Project ENAC

École polytechnique fédérale de Lausanne

Autumn 2022/23

How to avoid the danger of pollutants in Swiss biochar production and use?

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January, 2023

Executive summary

The study of pollutants found in biochar and its effects on agricultural soil was conducted in this paper. The aim of the research was to analyse organic and inorganic pollutants found in biochar which either originate from the biomass itself or are formed in the process of pyrolysis. Pollutants that were analysed are polycyclic aromatic hydrocarbons (PAHs), heavy metals, dioxins, metal cyanide, persistent free radicals and volatile organic compounds (VOCs). Biomass categories and pyrolysis conditions are examined and linked to pollutant concentrations found in biochar. Secondary aim of the study was to connect biochar types with the overall positive or negative effects that are observed when biochar is applied on one of the four Swiss soil types (silt loam, loam, sandy loam and silty clay) at a specific application rate. After assessing the previously stated, instructions for safe biochar production and use on agricultural soils will be provided. Heavy metals are identified as pollutants with the highest risk for the ecosystem due to their toxicity. Sewage sludge, animal manure and phytoremediation residues are non-woody biomass which are observed to be rich in heavy metals. Heavy metals can concentrate during the pyrolysis process in biochar so they end up having higher heavy metal concentrations than the biomass itself. Acid washing prior to the pyrolysis or co-pyrolysis with a heavy metals-poor biomass are mitigation strategies for heavy metal-rich biomass. Miscanthus and paper mill sludge are identified as non-woody biomass with high potential of forming PAHs during the pyrolysis process. Sawdust is a woody biomass identified to have high potential of forming PAHs and dioxins during the pyrolysis. Pyrolysis at high temperatures or with a long residence time is a potential solution. Correlation between heavy metal polluted biomass and its corresponding negative effects on the ecosystem is proposed due to observed results. Non-woody biomass is identified with larger overall negative effects on the ecosystem, when applied to the soil, than woody biomass. Biochar is identified to have overall more positive effects on the soil ecosystem than negative effects. Soil bulk density, soil water content, soil aggregate stability and water retention capacity are positively affected, while invertebrates and microorganisms are negatively affected. Soil erosion, soil salinity, soil pH, soil conductivity and plant biomass are categories which are influenced both positively and negatively, thus further studies are necessary in order to conclude on the specific overall effect of biochar when applied to the soil. Effects are highly contradictory as different studies observed different effects. Considering this, due to the inconsistent results, it is concluded that no specific recommendations can be given on safe use of biochar on the agricultural soils. One use of biochar that is significant and has a big potential is carbon sequestration which is used as a climate change mitigation tool. Long term effects, biochar stability in the soil, pollutants bioavailability and application rates of biochar are proposed topics for further research which is necessary to conduct a more thorough analysis.

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Introduction

Swiss soil has been characterised as depleted due to human activity and agricultural use which are not sustainable. The depletion of the soil, which has been occurring over the years, has become a serious problem for agriculture [1]. One of the solutions that has been identified to have great potential is the use of biochar[2]. Biochar is a product which serves as a soil amendment. Various benefits of biochar have been discovered over the years[3]. Carbon sequestration and serving as a climate change mitigation tool are reasons why biochar is considered to be beneficial[2]. When it comes to soil amendment, biochar can positively influence soil fertility and yield. It improves water retention capacity of the soil, soil structure, nutrients sorption and microbial interactions while supporting plant growth[4]. However, implications of its disadvantages exist and questions about biochar's long-term effects are emerging. Pollutants in the biochar which originate from different feedstocks are a subject which needs to be discussed [2]. They can cause phytotoxicity, neurotoxicity, cytotoxicity and ecotoxicity which is a serious issue[5]. If polluted biochar is applied to the soil, it can induce potentially negative effects which pose a risk for the whole ecosystem[5]. Therefore, it is important to assess the pollutants which are present in the biochar and effects that will occur after the biochar has been applied on the agricultural soil. The danger and the risk of pollutants need to be quantified and qualitatively explained. After the assessment, mitigation proposals and recommendations for biochar production and use will develop, while keeping in mind human and ecosystem health. The purpose of this study is to come to a conclusion on safe and sustainable Swiss biochar production and use. In order to do that, three research questions are stated.

Outline of the project and research questions

Biochar is a porous, carbonaceous material that is generated by pyrolysis of biomass[2]. It is widely used as a soil amendment nowadays. Research is currently ongoing regarding all possible uses of biochar which include various farming and agricultural uses, wastewater and drinking water treatment, industrial use, etc[6]. Pyrolysis is a process of burning the biomass in anoxic conditions and at high temperatures (200-1000°C). Three products are formed in the process which are: pyrogas, bio-oil and biochar. Ratio of given products depends mostly on the material that is used as biomass and the pyrolysis conditions[2]. Biochar is the focus of this project, as well as the pollutants in it which originate from polluted biomass material. Ten biomass types are taken into account which are subcategories of two biomass categories: Woody (waste wood, industrial wood residues, forest wood and wood from landscape maintenance) and Non-Woody (animal manure, agricultural crop by-products, sewage sludge, organic fraction of household garbage, green waste from households and landscape, commercial and industrial organic waste) biomass[7]. To understand exactly what type of biomass material under which pyrolysis conditions produces polluted biochar in Switzerland is one of the goals of this project and it is defined as first research question:

RQ1: What are the pollutants that are present in ten biomass types and how are they affected by pyrolysis?

Biochar's widest use currently is in soil amendment as it is associated with improvement of soil properties such as soil fertility and aggregate stability. It can cause plant growth and yield enhancement when applied to the soil. It is a strong adsorbent so it governs nutrient sorption processes and prevents the nutrient loss. Biochar is used to improve water retention capacity and available plant water. Additionally, it can reduce contaminant mobility and furthermore, have a positive impact on microbial interactions [4]. Nevertheless, biochar use on agricultural soils has shown some undesired effects which are considered as problematic. Some of them are input of pollutants, enhanced soil erosion and particulate matter emissions, reduced efficacy of agrochemicals, excessive increase in soil pH, increase in soil salinity and adverse effects on soil invertebrates (e.g. earthworms)[8]. Long-term effects of biochar application to soil are not investigated yet and it is a great uncertainty[2]. There is an ongoing debate whether the biochar use in agriculture is acceptable and brings benefits, or is it more harmful to the ecosystem in soil and people after long-term use which is sometimes improper.

After establishing the link between the biomass material and type of pollutants in produced biochar, it is necessary to closely look at the biochar properties and consequently altered soil properties to make a conclusion on the effect of polluted Swiss biochar on ecosystems in amended soil. Danger of having polluted biochar in soil exists, but the level of danger to ecosystems is not yet understood. This is to be described and it is formed in a second research question:

RQ2: How does polluted biochar affect Swiss ecosystems if applied to agricultural soils and what type of danger does it pose?

When describing and quantifying the danger of using polluted biochar on Swiss soils, the amount of risk it poses for the whole ecosystem is to be investigated. Trying to tackle the problematic pollutants in its biochar could mean safer biochar and wider application of biochar on the Swiss market. Management and available solutions on polluted biochar is looked at to investigate the possible opportunities for the Swiss market. Pollutants in the biochar have to be measured, monitored and tackled, while their effects need to be minimised. Third research question is formed as:

RQ3: Given the insights of RQ1 and RQ2, how should Switzerland produce and use biochar?

Investigation of the given questions provides results and further insight into the topic. After research questions have been answered and discussed, a conclusion on safe production and use of biochar in Switzerland is made to conclude this study.

Methodology

The methodology followed throughout this project was mainly based on scientific literature reviews and conducted interviews with people directly working with production or laboratory analysis of biochar.

Firstly, background investigation of pollutants in the biochar had been done and scientific papers were reviewed. Ten biomass types (waste wood, industrial wood residues, forest wood, wood from landscape maintenance, animal manure, agricultural crop by-products, sewage sludge, organic fraction of household garbage, green waste from households and landscape, commercial and industrial organic waste) [7] were explored. Gathering data on exact pollutants present in biomass feedstock and produced biochar and forming a connection between those including pyrolysis conditions analysis was the following step. Pollutants which are closely investigated were polycyclic aromatic hydrocarbons, heavy metals and dioxins. Additionally, metal cyanide, persistent free radicals and volatile organic compounds were analysed. Pyrolysis conditions such as temperature, reactor type and retention time in the pyrolysis reactor are information that was assessed. Concentrations of the pollutants in the biomass prior to the pyrolysis and in the biochar after the pyrolysis were observed and gathered from various studies and formed in a table for further analysis. EBC standards were used as a limit value for classifying pollutants[9]. This was done to answer the first research question.

Secondly, biochar effects after it has been applied to agricultural soil were assessed. Biochar's wide variety of positive and negative effects on the whole ecosystem was looked at. Switzerland has multiple soil types across the country, but four soil types were identified as main types and were further examined: silt loam, loam, sandy loam and silty clay[10]. Insight on the type of biochar produced under specific pyrolysis conditions and its application rates on the four Swiss soil types was found in various literature resources. Linking biomass category through biochar types with positive, negative and neutral effects was done. Following that, assessment and categorisation of effects and their significance was made and overall positive and negative effects for all biochar types were suggested. Overall effects were categorised as: neutral, positive, negative, significantly positive and significantly negative. Effects on the ecosystem were connected to the soil types and application rates as well. This was done to answer the second research question.

Lastly, more insight into the topic of every question was provided by qualitative discussion together with a quantitative analysis. There was a conclusion made linking the biomass subcategories/categories with pollutants that were found in the biochar and overall effects that were expected when that biochar is applied on the soil. The danger and the risk of applying polluted biochar to Swiss soil were examined. Safe production and use of biochar was instructed through recommendations and mitigation strategies. Sustainability was briefly discussed as well as economic aspect of the polluted biochar while considering two key factors: human and ecosystem health and plant growth. This was done to answer the third research question.

