C	6,5 ± 0,08 B	6,7 ± 0,01 B	6,6 ± 0,11 CD
E/ 10% CP	6,5 ± 0,02 CD	6,9 ± 0,01 B	7,1 ± 0,02 A	7,2 ± 0,01 AB	7,3 ± 0,04 AB
E/ 5% BC	5,8 ± 0,03 G	6,3 ± 0,01 D	6,1 ± 0,35 C	6,2 ± 0,43 C	6,3 ± 0,51 D
E/ 5% BCa	5,6 ± 0,10 F	5,9 ± 0,11 E	5,9 ± 0,10 C	6,1 ± 0,14 C	6,2 ± 0,15 D
E/ 5% BC/ 10% CP	6,7 ± 0,01 B	6,9 ± 0,01 B	7,2 ± 0,02 A	7,5 ± 0,13 A	7,5 ± 0,07 A
E/ 5% BCa/ 10% CP	6,6 ± 0,08 BC	6,9 ± 0,03 B	6,9 ± 0,13 A	7,4 ± 0,02 A	7,4 ± 0,19 AB
E/ 5% BCa/ 10% CP/ nHM	7,0 ± 0,03 A	7,3 ± 0,01 A	7,3 ± 0,02 A	7,5 ± 0,03 A	7,6 ± 0,10 A
T/ 5% BC / 10% CP	7,0 ± 0,01 A	7,4 ± 0,04 A	7,3 ± 0,05 A	7,5 ± 0,00 A	7,5 ± 0,14 A
T/ Control	6,3 ± 0,03 E	6,5 ± 0,01 C	6,5 ± 0,04 B	6,8 ± 0,07 B	6,9 ± 0,01 BC
P of ANOVA	p < 0,001	p < 0,001	p < 0,001	p < 0,001	p < 0,001

Table 19: Summary of the results of electric conductivity of soil samples. Legend to the table, see Table 9.

Electric conductivity (µS cm^{1}) Soil					
Treatment	**18.02.2016**	**04.03.2016**	**20.04.2016**	**23.05.2016**	**25.07.2016**
E Control	267,3 ± 19,9 B-D	196,7 ± 23,8 BC	-	173,5 ± 36,0 CD	-
E/ Lime	236,3 ± 23,4 CD	161,5 ± 35,4 BC	-	115,3 ± 4,7 DE	-
E/ 10% CP	356,8 ± 16,1 AB	242,5 ± 18,6 AB	-	222,8 ± 22,3 BC	-
E/ 5% BC	200,1 ± 22,6 DE	189,1 ± 107,0 BC	-	227,8 ± 90,0 BC	-
E/ 5% BCa	233,6 ± 29,8 CD	114,2 ± 47,5 C	-	146,6 ± 15,2 C-E	-
E/ 5% BC/ 10% CP	327,7 ± 59,5 A-D	243,0 ± 0,0 A-C	-	278,5 ± 12,9 AB	-
E/ 5% BCa/ 10% CP	397,5 ± 103,9 A	341,5 ± 36,6 A	-	277,0 ± 47,9 AB	-
E/ 5% BCa/ 10% CP/ nHM	267,0 ± 26,0 B-D	N.A.	-	219,0 ± 10,5 BC	-
T/ 5% BC / 10% CP	333,3 ± 62,0 A-C	265,0 ± 0,0 A-C	-	333,3 ± 11,7 A	-
T/ Control	107,8 ± 16,0 E	115,8 ± 2,5 C	-	67,7 ± 3,8 E	-
P of ANOVA	p < 0,001	p < 0,001	-	p < 0,001	-

6.1.7 Dissipation time 50% of pollutants

Table 20: Summary of the results of the dissipation time (DT50) for all four pollutants in soil samples. Legend to the table, see Table 9.

DT 50				
Treatment	**Zinc**	**Cadmium**	**Pyrene**	**Phenanthrene**
E Control	75 ± 8 A	149 ± 42 A	68 ± 6 A	6 ± 0 A
E/ Lime	11 ± 0 B	79 ± 5 B	56 ± 14 AB	5 ± 1 CD
E/ 10% CP	9 ± 1 B	44 ± 4 B	67 ± 4 A	2 ± 0 F
E/ 5% BC	8 ± 0 B	62 ± 33 B	50 ± 8 A-C	5 ± 0 B-D
E/ 5% BCa	26 ± 20 B	87 ± 11 B	55 ± 11 AB	3 ± 0 EF
E/ 5% BC/ 10% CP	19 ± 6 B	51 ± 5 B	35 ± 10 BC	3 ± 0 D-F
E/ 5% BCa/ 10% CP	20 ± 6 B	60 ± 11 B	37 ± 11 BC	4 ± 1 B-E
E/ 5% BCa/ 10% CP/ nHM	-	-	27 ± 13 CD	6 ± 0 AB
T/ 5% BC / 10% CP	-	-	6 ± 0 D	5 ± 0 B-E
T/ Control	-	-	5 ± 0 D	5 ± 1 A-C
P of ANOVA	p < 0,001	p < 0,001	p < 0,001	p < 0,001