Interviews were conducted with three people: Mr. Einar Stuve from Oplandske Bioenergi, Mr. Philipp Vögelin from IWB and Mr. Stefan Baumann from FiBL. Additionally, documents with information and written answers to interview questions on analysis of biochar were sent from Mr. Fabian Link from Bioenergie Frauenfeld. Topic of all interviews had been biochar analysis according to EBC standards. Questions on pyrolysis conditions, used feedstock for biochar production, pollutants in biochar and handling of biochar were discussed. EBC data sheets were shared to be used as part of the analysis for this study[11]–[13]. Concentrations of pollutants found in biochar were included in the table which was a part of the analysis done for the first research question. The interviews gave further insight into biochar production and practical information of the process which helped with better understanding of the topic.

Literature review

Pollutants in the biochar

Biochar is a product mostly used for soil amendment. It is a product which has been recognized to have great potential of converting depleted soil to nutrient-rich soil which can provide good crop yield[4]. Biochar can also be used for as a fertilizer in agriculture[5]. It is able to sequester carbon due to its capability to stabilise and store carbon in soil. Therefore, it acts as a climate change mitigation tool[8]. Additionally, biochar increases water retention capacity of the soil which, consequently, can induce healthier plant growth[8].

The quality of biochar is characterised by multiple parameters. Some of them are: elemental composition (carbon, hydrogen, oxygen, nitrogen and phosphorus content), ash and moisture content, pH value, percentage of mobile and fixed matter, micropore volume, BET surface area, cation exchange capacity, etc[9].

High quality biochar will provide the following parameters: high carbon content, high cation exchange capacity and low contaminant content. These are important to obtain since the price of biochar increases with the increase in its quality[14]. All of the parameters will determine the overall quality of biochar and its specific use.

Biochar is produced from pyrolysis of biomass. Specific characteristics of biochar mostly depend on the type of feedstock and pyrolysis conditions such as residence time, the type of reactor and the temperature. Type of biomass that is used as a feedstock is important since it will determine what type of biochar is produced[15]. Ten biomass types are taken into consideration in this study. Ten biomass types are divided in two biomass categories[7]:

- Woody biomass (waste wood, industrial wood residues, forest wood and wood from landscape maintenance)
- Non-Woody biomass (animal manure, agricultural crop by-products, sewage sludge, organic fraction of household garbage, green waste from households and landscape, commercial and industrial organic waste)

Biomass is sometimes analysed prior to pyrolysis and some pollutants are often found. Almost all types of biomass will have pollutants originating from their previous use[8]. Concentrations of pollutants in the biomass are still widely unknown since there is no legal requirement to analyse biomass content prior to pyrolysis treatment. Multiple types of pollutants can often be present in a single biomass type. Waste wood and industrial wood residues that come from construction often have paint and coatings which are rich in chemicals and heavy metals, as preservatives can be a source of heavy metals in woody biomass [16]. Animal manure and phytoremediation residues contain high levels of heavy metals[8], while animal manure can also be rich in antibiotics[17]. Agricultural crop by-products contain pesticides that have been used on the agricultural soil[9], while sewage sludge is full of polycyclic aromatic hydrocarbons (PAHs) originating from the sewage system[18], but also heavy metals[5]. PAHs are often occurring in almost all biomass types, same as VOCs[8]. On the other hand, forest wood is usually found to be a clean biomass since its pollutant content is quite low[11]. Some dioxins and heavy metals can potentially be formed from landscape wood biomass[5]. Dioxins can be formed from wood, crop and sewage sludge biomass[5]. Organic waste and crop by-products can contain heavy metals, while organic metal can be rich in metal cyanide[5]. Table 1 shows two main biomass categories, ten biomass types and pollutants found in them.

Table 1. Biomass categories, biomass types and pollutants found in them.

Biomass category	Biomass type	Pollutants	Reference
Woody	Waste wood	PAHs*, PTEs (heavy metals), dioxins, VOCs	[5], [8], [16]
	Industrial wood residues	PAHs*, PTEs (heavy metals), VOCs, dioxins	[5], [8], [16]
	Forest wood		[11]
	Wood from landscape maintenance	PTEs (heavy metals), VOCs, dioxins	[5], [8]
Non-Woody	Animal manure	PAHs*, PTEs (heavy metals), dioxins, antibiotics	[5], [8], [17]
	Agricultural crop by-products	PAHs*, PTEs (heavy metals), VOCs, dioxins, pesticides	[5], [8], [9]
	Sewage sludge	PAHs, PTEs (heavy metals), dioxins	[5], [8], [18]
	Organic fraction of household garbage	PAHs*, PTEs (heavy metals), dioxins, MCN	[5], [8]
	Green waste from households and landscape	PTEs (heavy metals), VOCs	[5], [8]
	Commercial and industrial organic waste	PAHs*, PTEs (heavy metals), dioxins, MCN	[5], [8]

*PAHs are not in the biomass itself (except in the case of the sewage sludge), but they are formed during the pyrolysis process from the marked types of biomass.

Antibiotics and pesticides are not the pollutants which are a focus of this study and therefore will not be discussed further in this paper.

Pyrolysis is a process in which biomass is thermally treated under anoxic conditions and at a high temperature. It produces biochar, bio-oil and pyrolysis gas (often referred to as syngas). Temperature range, residence time and the reactor type can vary for different types of pyrolysis[2]. Pyrolysis conditions play a significant role in producing good quality biochar[14]. Processes with low temperature, between 180°C and 300°C, together with long residence time, ranging between 10 minutes and 16 hours, yield higher amount of biochar in comparison to processes with high temperature and short residence time[15]. For example, hydrothermal carbonization (HTC) and torrefaction processes have 50-80% of the yields in the form of biochar. Other pyrolysis types, such as fast and slow pyrolysis or gasification, tend to have up to 35% of yields in the form of solid biochar. Nowadays, slow and fast pyrolyses are used for production of biochar even though they do not yield a significant amount of biochar[15].

Pyrolysis temperature can be set anywhere between 180°C and 1600°C, but usually it is set between 300°C and 700°C. Pyrolysis either destroys or partially destroys pollutants at high temperatures, but in some cases pollutants can be formed during pyrolysis as a result of chemical reactions occurring at a certain temperature range[19]. The residence time ranges from seconds to days, depending on the type of feedstock. Pyrolysis systems use kilns and retorts as specialized equipment to contain the baking biomass while excluding oxygen[15]. Three types of reactors are used: batch, continuous and semi-continuous[15], [19]. All three reactors have specific subcategories of reactors such as: conventional pyrolysis reactor, microwave pyrolysis reactor, rotary reactor, kiln reactor, tubular reactor, fluidized bed reactor, muffle furnace, tube furnace, auger reactor, ablative reactor etc. Auger reactor, rotary kiln reactor and fixed bed reactor are the most efficient technologies for production of solids, including biochar[14], [15], [19].

Biochar is considered as a good solution for soil amendment with high scale-up potential[15]. Novel studies show that not all biochar effects are positive when applied to soil, especially long-term effects[2]. One of the concerns are pollutants in the biochar. Pollutants in biochar originate from the polluted biomass and are affected by the pyrolysis temperature and reactor type in different ways[5], [20]. They are characterised as phytotoxic, neurotoxic, cytotoxic and ecotoxic substances. Organic and inorganic pollutants that are investigated throughout the years are[5]:

- organic pollutants: polycyclic aromatic hydrocarbons (PAHs), dioxins, volatile organic compounds (VOCs), persistent free radicals (PFRs)
- inorganic pollutants: potentially toxic elements (PTEs) referred to as heavy metals, metal cyanide (MCN)

Both can include some novel and emerging pollutants. Pollutants are problematic when biochar is applied to the soil. They can become bioavailable for the plant uptake or can leach into the soil[21]. When those processes occur, pollutants may endanger plants and microorganisms in the soil, therefore negatively affecting the whole ecosystem.

PAHs (**polycyclic aromatic hydrocarbons**) are often found in biochar[8]. The USEPA classifies a sum of the 16 PAHs that are considered to be dangerous for the environment and their concentrations are carefully monitored. The sum of the 16 PAHs are: naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IPY), dibenz[a,h]anthracene (DBA) and benzo[g,h,i]perylene (BPE)[19]. PAHs formation is mostly influenced by pyrolysis temperature and reactor type[19], but the feedstock influence is negligible because they are often formed during the pyrolysis process[9]. It is found that only feedstock which contains PAHs prior to the pyrolysis process is sewage sludge[18]. Separation of biochar and formed gases in the reactor also plays an important role in PAHs content of biochar[19].

Total 16 PAHs concentration in biochar in general varies in range from 0.07 mg/kg to 100 mg/kg[5]. Although a study[22] found the concentration of PAHs of 355 mg/kg in biochar made from coniferous residues at 750°C, while all other concentrations were below 62.7 mg/kg.

It is found that concentrations of PAHs are in range between 1.124 mg/kg to 28.339 mg/kg[20]. Phenanthrene and fluorene are found as dominant compounds in all four different biochars derived from miscanthus, coconut shell, wicker and wheat straw at a temperature range of 350-650°C. Naphthalene is found as a dominant compound in another research paper[23] which studied sawdust biochar produced at temperature range from 250°C to 700°C. For paper mill sludge biochar, the peak PAHs concentration is at 500°C where dominant substance is phenanthrene (3.7 mg/kg) followed by benzo[b]fluoranthene, benzo[k]fluoranthene and pyrene[24]. However, dominant substances in paper mill sludge prior to pyrolysis are phenanthrene, chrysene, pyrene and benz[a]anthracene. Naphthalene, phenanthrene and anthracene are found to be the most abundant PAHs in all the biochars derived from rice husk, wood, wheat and sewage sludge using three pyrolytic reactors at 400°C, 500°C and 600°C[19].

Study[25] on pyrolysis of vineyard wood, rice husk, wood chips, sewage sludge and wheat husk. The sum of 16 PAHs varies between 0.799 mg/kg and 6.364 mg/kg. PAHs concentration reaches maximum in a batch reactor at 400°C and then decreases with increasing temperature. In a slow-pyrolysis reactor (3h residence time), PAHs concentration reaches maximum at a lower temperature (300°C-400°C). Rice husk is pyrolyzed at 400°C, 500°C and 600°C. With increasing temperature in the batch reactor, with residence time of 1 hour, PAHs concentration is found to decrease from 6.364 mg/kg to 1.291 mg/kg. Keeping the same temperature, 400°C, in a batch reactor but changing the residence time from 1 hour to 4 hours decreases PAHs concentration from 6.364 mg/kg to 5.653 mg/kg (approximately 11%). Keeping the temperature at 600°C with the same conditions will decrease the PAHs concentration in biochar by 28.5% (from 1.291 mg/kg to 0.923 mg/kg). Higher temperature pyrolysis will decrease PAHs concentration in biochar more than lower temperature pyrolysis with the same residence time. PAHs concentration in biochar produced in a continuous rotary reactor at a temperature of 500°C is 1.395 mg/kg, while setting temperature at 600°C will yield concentration of 0.799 mg/kg. In every case, increased temperature decreases PAHs concentration in biochar. Total toxic equivalent concentration (TTEC) evaluates the rotary reactor as the one for producing the safest biochar when all parameters (temperature, residence time, feedstock) are taken into account. Batch reactors at 400°C-500°C are considered to produce biochar with the greatest hazard potential[25].

European biochar certificate (EBC) is a voluntary standard for biochar production in Europe, while it is obligatory for Swiss biochar sold for use in agriculture. With its rules and instructions, it ensures safe and sustainable production of biochar. EBC has pollutant concentration requirements for every type of biochar according to their purpose. Switzerland requires biochar for agricultural use to be certified with EBC-AgroOrganic and EBC-Agro. Table 2 shows limit values for PAH contents in biochar that must not be exceeded[9].

Table 2. EBC limit values for PAHs in biochar[9].

Certification Class	EBC-Feed	EBC-AgroOrganic	EBC-Agro	EBC-Urban	EBC-ConsumerMaterials	EBC-BasicMaterials
16 EPA PAH	declaration	4±2 g t^{-1} DM	6.0+2.2 g t^{-1} DM	declaration	declaration	not required
8 EFSA PAH	1.0 g t^{-1} DM					4 g t^{-1} DM
benzo[e]pyrene benzo[*j*]fluoran-thene	< 1.0 g t^{-1} DM for each of both substances					

PAHs concentrations are examined in biochar derived from 12 biomass types[5]. Between 400°C and 500°C there is a peak of PAHs formation which decreases rapidly with increasing temperature. Wheat straw, maize, miscanthus and paper mill sludge biochar have PAHs concentrations above EBC requirements (max. 6 mg/kg[9]). Well-designed pyrolysis unit at a higher temperature range (550°C-700°C) should decrease formation of organic contaminants[5].

PAHs are identified to be bound in the biochar matrix and they are not readily bioavailable when applied to the soil, therefore they do not pose a risk for the environment according to the EBC[9]. But previously mentioned concentrations of PAHs in the biochars in some cases exceed EBC requirements (4±2 mg/kg) which makes it a debatable matter. Content of PAHs may pose a real threat.

PTEs (**potentially toxic trace elements**), also known as **heavy metals**, are the following elements: Pb, Zn, Cd, Cu, Ni, Hg, Cr, As and Ag. They have high density and are considered highly toxic and poisonous at low concentrations[9]. Biomass that is rich in PTE is sewage sludge, animal manure, food waste, phytoremediation residues and industrial wood residues according to Table 1. Table 3 shows limit values for heavy metals according to the EBC application classes. In this case, EBC-AgroBio and EBC-Agro are taken into account for Swiss biochar[9].

Table 3. EBC limit values for heavy metals in biochar[9].

	EBC-Feed	EBC-AgroBio	EBC-Agro / EBC-Urban / EBC-ConsumerMaterials	EBC-BasicMaterials
Pb	10 g t^{-1} (88%DM)	45 g t^{-1} DM	120 g t^{-1} DM	no limit value, only declaration required
Cd	0.8 g t^{-1} (88% DM)	0.7 g t^{-1} DM	1,5 g t^{-1} DM	
Cu	70 g t^{-1}DM	70 g t^{-1}DM	100 g t^{-1} DM	
Ni	25 g t^{-1} DM	25 g t^{-1} DM	50 g t^{-1} DM	
Hg	0.1 g t^{-1} (88% DM)	0.4 g t^{-1} DM	1 g t^{-1} DM	
Zn	200 g t^{-1} DM	200 g t^{-1} DM	400 g t^{-1} DM	
Cr	70 g t^{-1} DM	70 g t^{-1} DM	90 g t^{-1} DM	
As	2 g t^{-1} (88% DM)	13 g t^{-1} DM	13 g t^{-1} DM	
Ag	no limit value, only declaration required			

According to an author[8], plant biomass and manure (mangrove biomass, sugar cane straw, cow and pig manure) and waste (sewage sludge, textile dye sludge) pyrolysis is researched. Concentration of Cr, Cu, Ni, Pb and Zn in both biochars slightly increases with the increasing temperature in range from 300°C to 700°C. Cd concentration for waste biochar decreases from 0.79 mg/kg to 0.14 mg/kg, while it increases for plant biomass and manures biochar from 0.2 mg/kg to 0.53 mg/kg with increasing temperature. Waste biochar has higher PTE content than plant biomass and manures biochar, except for the higher Cu content in the plant biomass and manures biochar. Cd content is generally low in comparison to other heavy metals (0.79 mg Cd/kg for waste biochar), but it doesn't comply with the EBC standard (0.7 mg Cd/kg[9]). Zn content is high in comparison to other heavy metals (up to 7790 mg Zn/kg for waste biochar and 2371 mg Zn/kg for plant biomass and manures) which is also above EBC requirements (<200 mg Zn/kg[9]). Cd content in a temperature range from 300°C to 700°C and Ni content at lower temperatures (up to 500°C) of plant biomass and manure biochar comply with the EBC standard.

According to another study[20], biochar derived from miscanthus, coconut shell, wicker and wheat straw at a temperature range from 350°C to 650°C is studied. All biochars comply with the EBC standard except for the Cd content (0.87 mg/kg) in the miscanthus biochar. Biochar heavy metal content decreases in the order: Zn>Pb>Cr>Cu>Ni>Cd[20].

Solar pyrolysis in a fluidized bed reactor of a raw and heavy metals impregnated willow at temperatures of 600°C, 800°C, 1000°C, 1200°C, 1400°C and 1600°C is investigated[25]. Heavy metals content is the highest at 800°C (total element concentration almost equal to 50000 mg/kg). As pyrolysis temperature increases, the content of Ni and Cu in the biochar will increase, but the total element concentration will slightly decrease. Raw willow biochar at 1600°C has Ni content of 1.7%, while Ni impregnated willow biochar has Ni content of 14.3% at the same temperature. Same Cu content increase applies for the raw and the Cu impregnated willow biochar. Pyrolysis of heavy metal contaminated biomass ensures that more than 98.5% of heavy metals are retained in the biochar already at 600°C[25].

Pyrolysis can cause PTEs enrichment in biochar due to their embedment into the biochar structure[5]. International Biochar Initiative (IBI)[26] proposes guideline values for heavy metal content of biochar. According to one study, biochar derived from redwood, rice straw, maize, and bamboo which are biomass containing low PTE levels have lower concentration than ambient background soil concentration (0.89 mg/kg)[27]. On the other hand, sewage sludge biochar exceeds IBI requirements for every element (Zn, Cu, Cr, Ni and Pb). The IBI threshold for Zn is 480 mg/kg[26], while biochar pyrolyzed at 600°C has Zn content of approximately 3400 mg/kg. Sewage sludge biochar pyrolyzed at 600°C has higher content of heavy metals than the one pyrolyzed at 400°C[5]. EBC requirements[9] are generally more strict when it comes to limit concentrations that IBI[26].

Research is conducted on pyrolysis of Cu(II)-laden cotton leaf biomass[28]. The temperature range is 350°C-750°C. At >550°C, pyrolysis of Cu polluted biomass produces Cu nanoparticles embedded biochar. The Cu levels in biochar obtained at temperatures of 350°C, 550°C and 750°C are 16290 mg/kg, 19240 mg/kg and 22110 mg/kg, which is about 1.6, 1.9 and 2.2 times more than in raw Cu cotton leaf biomass (10160 mg/kg), respectively. Highest Cu fraction in biochar is in non-available and stable form, while lowest Cu fraction of polluted biochar is in bioavailable form[28].

Phytoremediation crop residue is a problematic biomass because it has high content of heavy metals. Flash pyrolysis of phytoremediation residues (plants, leaves and stems) is done in a semi-continuous reactor at temperatures of 350°C, 450°C, 550°C with hot gas filtration[29]. Temperature is an important factor which determines the transfer of heavy metals into volatile pyrolysis products, therefore determining the heavy metal content of solids (biochar). Cd is volatilised at elevated temperatures, while Zn, Pb and Cu are not prone to volatilisation. Only the strongest and most stable metal compounds will stay in biochar at elevated temperatures. Lowest concentration of heavy metals found at 350°C and the highest concentration of heavy metals in the biochar is found at 550°C. Recovery of heavy metals in the biochar is the same at 350°C and 450°C, but at 550°C heavy metal content in biochar is low, same as the biochar yield itself. Metals in biochar are more strongly bound than in originating biomass because they embed into the biochar matrix. Pyrolysis chars from 400°C and 500°C pyrolysis in an Auger-fed reactor have been found to be able to sorb heavy metals from wastewater streams[29].

One EDTA leaching test shows that up to 35% of elements in biochar are still bioavailable[29]. According to another author[21], higher pyrolysis temperature leads to more loss of Cd from the biochar due to Cd evaporation. Most of Cd adsorbed by biomass is readily leachable and bioavailable, but pyrolysis of polluted biomass can significantly increase the stability of Cd in biochar. Direct pyrolysis reduces leachable Cd in the biochar to 23.7% for peanut husk and 14% for rice straw biochar, but also reduced bioavailable Cd in both biochars to less than 5%. Rice straw biomass has higher content of leachable and bioavailable Cd when compared to peanut husk biomass, but rice straw biochar has lower content of leachable Cd when compared to peanut husk biochar[21]. Additional study[30] shows that effective 93% reduction in Cd and 90% reduction in Zn leachability occurs after heat treatment of 1h at 400°C. Metal contaminated biomass is pyrolyzed together with sawdust which, the study claims, is the reason of such leachability reduction. Pb leaching is reduced by 43% after the same treatment, without the sawdust addition[21].