6.2 Tables with the summarized results of soil pore water analysis

6.2.1 Sum of 16 PAHs

Table 21: Summary of the results of the concentration of the sum of 16 PAHs extracted (n- hexane) from soil pore water samples over five sampling time points. Legend to the table, see Table 9.

Sum 16 PAHs (mg L^{-1})					
Treatment	**29.02.2016**	**11.03.2016**	**27.04.2016**	**31.05.2016**	**27.07.2016**
E Control	-	-	-	-	-
E/ Lime	-	-	-	-	-
E/ 10% CP	-	-	-	-	-
E/ 5% BC	-	-	-	-	-
E/ 5% BCa	-	-	-	-	-
E/ 5% BC/ 10% CP	-	-	-	-	-
E/ 5% BCa/ 10% CP	-	-	-	-	-
E/ 5% BCa/ 10% CP/ nHM	-	-	-	-	-
T/ 5% BC / 10% CP	142,0 ± 2,4 B	<0,253	<0,253	<0,000032	<0,000032
T/ Control	243,5 ± 13,8 A	<0,253	<0,253	<0,000032	<0,000032
P of ANOVA	p < 0,001	-	-	-	-

6.2.2 Pyrene

Table 22: Summary of the results of pyrene concentration extracted (n- hexane) from soil pore water samples over five sampling time points. Legend to the table, see Table 9.

Pyrene (µg L^{-1})					
Treatment	**29.02.2016**	**11.03.2016**	**27.04.2016**	**31.05.2016**	**27.07.2016**
E Control	107571,6 ± 11231,2 AB	4166,4 ± 775,7 AB	<13,33	<13,33	<13,33
E/ Lime	110957,8 ± 3760,2 AB	6221,0 ± 4518,4 A	<13,33	<13,33	<13,33
E/ 10% CP	94231,7 ± 10151,8 B	5400,0 ± 206,1 AB	<13,33	<13,33	<13,33
E/ 5% BC	98753,0 ± 20831,9 AB	6487,5 ± 1465,3 A	<13,33	<13,33	<13,33
E/ 5% BCa	104690,3 ± 4439,9 AB	5115,0 ± 794,0 AB	<13,33	<13,33	<13,33
E/ 5% BC/ 10% CP	114930,7 ± 2077,6 AB	1725,6 ± 334,7 B	<13,33	<13,33	<13,33
E/ 5% BCa/ 10% CP	124889,7 ± 2355,0 AB	4533,8 ± 745,7 AB	<13,33	<13,33	<13,33
E/ 5% BCa/ 10% CP/ nHM	132100,2 ± 15298,6 A	<13,33	<13,33	<13,33	<13,33
T/ 5% BC / 10% CP	14313,0 ± 2405,4 D	<13,33	<13,33	<13,33	<13,33
T/ Control	19425,7 ± 2065,0 C	<13,33	<13,33	<13,33	<13,33
P of ANOVA	p < 0,001	p = 0,041	-	-	-

6.2.3 Phenanthrene

Table 23: Summary of the results of phenanthrene concentration extracted (n- hexane) from soil pore water samples over five sampling time points. Legend to the table, see Table 9.

Phenanthrene (µg L^{-1})						
Treatment	**29.02.2016**		**11.03.2016**	**27.04.2016**	**31.05.2016**	**27.07.2016**
E Control	93401,5	± 5769,2 AB	< 10,0	< 10,0	< 10,0	< 10,0
E/ Lime	99417,4	± 862,2 AB	< 10,0	< 10,0	< 10,0	< 10,0
E/ 10% CP	76693,5	± 714,7 B	< 10,0	< 10,0	< 10,0	< 10,0
E/ 5% BC	79984,0	± 17629,0 B	< 10,0	< 10,0	< 10,0	< 10,0
E/ 5% BCa	85924,5	± 4119,4 AB	< 10,0	< 10,0	< 10,0	< 10,0
E/ 5% BC/ 10% CP	92297,1	± 6759,7 AB	< 10,0	< 10,0	< 10,0	< 10,0
E/ 5% BCa/ 10% CP	107592,1	± 4303,8 AB	< 10,0	< 10,0	< 10,0	< 10,0
E/ 5% BCa/ 10% CP/ nHM	113546,8	± 29566,8 A	< 10,0	< 10,0	< 10,0	< 10,0
T/ 5% BC / 10% CP	7356,1	± 849,8 C	< 10,0	< 10,0	< 10,0	< 10,0
T/ Control	12902,6	± 428,4 C	< 10,0	< 10,0	< 10,0	< 10,0
P of ANOVA	p < 0,001		-	-	-	-