There is a strong correlation between potential ecological risk and the pyrolysis temperature for heavy metals. Pyrolysis of four biochars derived from heavy metal rich biomass (cow manure, sewage sludge, sewage sludge and cotton stalk, textile dyeing sludge) is investigated[8]. Cow manure biochar is the only one that is categorised as a high potential ecological risk type of biochar, while the ecological risk of sewage sludge biochar is considerable at 350°C. At 650°C, all four types of biochar are considered medium or low risk. When it comes to a particular potentially toxic element, it can be quantified by risk assessment code (RAC). Relationship between RAC and pyrolysis temperature for heavy metals shows that Zn poses a medium risk at a temperature range 400-580°C, while other heavy metals show low risk for the same temperature range. Cd is identified as a medium risk at lower temperatures (<400°C) together with Zn. At higher temperatures (>580°C) all elements are considered to pose a low risk[8].

Dioxins are classified as persistent organic pollutants (POPs)[31]. They are considered to be highly toxic and cancerogenic. They are usually found in woody biomass such as sawdust, soft wood or wheat straw biomass. Dioxins can even be found in food waste or digested dairy manure[5]. A study[32] shows a test of 14 biochars and their dioxin levels. Their toxic equivalency (TEQ) ranged from 0.008 ng/g to 1.2 ng/g. The EBC requirement for dioxin concentration is 0.02 ng/g[9], which means the concentration of 1.2 ng/g is exceeding the standards. Biochar derived from sawdust has TEQ of 7 ng/kg, which is below the EBC requirement (20 ng/kg). Pyrolysis of sawdust is obtained in a range from 250°C to 700°C[5]. Maximum concentration of dioxins (7 ng/kg) is found at a temperature of 300°C and it decreases with increasing temperature. Pyrolysis of 8 biomass types [5](switch grass, pine wood, eastern gamma grass, laurel oak, lodgepole pine, paper mill waste, digested dairy manure and food waste) shows that dioxins concentrations found in pine wood, lodgepole pine, digested dairy manure and food waste biochars are exceeding IBI (10 ng/kg[26]) and EBC (20 ng/kg[9]) requirements. Their dioxin concentrations are in the range of approximately 85 ng/kg – 92 ng/kg[32]. They are considered to represent a low environmental risk at the moment due to their generally low concentrations, but they could be dangerous for the ecosystem due to their high toxicity[5].

Persistent free radicals (**PFRs**) are emerging pollutants in biochar which are still being investigated. They are considered potentially toxic. They are found in woody biomass (pine needles) since they originate from lignin which is a main wood component[5]. One paper[33] shows PFR content in pine needles biochar pyrolyzed at 200-600°C is $(0.06 - 37.1) \times 10^{18}$ another onepins g^{-1}, while another study[34] suggests PFR content in pine needles, wheat straw and maize straw biochar pyrolyzed at 300-500°C is $(1.25 - 22.3) \times 10^{18}$ spins g^{-1}. Content of PFRs in biochar increases with elevated temperatures (300°C-600°C) and then decreases sharply at 700°C. PFRs are still an ongoing research topic[5].

Volatile organic compounds (**VOCs**) are compounds that evaporate at >350°C during pyrolysis. Slow pyrolysis biochar contains lower and highly variable levels of VOCs[5]. VOCs are usually organic acids, aldehydes, furans, ketones, alcohols, phenols, o-, m-, and p-cresol, and 2,4-dimethylphenol[35]. Their concentration can exceed 100 mg/kg in biochars which have been in contact with pyrolysis vapours as a result of a non-optimized pyrolysis unit[5]. They can pose a risk due to their high mobility in the soil[8].

Metal cyanide (**MCN**) can be found in biochar derived from food waste, sludge, fungi residues and alga. Maximum concentration of MCN in 18 different feedstocks pyrolyzed at 800°C is found to be 85870 mg/kg by one author[36]. Biochar from sawdust, wheat straw and livestock manure contain only small amounts of cyanide ions[5].

There are no official limit values on concentrations of VOCs, PFRs and MCN presented by EBC. It is, however, required to do thermogravimetric analysis (TGA) in the first control year of a pyrolysis unit to measure VOCs[9]. PFRs, VOCs and MCN need further research as potentially dangerous pollutants in the biochar.

Biochar effects on the soil ecosystem

Pollutants in the biochar are identified as a hazard for the whole ecosystem when biochar is applied on the soil. If polluted biochar is applied on the soil in an inadequate way, it could lead to dangerous consequences which would affect the ecosystem in a negative way. Long-term effects of biochar are still unknown[2]. Major concern when it comes to biochar application is the effect that it has on soil and its physicochemical properties. Additionally, potential leaching of the pollutants into the soil is considered problematic as it may affect the plants, microorganisms or invertebrates if the pollutants are bioavailable[8]. Those concerns exist due to current lack of understanding of mechanisms affecting soil and organism health.

There are various positive, negative and neutral effects and observations when it comes to biochar application on agricultural soils[8], [37]–[40]. Soil type (Swiss soil types: silt loam, loam, sandy loam and silty clay[10]) and application rate together with the type of biochar that is used on the soil are key parameters which determine the overall effect[8]. One of the key factors in having an overall positive effect is pairing a suitable biochar with a suitable soil[38], [40].

Effects within these categories will be discussed:

- Availability of soil water
- Soil erosion
- Soil salinity
- Soil pH and bioavailability of nutrients
- Soil biota and microbiome
- Soil invertebrates

Soil water availability[8] is related to moisture content, hydraulic conductivity and water infiltration. It is important for healthy plant growth[8]. Research has been conducted with biochar derived from cattle manure (600°C)[41], Red oak hardwood (450-600°C)[42], *Carpinus betulus* I. wood chips (450-500°C)[43], *Robinia pseudoacacia* I. wood (500°C)[8], herbaceous plant cuttings (400, 600°C)[44], *Pinus radiate* D.Don woodchips (700°C)[45], Fir woodchip (1200°C)[46], Acacia whole tree green waste (550°C)[47] and mixed feedstock-prunings of fruit trees (500°C)[48]. Biochar has a neutral effect in some situations when it comes to availability of soil water. For *Carpinus betulus* I. wood chips[43] applied on clay loam soil, biochar application has a positive effect on soil water retention capacity and an increase of plant biomass of 73%. For *Pinus radiate* D.Don wood chips[45] applied to market garden soil, a positive effect on soil moisture content and water retention capacity is suggested. Positive, and simultaneously negative effect, are observed for *Robinia pseudoacacia* I. wood[8] applied to sandy soil where water capacity is increased by 97% and water content by 56%, but reduced hydraulic conductivity is present. Biochar increases available water content by 45% in coarse-textured soils and by 14% in fine textured soils[39]. High doses of biochar in clay soils are likely to decrease available water content[8].

Soil erosion[8] is detected by signs as particulate matter emissions, loss of soil and biochar mass, accelerated biochar degradation and loss of soil fertility. It is caused by improper application of biochar to a specific soil surface[2]. Studies claim that positive effects on soil erosion are seen in case of *Leucaena leucocephala* (Lam.) de Wit wood (700°C)[49] application on loamy soil, carbonised bamboo (600°C)[50] application to sandy-silt soil and *Panicum virgatum* I. (375°C-475°C)[51] application to multiple types of loamy soil. Reduced soil loss by 50% and 64% and increased mean weight diameter of soil aggregates occur if *Leucaena leucocephala* (Lam.) de Wit wood[49] biochar is applied. If carbonised bamboo[50] biochar is applied, decrease in runoff, leachate and soil detachment occurs. For application of *Panicum virgatum* I. [51] biochar, no impact on soil enzyme activities and on soil bacterial and fungal communities is observed. Biochar derived from apple branches (550°C)[52] and pine wood (300°C)[53] when applied to loam soil increases total erosion and significantly increases particulate matter concentrations and emissions, respectively. Application rate and the size of biochar particles are crucial parameters that influence the effect on soil erosion. Smaller particles have a higher chance of being picked up by the wind and therefore, causing erosion. Surface application to sandy soils is likely to increase erosion and particulate matter emissions[8].

Trace elements (Na, Ca, Mg, K) govern the equilibrium of **soil salinity**[8]. Accumulation of those elements results in an increase in soil salinity which can lead to plant growth inhibition and can affect crop yields. Salinity of soil will depend on the feedstock that biochar is derived from. Poultry litter (400°C)[54] biochar applied to red tropical soil, peanut shell (350°C)[55] biochar applied to degraded coastal soil and cattle manure (600°C)[41] biochar applied to silty clay soil have negative impacts on the soil salinity. Increase in salinity parameters is observed and the plant growth is inhibited. Wheat straw (350-550°C)[56] biochar when applied to silt loam soil mitigates and eliminates stress effects of salt on okra plant specifically, while soil bulk density is decreased and water content is increased in general. Similar happens when applying *Fagus grandifolia* sawdust (378°C)[57] biochar to commercial potting soil and wood chips (600°C)[58] biochar to coastal soil. Application of *Acer pseudoplatanus* I. residues (560°C)[59] biochar on silty loam soil alleviates salinity-induced oxidative stress and enhances shoot and root dry weight[8].