6.2.4 Cadmium

Table 24: Summary of the results of the extractable (65 % nitric acid) cadmium concentration from soil pore water over five sampling time points. Legend to the table, see Table 9.

Extractable cadmium (µg L^{-1})										
Treatment	**29.02.2016**		**11.03.2016**		**27.04.2016**		**31.05.2016**		**27.07.2016**	
E Control	1446,3 ± 97,2	A	380,4 ± 137,6	A	138,0 ± 85,1	A	113,3 ± 4,9	A	110,3 ± 12,5	A
E/ Lime	533,7 ± 101,0	B	202,2 ± 49,6	B	54,2 ± 10,5	A	32,6 ± 7,1	BC	33,7 ± 0,7	B
E/ 10% CP	222,1 ± 29,4	C	94,2 ± 6,6	C	41,9 ± 0,0	A	12,5 ± 4,8	D	11,5 ± 6,3	C
E/ 5% BC	374,2 ± 85,6	BC	131,9 ± 26,5	BC	66,4 ± 23,2	A	25,1 ± 5,4	BC	28,8 ± 6,0	B
E/ 5% BCa	569,3 ± 166,8	B	114,2 ± 4,0	C	87,4 ± 36,8	A	41,9 ± 0,0	B	48,5 ± 16,9	AB
E/ 5% BC/ 10% CP	191,1 ± 52,6	C	86,8 ± 7,9	C	47,2 ± 15,5	A	22,8 ± 5,7	C	24,1 ± 2,0	B
E/ 5% BCa/ 10% CP	163,0 ± 4,0	C	380,4 ± 23,3	C	43,7 ± 24,5	A	33,9 ± 8,1	BC	25,6 ± 5,4	B
E/ 5% BCa/ 10% CP/ nHM	< 34,4		< 34,4		< 34,4		< 34,4		< 34,4	
T/ 5% BC / 10% CP	< 34,4		< 34,4		< 34,4		< 34,4		< 34,4	
T/ Control	< 34,4		< 34,4		< 34,4		< 34,4		< 34,4	
P of ANOVA	p < 0,001		p < 0,001		p = 0,078		p < 0,001		p = 0,001	

6.2.5 Zinc

Table 25: Summary of the results of the extractable (65 % nitric acid) zinc concentration from soil pore water over five sampling time points. Legend to the table, see Table 9.

Extractable zinc (mg L^{-1})					
Treatment	**29.02.2016**	**11.03.2016**	**27.04.2016**	**31.05.2016**	**27.07.2016**
E Control	240,4 ± 68,6 A	60,3 ± 1,1 A	24,8 ± 16,7 A	13,9 ± 2,1 A	15,9 ± 2,4 A
E/ Lime	58,3 ± 2,4 BC	21,7 ± 4,3 AB	4,4 ± 0,5 B	1,4 ± 0,3 D	1,1 ± 0,2 CD
E/ 10% CP	18,5 ± 3,1 DE	10,4 ± 1,3 BC	3,9 ± 0,0 B	2,0 ± 0,6 CD	0,8 ± 0,5 D
E/ 5% BC	33,1 ± 15,8 CD	15,1 ± 6,0 AB	6,7 ± 3,5 AB	2,4 ± 0,6 C	2,6 ± 0,1 BC
E/ 5% BCa	74,7 ± 11,6 B	16,5 ± 2,1 AB	7,8 ± 1,1 AB	4,3 ± 0,5 B	3,6 ± 1,9 B
E/ 5% BC/ 10% CP	11,7 ± 3,2 DE	4,8 ± 3,3 C	2,5 ± 0,2 B	1,8 ± 0,0 CD	1,2 ± 0,0 B-D
E/ 5% BCa/ 10% CP	19,2 ± 7,2 E	10,9 ± 2,6 BC	5,3 ± 1,8 B	2,9 ± 0,7 BC	1,3 ± 0,4 B-D
E/ 5% BCa/ 10% CP/ nHM	< 0,034	< 0,034	< 0,034	< 0,034	< 0,034
T/ 5% BC / 10% CP	< 0,034	< 0,034	< 0,034	< 0,034	< 0,034
T/ Control	< 0,034	< 0,034	< 0,034	< 0,034	< 0,034
P of ANOVA	p < 0,001	p < 0,001	p = 0,002	p < 0,001	p < 0,001

6.2.6 Dissolved organic carbon, pH value and electric conductivity

Table 26: Summary of the results of dissolved organic carbon in soil pore water samples. Legend to the table, see Table 9.

Dissolved organic carbon (mg L^{-1})					
Treatment	**29.02.2016**	**11.03.2016**	**27.04.2016**	**31.05.2016**	**27.07.2016**
E Control	29,1 ± 2,5 CD	32,3 ± 0,6 C	30,1 ± 7,8 C	32,6 ± 7,2 D	29,9 ± 3,0 D
E/ Lime	29,0 ± 2,0 CD	33,4 ± 0,4 C	39,6 ± 0,2 BC	38,4 ± 11,9 D	41,9 ± 1,1 CD
E/ 10% CP	221,9 ± 28,6 C	251,4 ± 26,7 A	186,0 ± 43,6 A	142,9 ± 65,8 AB	77,6 ± 25,4 AB
E/ 5% BC	23,9 ± 3,4 D	27,3 ± 0,4 D	56,0 ± 13,8 B	71,3 ± 24,7 CD	75,0 ± 3,7 AB
E/ 5% BCa	25,1 ± 3,0 CD	34,5 ± 1,4 C	47,7 ± 6,4 B	64,0 ± 11,2 CD	50,6 ± 9,1 B-D
E/ 5% BC/ 10% CP	237,6 ± 2,1 BC	246,0 ± 4,4 A	223,4 ± 25,2 A	200,3 ± 7,5 A	100,1 ± 18,4 A
E/ 5% BCa/ 10% CP	244,3 ± 15,1 BC	222,7 ± 9,4 A	207,3 ± 11,6 A	196,0 ± 19,9 A	85,8 ± 10,0 A
E/ 5% BCa/ 10% CP/ nHM	277,5 ± 10,4 AB	194,9 ± 4,7 B	184,8 ± 8,7 A	163,8 ± 8,7 AB	88,0 ± 6,7 A
T/ 5% BC / 10% CP	325,1 ± 5,5 A	247,4 ± 1,0 A	146,2 ± 13,7 A	124,5 ± 3,5 BC	71,0 ± 14,6 A-C
T/ Control	30,1 ± 2,0 D	31,4 ± 2,5 C	29,5 ± 2,9 C	31,6 ± 1,1 D	28,7 ± 0,6 D
P of ANOVA	p < 0,001	p < 0,001	p < 0,001	p < 0,001	p < 0,001

Table 27: Summary of the results of pH values of soil pore water samples. Legend to the table, see Table 9.

pH- Value					
Treatment	**29.02.2016**	**11.03.2016**	**27.04.2016**	**31.05.2016**	**27.07.2016**
E Control	6,5 ± 0,1 E	7,0 ± 0,0 G	6,6 ± 0,2 E	6,6 ± 0,0 E	6,9 ± 0,2 D
E/ Lime	6,8 ± 0,1 D	7,6 ± 0,0 E	7,3 ± 0,0 CD	7,2 ± 0,1 CD	7,6 ± 0,0 BC
E/ 10% CP	7,3 ± 0,1 BC	7,8 ± 0,1 D	7,8 ± 0,1 AB	7,7 ± 0,3 AB	8,2 ± 0,2 A
E/ 5% BC	7,2 ± 0,1 C	7,5 ± 0,0 E	7,2 ± 0,0 D	7,2 ± 0,2 CD	7,6 ± 0,2 BC
E/ 5% BCa	6,8 ± 0,1 D	7,3 ± 0,0 F	7,2 ± 0,1 CD	6,9 ± 0,0 DE	7,4 ± 0,3 C
E/ 5% BC/ 10% CP	7,7 ± 0,2 A	7,9 ± 0,0 C	8,1 ± 0,0 AB	7,8 ± 0,1 A	8,0 ± 0,0 AB
E/ 5% BCa/ 10% CP	7,3 ± 0,0 BC	8,0 ± 0,0 B	7,6 ± 0,2 B	7,4 ± 0,1 A-C	7,9 ± 0,1 AB
E/ 5% BCa/ 10% CP/ nHM	7,7 ± 0,1 A	8,5 ± 0,0 A	8,1 ± 0,1 A	7,7 ± 0,2 AB	8,1 ± 0,1 A
T/ 5% BC / 10% CP	7,5 ± 0,1 AB	8,0 ± 0,0 B	8,1 ± 0,3 A	7,8 ± 0,1 A	8,2 ± 0,2 A
T/ Control	7,6 ± 0,1 AB	8,1 ± 0,0 B	7,8 ± 0,0 AB	7,3 ± 0,1 BC	8,0 ± 0,0 AB
P of ANOVA	p < 0,001	p < 0,001	p < 0,001	p < 0,001	p < 0,001

Table 28: Summary of the results of electric conductivity of soil pore water samples. Legend to the table, see Table 9.