Soil pH affects the stability of soil organic matter, regulates the **nutrient bioavailability**, controls leaching of nutrients and affects soil fertility and crop yield. Biochar has neutral or slightly alkaline pH[8]. Nutrients may precipitate at alkaline pH resulting in their decreased bioavailability for the plants. High sorption capacity, porosity, and large specific surface area, together with high surface charge density and numerous polar and nonpolar surface sites, define biochar as a substrate with a high potential for nutrient association[8]. Effects on soil nutrients are highly dependent on biochar feedstock. Generally, there are more nutrients available in biochar derived from animal products than from plant biomass. Using nutrient-rich biochar can increase nutrient content of the soil if the nutrients are bioavailable. Wheat, rice and peanut (300°C)[60] biochar applied to acid forest soils significantly increases soil pH, exchangeable cations and reduces acidity production from N-cycle. Application of corn straw[61] biochar to saline-alkali soil can reduce the adverse effects of pH decrease. On the other hand, poultry litter manure (700°C)[62] biochar applied to acidic sandy loam soil excessively raises pH and endangers the plant nutrients availability. Soil pH can significantly decrease by 0.92 and 0.95 units when pine sawdust (400°C) biochar is applied to alkaline sandy soils[63]. There is a possibility of As bioaccumulation in rice shoot by up to 327% as a result of pH increase in contaminated soils[8].

Microbial community is the foundation of the ecosystem. Fungi-to-bacteria ratio and microbial activity can be endangered by polluted biochar application. High doses of coarse biochar applied to sandy soil with low SOC content can inhibit degradation of the organic matter and reduce microbial activity[8]. N mineralisation and SOC sequestration cycles are also important for sufficient microbial activity. Negative effects are observed from application of biochar to the soil when it comes to microbiome. Decreased microbial activity, soil organic matter decomposition and N mineralisation are observed when *Eucalyptus marginata* (600°C)[64] biochar is applied to sandy soil. Significantly reduced soil microbial biomass, changed fungi and bacteria content, altered microbial community composition and negatively impacted biodiversity is observed and leads to crop biomass decrease when maize corn cob rachis (450-500°C)[65] biochar is applied to sandy loam, maize straw (450°C)[66] biochar is applied to fluvo-aquic loamy soil and when *Panicum virgatum* l.[67] is applied to dry soils. Biochars with smaller particle sizes have a higher positive effect on microbial functioning but also lower carbon storage and a faster decomposition rate. The effect of biochar on microbiome is highly variable. Short-term application of biochar significantly changes bacterial diversity, while long-term use can increase the diversity and complexity of the microbial communities. Biochar may boost soil microbial activity because of the introduction of labile carbon present in biochar[8].

Soil invertebrates, most often earthworms, break down dead organic matter by feeding on it in a process of decomposition. They keep the soil structure stable, increase nutrient availability and fertilise the soil[8]. Earthworms are negatively affected by biochar application in most cases. Significant weight loss is observed when corn stover (600°C)[68] biochar is applied to agricultural loamy soil and when apple wood sawdust (525°C)[69] biochar is applied to artificial soil. Reduction in earthworm mean mass after 2 weeks can be caused by rice husk (550°C)[70] biochar application to loamy soil. When wheat straw (500°C)[8] biochar is applied to artificial soil, significant decrease of earthworm growth and DNA damage occurs. Mortality and weight loss reaches 100% in artificial soil when poultry litter (400°C)[71] biochar is applied. Mortality is also increased when rice husk (>480°C)[72] biochar is applied to pristine agricultural soil. For springtails, application of pine and spruce chips (300°C)[73] biochar to sandy loam soil will reduce mortality by 20%. Reproduction rates are reduced by 38% and 27% in comparison to unamended soil when wood biochar (700°C)[74] and rice husk biochar (600°C)[74] is applied to sandy loam soil. Stimulated reproduction of earthworms and increase in digestive enzyme activities are possible effects if wastewater sludge (500-550°C)[75] biochar is applied to calcareous soil and spent coffee grounds (450°C)[76] biochar is applied to Anthrosol, respectively. The biochar particles itself could be problematic because they stick to invertebrate's body[8]. Invertebrates are possibly affected by the pH changes, structural changes and nutrients changes in soil when biochar is applied to the soil. One of the problems is the sorption potential of the biochar since important nutrient for the health of the invertebrates can be sorbed by the biochar and not bioavailable for their intake[8].

Some of the effects are contradictory, thus one biochar type can be identified as having a positive and a negative effect for the same soil properties, soil functions or the soil organisms. Soil ecosystem is inevitably affected by the application of biochar, but further investigation needs to be carried out to have more knowledge on possible positive and negative effects.

Results

Results of this study aim to reflect on the three research questions which have been attempted to answer through this study. Data is collected through literature review and interviews that have been done in order to gain further understanding of this topic. All Tables with results can be found in Annexes.

Table 4, Table 5 and Table 6 represent an analysis of the first research question. Study of pollutants and their transformations during the pyrolysis process has been conducted. Table 4 is related to PAHs concentrations found in the biomass prior to the pyrolysis and in the biochar after the pyrolysis. Various woody and non-woody biochar types are considered with different pyrolysis temperature ranges. PAHs are formed in the process of pyrolysis so there is usually no PAHs concentration found in the biomass, except when it comes to the sludge (sewage sludge or paper mill sludge). Concentrations found in the biochar are compared to EBC limit values[9]: EBC-AgroOrganic (4±2 ppm) and EBC-Agro (6±2.2 ppm). It is found that 10.2% of the samples (coloured in yellow) are exceeding the EBC-AgroOrganic requirement and 15.3% (coloured in red) are exceeding the EBC-Agro requirement. Which makes around 75% of the samples within the EBC requirements. 18.2% of woody samples exceed the EBC limit and 29.7% of non-woody samples exceed the EBC limits. Coniferous wood residues and miscanthus biochars seem to have the highest risk of exceeding the EBC standards. Rice husk and paper mill sludge biochars have a medium risk of exceeding EBC standards, while pine wood biochar is found to have exceeding concentrations is some cases, and in other cases its concentrations are within the EBC limits. This can be seen in Figure 1.

Table 5 represents heavy metal concentrations (Cd, Cr, Cu, Ni, Pb, Zn, As and Hg) in the biomass prior to the pyrolysis and in the biochar after the pyrolysis including various biochar types and their pyrolysis conditions. Biochar heavy metal concentrations are compared to EBC-AgroBio limit (Cd-0.7 ppm, Cr-70 ppm, Cu-70 ppm, Ni-25 ppm, Pb-45 ppm, Zn-200 ppm, As-13 ppm, Hg-0.4 ppm) and to EBC-Agro limit (Cd-1.5 ppm, Cr-90 ppm, Cu-100 ppm, Ni-50 ppm, Pb-120 ppm, Zn-400 ppm, As-13 ppm, Hg-1 ppm)[9]. Heavy metals contaminated (Ni and Cu) willow and phytoremediation residues are biomass that is rich in heavy metals. Heavy metal concentrations of biochar that originates from plant biomass mixed with manures and sewage or textile dye sludge exceeds EBC limits (red and yellow fields in Table 5) when it comes to all heavy metals except As and Hg. Sewage sludge biochar Ni concentrations exceed EBC limits more than any other Ni polluted biochar. Manures biochar is the source of heavy metals and manures biochar itself exceeds the EBC limits. Organic waste biochar also has high concentrations of Cd, Cu, Ni and Zn while exceeding EBC limits. Phytoremediation residues biochar concentrations are exceeding EBC limits for Cd, Cu and Zn. Biochar derived from wood that is impregnated with preservatives has typically high concentrations of heavy metals and its Cr and Cu concentrations are exceeding EBC limits. Pine sawdust also exceeds the Cr and Cu EBC limits. Biochars derived from sewage sludge, manures and plant biomass are rich in Pb and Zn as their Pb and Zn concentrations exceed the EBC limits. Non-woody biochar tends to be rich in Cd, Cu, Ni, Zn and Pb, while woody biochar tends to be rich in Cr and Cu. Arsenic concentrations in pine sawdust (500°C) biochar exceeds the EBC limit, while molded wood pallet (600°C) and compost (600°C) biochars exceed the Hg concentration EBC limit as seen in Table 5. From non-woody biochars, phytoremediation residues and sludge biochars have the highest overall concentrations of heavy metals, while impregnated and coated wood biochars have the highest overall heavy metals concentrations from woody biochars. All of this can be seen in Figure 5 and Figure 6 down below and in Figure 7, Figure 8, Figure 2 and Figure 3 in Annexes Figure 1. PAHs concentrations found in the biochar after the pyrolysis including the biochar types and their pyrolysis conditions together with EBC limits for PAHs.