Electric conductivity (µS cm^{1})			
Treatment	**29.02.2016**	**11.03.2016**	**27.04.2016**
E Control	7506,7 ± 349,5 BCD	2902,5 ± 9,6 E	1375,5 ± 641,5 C
E/ Lime	5750,0 ± 103,9 D	2116,7 ± 15,3 G	974,0 ± 129,7 C
E/ 10% CP	9045,0 ± 267,6 AB	4640,0 ± 181,9 C	2370,0 ± 144,5 B
E/ 5% BC	7032,5 ± 1012,6 CD	2570,0 ± 60,8 F	1257,5 ± 77,2 C
E/ 5% BCa	6043,3 ± 162,0 D	1717,0 ± 27,1 H	1018,3 ± 140,5 C
E/ 5% BC/ 10% CP	9474,5 ± 622,4 A	5672,5 ± 92,9 A	3040,0 ± 501,0 AB
E/ 5% BCa/ 10% CP	9367,5 ± 1367,2 A	5570,0 ± 55,7 A	4035,0 ± 902,3 A
E/ 5% BCa/ 10% CP/ nHM	8710,0 ± 43,6 ABC	3173,3 ± 20,8 D	2727,5 ± 188,9 AB
T/ 5% BC / 10% CP	8815,0 ± 341,9 AB	4891,5 ± 86,8 B	2713,3 ± 72,3 AB
T/ Control	3625,0 ± 200,3 E	843,8 ± 6,6 I	791,3 ± 6,1 C
P of ANOVA	p < 0,001	p < 0,001	p < 0,001

Treatment	**31.05.2016**	**27.07.2016**
E Control	582,0 ± 43,0 C	652,0 ± 21,1 E
E/ Lime	564,8 ± 146,5 C	758,0 ± 6,6 DE
E/ 10% CP	1313,0 ± 498,2 B	1403,0 ± 148,5 BC
E/ 5% BC	513,3 ± 18,0 C	836,0 ± 127,7 DE
E/ 5% BCa	539,8 ± 173,6 C	715,3 ± 42,3 E
E/ 5% BC/ 10% CP	1744,8 ± 327,3 AB	1597,8 ± 157,9 B
E/ 5% BCa/ 10% CP	2417,0 ± 601,2 A	1780,5 ± 174,4 B
E/ 5% BCa/ 10% CP/ nHM	2091,5 ± 317,5 AB	1726,0 ± 61,6 B
T/ 5% BC / 10% CP	2053,5 ± 682,5 AB	2208,5 ± 388,0 A
T/ Control	542,3 ± 149,3 C	1129,0 ± 104,3 CD
P of ANOVA	p < 0,001	p < 0,001

6.2.7 Dissipation time 50% of pollutants

Table 29: Summary of the results of the dissipation time DT50 of three pollutants in soil pore water samples. Legend to the table, see Table 9.

Dissipation time 50 %				
Treatment	**Zinc**	**Cadmium**	**Pyrene**	**Phenanthrene**
E Control	10 ± 7 A	6 ± 2 B	2 ± 0 AB	-
E/ Lime	13 ± 5 A	10 ± 4 B	3 ± 1 AB	-
E/ 10% CP	23 ± 4 A	10 ± 1 AB	3 ± 0 AB	-
E/ 5% BC	24 ± 18 A	7 ± 1 B	3 ± 0 A	-
E/ 5% BCa	5 ± 0 A	10 ± 7 B	3 ± 0 AB	-
E/ 5% BC/ 10% CP	11 ± 10 A	20 ± 12 AB	2 ± 0 B	-
E/ 5% BCa/ 10% CP	28 ± 6 A	35 ± 13 A	2 ± 0 AB	-
E/ 5% BCa/ 10% CP/ nHM	-	-	-	-
T/ 5% BC / 10% CP	-	-	-	-
T/ Control	-	-	-	-
P of ANOVA	p = 0,031	p = 0,002	p = 0,051	-

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