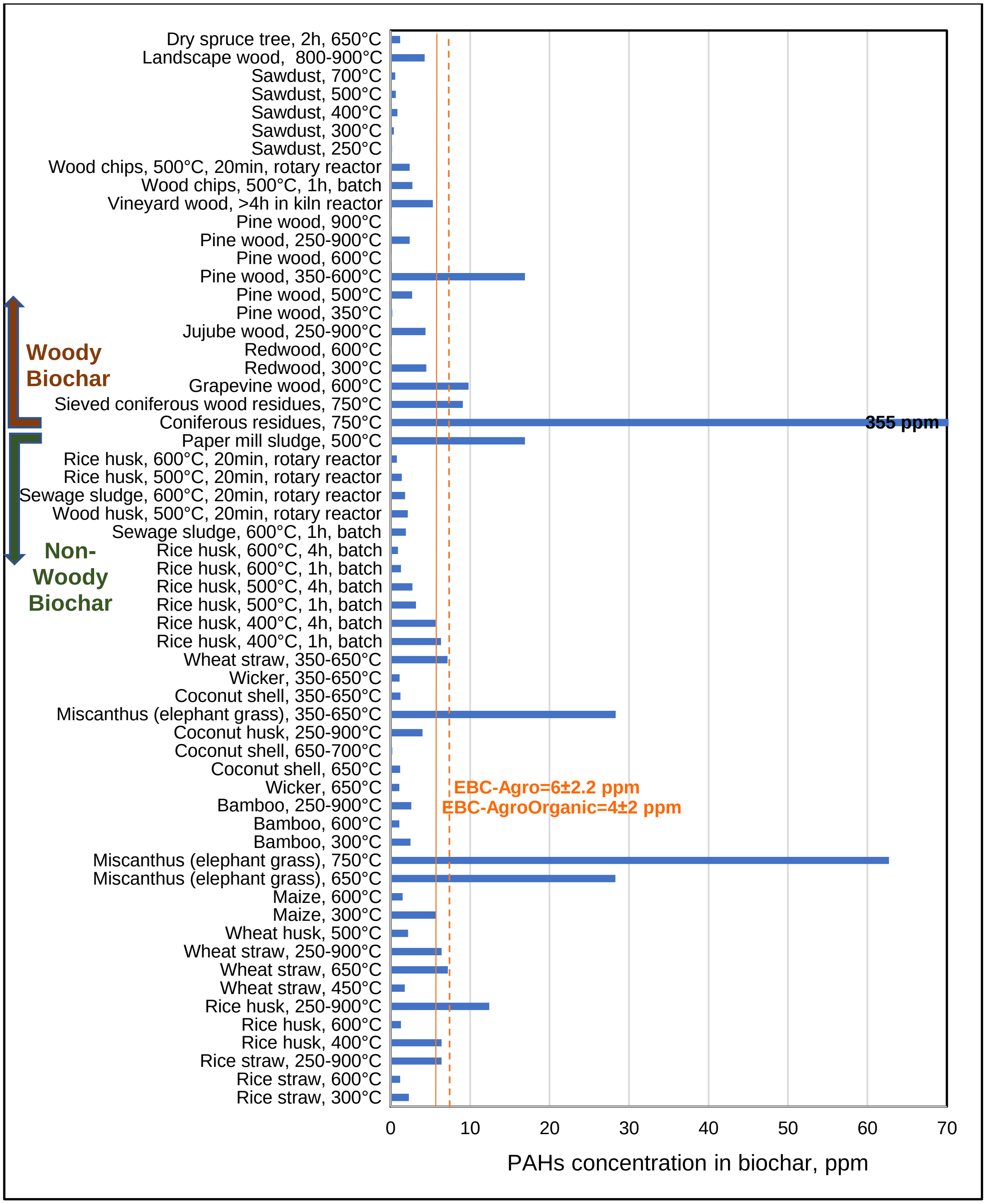

Figure 1. PAHs concentrations found in the biochar after the pyrolysis including the biochar types and their pyrolysis conditions together with EBC limits for PAHs. The graph is limited at 70 ppm on x-axis so lower concentrations can be seen better, however there is one PAHs concentration of 355 ppm (coniferous residues, 750°C) as marked on the graph.

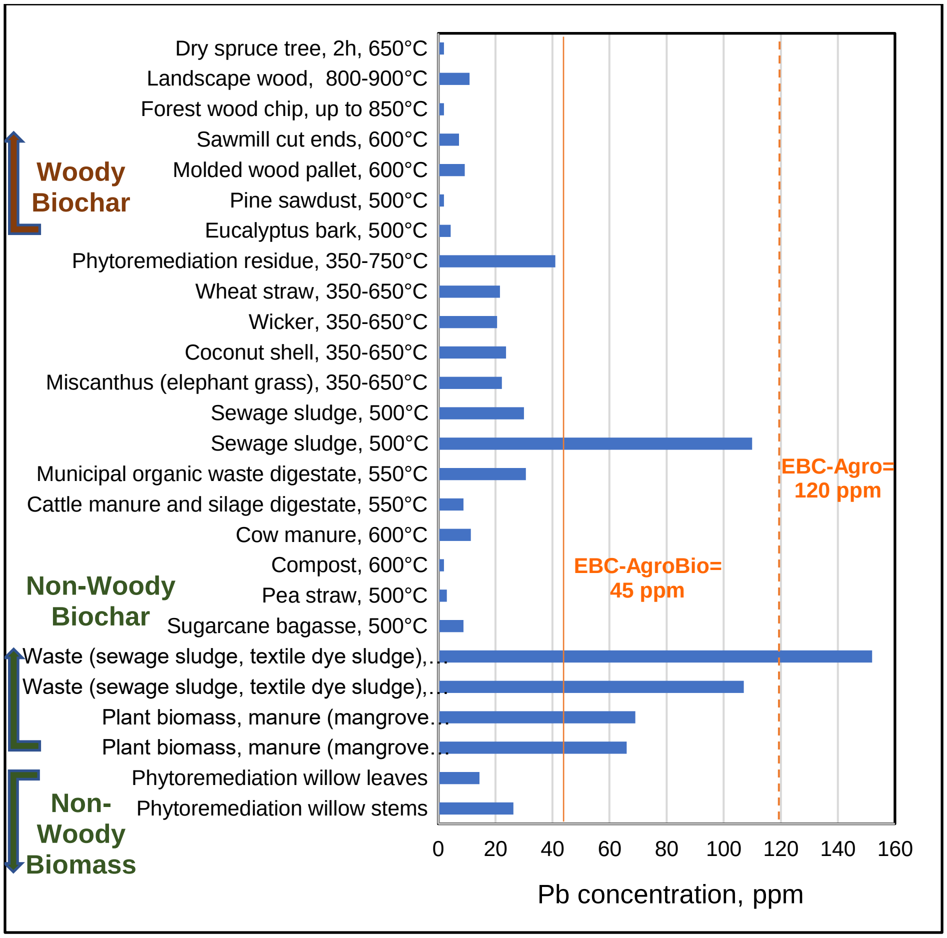

Figure 2. Pb concentrations of various biochars and EBC limits for Pb.

Table 6 describes dioxins concentrations in various biochar types after the pyrolysis including pyrolysis conditions. Dioxins are mostly found in woody biochars. 78.5% of dioxins concentrations (red colored in Table 6) found in biochars exceeded the EBC-PCDD/F limit (0.00002 ppm)[9] but no concentrations exceed EBC-PCB limit (0.2 ppm) [9]. Dioxins are seen in sawdust, especially pine sawdust, no matter the pyrolysis temperature. This is seen in the Table 6 and Figure 9 in Annexes.

Table 7 represents the analysis of the second research question. Study of positive, negative, neutral and overall effects of various biochars applied to specific soils including different application rates has been done. Focus is put on data related to Swiss most common soil types: silt loam, loam, sandy loam and silty clay. Biochar application rate vary in range 2-200 000 ppm. Overall effect (positive or negative) is estimated from literature sources which have defined effect either as a significant effect or as an effect that is not so significant, but still important to be noticed. Literature sources are visible in Table 7 which represents the results. For both woody and non-woody biomass, all kinds of effects are observed. Non-woody biomass, especially crop by-products, are characterised with more significantly negative effects (56.5% of all non-woody biochars) than woody biomass. This is due to mortality, weight loss, reduction in size and decreased growth effects on invertebrates, changes in fungi-to-bacteria ratio and decrease in microbial biomass. 5% dose of miscanthus (350-650°C) biochar inhibits the plant root growth by 48% and 10% dose causes inhibition by 92%, additionally causing bacterial luminescence inhibition by 99%. The highest dose of coconut shell (350-650°C) biochar inhibits plant root growth by 4%, bacterial luminescence is inhibited by 12% and alga and protozoa mortality rate go up to 26.5% and 16.8%, respectively. Wicker (350-650°C) biochar, however, inhibits bacterial lumincence by 40% and causes alga mortality rate of 21%. For wheat straw (350-650°C) biochar, the 5% dose corresponds to 33% inhibition of plant root growth and 58% inhibition when 10% dose is applied. Bacterial luminescence is inhibited by 85% and mortality rates for alga and protozoa are 2% and 15.1%, respectively. All of the mentioned biochars cause 100% mortality rate for crustaceans, except for the coconut shell biochar (10% mortality rate). Other significantly negative effect is decrease in soil conductivity by 70.9%, 20.9% and 42.1% and 6.6% for biochars derived from straw (525°C), vineyard (400°C) and vineyard (525°C), respectively. Significantly positive effects (21.7% of all non-woody biochars) are related to mitigation of stress effects of salt on okra plant and soil bulk density decrease together with water content increase which occur when wheat straw (350-550°C) biochar is applied to the soil. For spent coffee grounds (450°C) biochar a significant increase in digestive enzymes of earthworms is observed. When rainbow eucalyptus (350°C) biochar is applied, a rice root biomass is increased by 1-10%, above-ground biomass by 1-152% and shoot-to-root ratio by 2-200%. Additional significantly positive effects observed for non-woody biomass are decrease in soil bulk density (8.6% for straw (525°C) biochar), increased microbial biomass (>25% for rice husk (>480°C) biochar) and increased soil aggregate stability which is connected to increased plant available water.

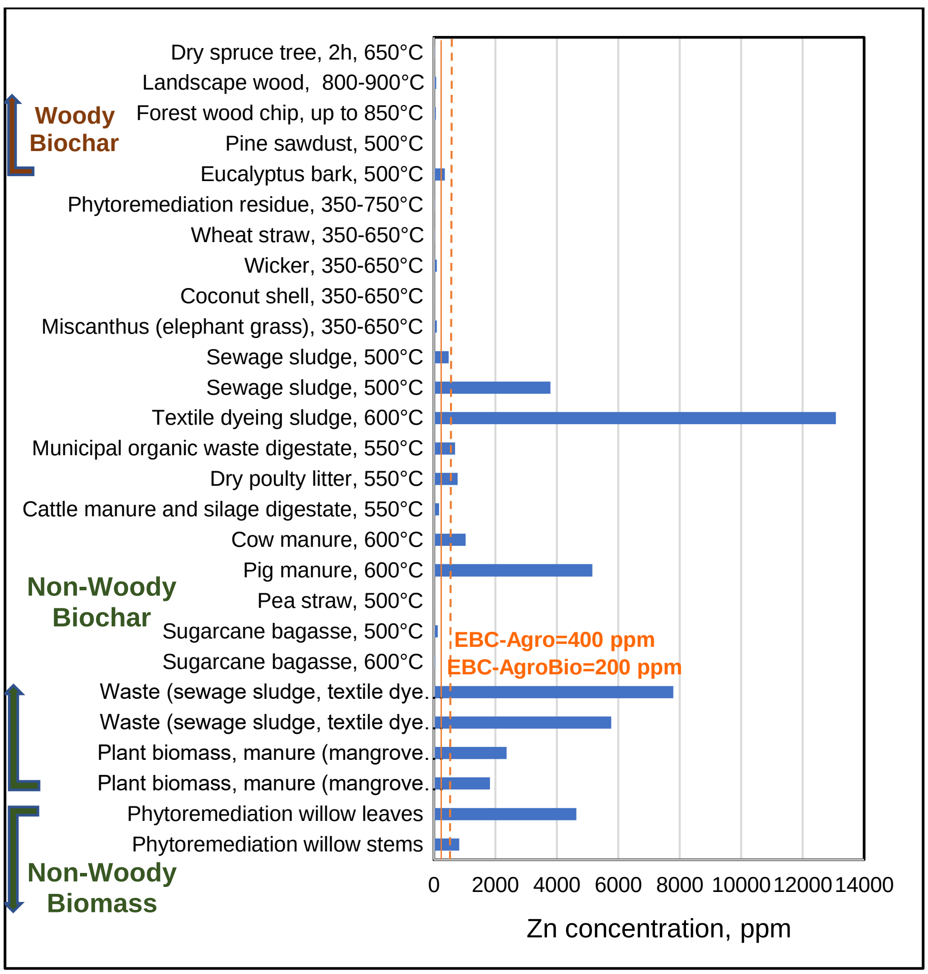

Figure 3. Zn concentrations of various biochars and EBC limits for Zn.

Woody biomass is characterised with more significantly positive effects (55.5% of all woody biochars). *Leucaena leucocephala* (Lam.) de Wit wood (700°C) biochar causes significant soil loss reduction of 50-64% and increased soil aggregate stability. Increase in soil conductivity by 11-22.8% and decrease in soil bulk density by 0.8-6.1% are observed for woodchip (525°C) biochar. Increased shoot and root biomass and alleviation of salinity-induced oxidative stress is observed when *Acer pseudoplatanus* l. residues (560°C) biochar is applied to the soil. However, significantly negative effects (22.2% of all woody biochars) observed for woody biomass include significant weight loss in earthworms observed for apple wood sawdust (525°C) biochar and a decrease in soil conductivity by 6.6% observed for woodchip (525°C) biochar. Mixed woody and non-woody biochar has a significantly negative effect on reproduction rates of springtails which are reduced by 27-38%. All this can be seen in Figure 4.

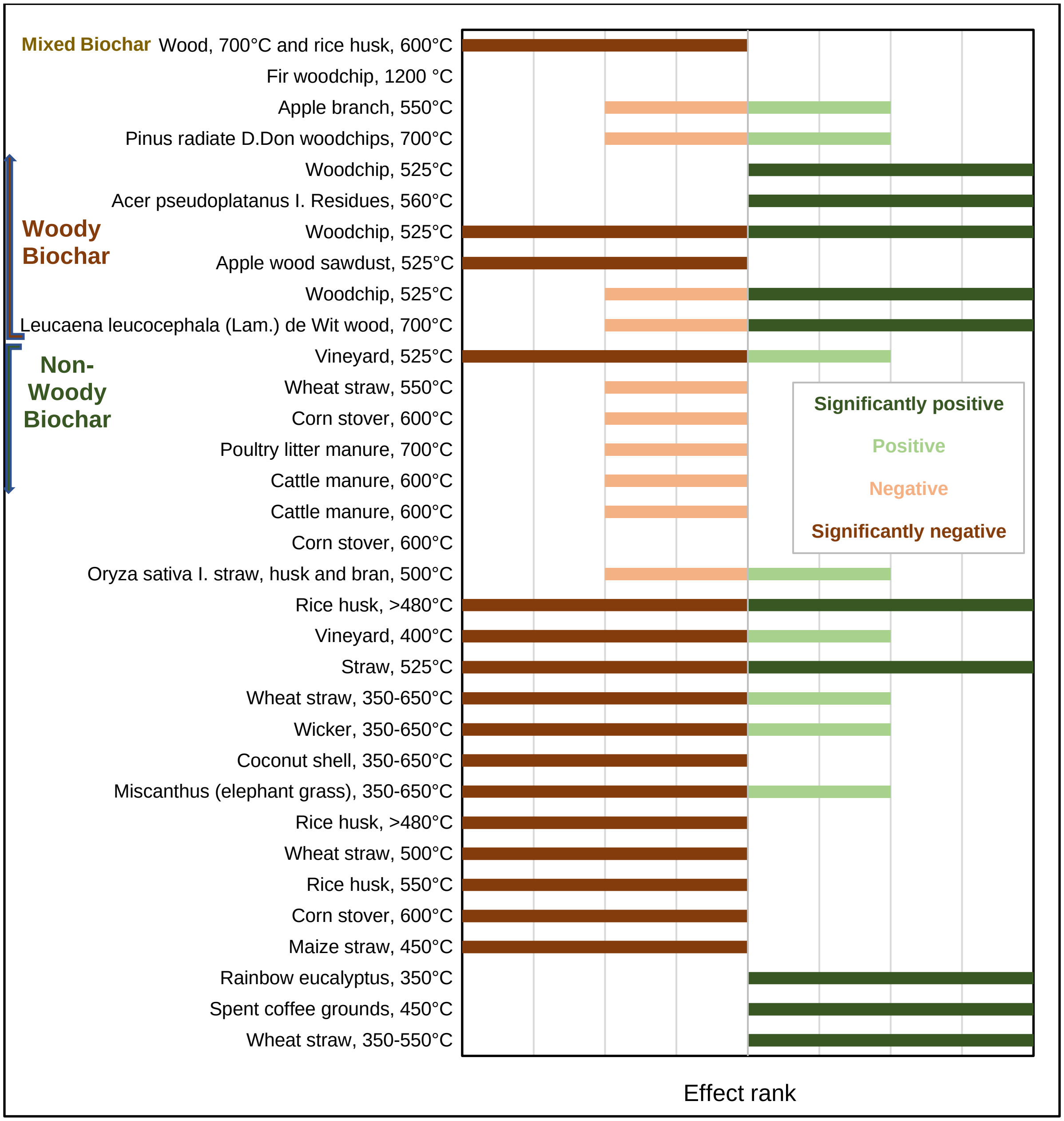

Figure 4. Overall effects of various biochar types.

Discussion

The analysis of the first research questions provides answers on connecting pollutants, which originate from a specific biomass or which occur in the process of pyrolysis by mechanisms of chemical transformation, with the polluted biochar. Inorganic compounds like heavy metals and MCN are found in biomass prior to the pyrolysis[5]. Heavy metals are identified as the biggest threat. In the results, it is clearly shown that heavy metals concentrations in biochar often exceed EBC standard limit values and therefore can be identified as potentially dangerous (Table 5). Additionally, they tend to concentrate in the process of pyrolysis and biochars derived from heavy metals rich biomass usually have higher heavy metal content than the biomass itself[5], [25]. Three biomass types are identified as heavily polluted with heavy metals: sewage sludge, animal manure and phytoremediation residues. Temperature is not a crucial parameter, but a feedstock is when it comes to heavy metals polluted biochars[8]. Therefore, non-woody biomass is defined as questionable for safe biochar production. PAHs are formed during the process of pyrolysis mostly around 400°C, but they tend to be destroyed by the higher pyrolysis temperature or longer residence time in the reactor[19], [20], [23]. When analysing PAHs concentrations in the biochar, they are below the EBC limits defined for the biochar which puts them in a category of less problematic pollutants which do not pose a risk for the environment and the humans because they follow the guidelines[5], [9]. Nevertheless, woody biochars (coniferous wood residues, pine wood, grapevine wood), paper mill sludge and miscanthus are biomass types that have shown PAHs concentrations which are exceeding the EBC limit values (Table 4). Dioxins are also formed during the pyrolysis process and can be partially destroyed or fully destroyed if pyrolysis conditions are optimized[5]. However, dioxins concentrations in sawdust biochars are still measured as exceeding when compared to EBC standards which makes them problematic (Table 6). Choosing a biomass with less than 1% chlorine content does not promote formation of dioxins during the pyrolysis process, therefore it can be used as a mitigation strategy for dioxins concentrations in the biochar[5]. MCN and PFR are novel pollutants for which data is lacking and further research and analysis need to be conducted in order to gain more insight into the mechanisms of these pollutants. VOCs are usually destroyed in the process of pyrolysis and are not found in biochars. Woody biochars can contain PAHs and dioxins, but they can be destroyed in an optimized pyrolysis process[5], [8].

The analysis of the second research question provides answers on connecting effects that are occurring in the soil when polluted biochar is applied to it with specific application rates. Swiss soil types that are considered are: silt loam, loam, sandy loam and silty clay[10]. Application rates highly vary between found data in the scientific literature (Table 7). It is observed that negative effects on microorganisms and invertebrates are stronger when the application rate is higher after non-woody biochar is used on the soil[20]. When it comes to soil water availability, woody biochar has shown positive effects, even though one study reports an increase in bulk density[40]. Plant biochars are observed to decrease bulk density due to dilution of the soil with a porous material and increase water content and aggregate stability because biochar surface attracts organic matter, thus it can be a start of building further aggregates [40], [56]. Woody biochars can reduce the effect of soil erosion and soil loss, while non-woody biochars usually contribute to soil erosion[49]. Woody biochars have a decreased erosion potential with an increase in biochar particles[52]. However, some studies enhance the improved soil erosion potential after an increase of application rate of a woody biochar[52]. Soil salinity, besides the pH, governs chemical equilibrium in the soil which is necessary for the healthy plant growth. Sawdust as woody biochar, and various crops, as non-woody biochars, eliminate stress which occurs from excessive soil salinity[56], [59], [77], while animal manure biochars content is usually rich in salts which causes stress for the plants and endangers the nutrient bioavailability[41], [62]. Soil nutrients are governed by the soil pH which can vary from alkaline to acidic. Excessively decreased pH can endanger the equilibrium in the soil and plants[8]. Crop by-products biochar is observed as a good buffering tool in the situations of highly decreased pH[61]. Manure biochars usually excessively raise the soil pH, while wood biochars tend to lower the soil pH, however pH itself is very dependent on the type of biochar feedstock[8], [62], [63]. Plant biochar is reported to cause an increase in pH, therefore decreasing Cd, Zn and Pb concentrations and increasing As concentrations[77]. Manure biochars contain more available nutrients than crop by-products biochars, therefore they are used for depleted soils to increase the nutrient content[8]. Invertebrates can be positively influenced by sludge biochars[75], while manure and wood biochars tend to have a negative impact[71], [72]. Plant and wood biochars have shown both negative and positive impacts on invertebrates mortality rate, reproduction and mass[8], while plant biochar has only negative effects on the microorganisms due to its heavy metals content[20]. Short-term biochar application influences bacterial diversity, but long-term use may increase the diversity and complexity of the microbial communities[8]. Plant biomass is increased when crops biochar is added to the soil[78], however some studies report plant growth inhibition as well[20]. One study reports increased shoot and root biomass after woody biochar application[79], but another study reports a decrease in plant biomass with increase in biochar application rate[45]. Soil conductivity is decreased by plant and woody biochars, although one study shows an increase in soil conductivity after woody biochar is applied to the soil[40].

Microbiome and soil invertebrates happen to be two categories which are mostly endangered by the improper biochar application as majority of significantly negative effects are observed when they are being assessed. This happens due to their high sensitivity to pH, soil structure and nutrient content change which occurs when biochar is added to the soil[8]. Additionally, biochar particles tend to stick to their bodies which can reduce their growth and effect their everyday functions[8]. Biochar application has a significantly positive effects on soil bulk density, water content, increase in shoot and root biomass, soil aggregate stability, soil erosion and water retention capacity. Soil salinity and pH are positively and negatively influenced by the biochar application because those properties highly depend on the type of biochar feedstock, without having a correlation to a specific biochar/biomass category[8]. Both decrease and increase in soil conductivity is reported as it highly varies between studies, even for the same type of biochar applied to the soil[40]. Plant growth is positively stimulated by the biochar, however some studies show significantly negative effect on the plant growth[20]. Biochars derived from non-woody biomass are defined as having more significantly negative effects than biochars derived from the woody biomass. Woody biochars positively influence soil properties like bulk density, aggregate stability and water capacity, but have a negative effect on the invertebrates[40], [69]. Non-woody biochars have a significantly negative effect on the invertebrates and soil microorganisms, but they stimulate the plant growth and some soil properties[20], [78].

After analysing the first two research question, an answer to the third research question can be discussed in a form of recommendations for safe and sustainable biochar production and use on agricultural soils in Switzerland. Optimization of the pyrolysis process in terms of condition adjustments according to the biomass type is very important as it can destroy PAHs and dioxins and evaporate some of the heavy metals, e.g. Cd[29]. Regular analysis needs to be carried out to measure and monitor PAHs and dioxins concentrations so their concentrations do not end up exceeding the EBC limits. Feedstock for the biochar production should be carefully chosen. Currently, it is legal to produce biochar only from an untreated woody biomass in Switzerland[80]. Woody biomass is prone to forming PAHs and dioxins (especially sawdust)[23], thus pyrolysis temperature should be adjusted to a higher temperature and/or residence time to a longer residence time if exceedance of EBC limits is observed after sampling and analysing the biochar[20]. Manure and sludge non-woody biomass are contaminated with heavy metals and PAHs (only the sludge). Therefore, animal manure is not recommended for the biochar production since it is heavily contaminated, causes excessive salinity and changes in pH in the soil as well as mortality in the invertebrates[41], [62], [71]. Whole amount of animal manure biomass can be used instead for production of primary energy, as it is estimated to a value of 4.42% of the total gross energy consumption in Switzerland and the production cost is low (<2.5 CHF/GJ) when compared to other biomass types[7]. Handling sewage sludge biomass and biochar should be done with caution since it is contaminated with PAHs and heavy metals. I would not recommend it as a first choice when choosing feedstock for the biochar production because heavy metals can concentrate in the biochar and PAHs have been measured from a study as higher in the biochar than in the biomass after the pyrolysis[5]. Strictly monitoring pollutants values if it must be used for biochar production. It should be kept in mind that sludge biochar does have a positive effect on the invertebrates when applied to the soil[75]. Non-woody biochar, especially phytoremediation residues biochar, should be carefully monitored for heavy metals concentrations. Miscanthus biomass should be avoided for biochar production as it has shown high PAHs concentrations[20], [22]. Mitigation strategies for PAHs can include a thermal post-treatment or biological aging of the biochar as it is found that these processes reduce PAHs concentrations in biochar by 33.8-100% and 30-100%, respectively[5]. For the heavy metals, co-pyrolysis of heavy metals-rich biomass with heavy metals-poor biomass provided good results when it comes to reducing heavy metals concentration in the biochar (e.g. pairing sewage sludge with a rice straw biomass). Another strategy is pre-treatment of the biomass through acid washing which lowers the overall heavy metals concentration in the biomass itself[5].

Taking all effects into account, non-woody biochars are observed to have an overall more negative effect on the whole ecosystem than woody biochars. Invertebrates and microorganisms are significantly negatively influenced by both woody and non-woody biochar[8]. Further research into mechanisms on that topic should be conducted to explore whether this is mostly connected to the biochar feedstock, pyrolysis conditions for biochar production or the biochar application rate. Non-woody biochar has a positive effect on soil water availability (crops biochar), soil conductivity (crops biochar) and nutrients in the soil (manure biochar). It has a negative effect on the soil erosion and microorganisms (crops biochar). Positive and negative effects are observed in the case of salinity (crops biochar-positive, manure biochar-negative), invertebrates (sludge biochar-positive, manure biochar-negative, crops biochar-positive, negative) and plant biomass (crops biochar-positive, negative). Woody biochar has a positive effect on soil water availability and salinity (sawdust biochar). It has a negative effect on the bulk density. Positive and negative effects are observed in the case of soil erosion, invertebrates, plant biomass and soil conductivity. Soil pH is highly dependent on various factors. Non-woody biochar (crops) tends to have good buffering effect in soils with decreased pH. Crops and manures biochar increases soil pH, while woody biochar decreases soil pH. Crop biochar can influence heavy metals concentrations and their bioavailability when pH is increased. It lowers the Cd, Zn and Pb and raises the As concentrations and bioaccumulation. Correlation between heavy metals polluted, woody and non-woody, biochar and negative biochar effects on the soil might be proposed given the obtained results. Biochar has overall more positive effects on the soil ecosystem than negative effects. Positive effects are observed considering soil bulk density, soil water content, soil aggregate stability and water retention capacity. Overall negative effects on the ecosystem are considering invertebrates and microorganisms. Soil erosion, soil salinity, soil pH, soil conductivity and plant biomass are categories which are influenced both positively and negatively and further research needs to be conducted on biochar effects so deeper knowledge can be obtained. Biochar application rates and their link to the biochar effects is a study which would be beneficial for the overall conclusion on safe use of biochar on the agricultural soil, but due to lack of data is not conducted. Long-term effects are most important topic that need further research as there is data lacking so they are unknown. There are indications long-term effects could be positive, but negative as well[8]. Specific recommendations on safe use of biochar would require further analysis since biochar effects are so different and sometimes contradicting. Human and environmental health together with plant growth are important factors to keep in mind whilst doing such analysis. Human health can be influenced if polluted biochar decomposes in the soil and pollutants become bioavailable for the crop uptake which are used for food production[21]. Further research is suggested on the topic of biochar stability and pollutants bioavailability in the soil because decomposition rate of the biochar can influence the concentrations of the pollutants in the soil and their bioavailability for the ecosystem[38].

Some of the observed effects, if not significant, can under specific circumstances be overlooked when it comes to the overall impression of the biochar effects because of biochar's capability to sequester carbon. Carbon sequestration is a powerful tool when it comes to climate change mitigation. In Switzerland, there is a capacity to produce 779109 tonnes of biochar per year only from the woody biomass. This is equal to 2050000 tCO_2eq negative emissions per year which is a significant value[2]. One suggested use of biochar on the agricultural soils would be intended for the carbon sequestration.

Conclusion

This study has been conducted to assess the danger of pollutants in biochar and the effects biochar has when applied to agricultural soils. The aim was to identify the pollutants which originate from specific biomass or form in certain biochar types. Pyrolysis type and conditions, such as temperature range, reactor type and residence time, were examined as they can provide a deeper understanding of the process which pollutants go through. Biochar effects were assessed by analysing the biochar types and connecting them with four Swiss soil types and certain application rates while observing the overall positive and negative effects when biochar is applied to the soil. This study identified sewage sludge, manure and phytoremediation residues as non-woody biomass that is rich in heavy metals and potentially poses a risk for the ecosystem because heavy metals concentrate in the biochar matrix during the pyrolysis process. Miscanthus and paper mill sludge are identified as non-woody biomass with high potential of forming PAHs during the pyrolysis, therefore should be pyrolyzed at a higher temperature or longer residence time. Woody biomass tends to form PAHs during the pyrolysis, but they can be managed as described above. Sawdust is a woody biomass which is prone to dioxins formation during the pyrolysis process and therefore should be analysed often. A correlation between heavy metals polluted biomass and its observed negative effects on the ecosystem is proposed. Non-woody biomass is identified with larger overall negative effects on the ecosystem when applied to the soil than woody biomass. Biochar is identified to have overall more positive effects on the soil ecosystem than negative effects. Soil bulk density, soil water content, soil aggregate stability and water retention capacity are positively affected. Overall negative effects on the ecosystem are identified as effects on invertebrates and microorganisms. Soil erosion, soil salinity, soil pH, soil conductivity and plant biomass are categories which are influenced both positively and negatively and further research needs to be conducted on biochar effects so deeper knowledge can be obtained. Effects are highly contradictory as different resources observed different effect, therefore it is concluded that no specific recommendations can be given on safe use of biochar on agricultural soils. One use of biochar that is important and has a big potential is carbon sequestration to fight climate change. Long term effects, biochar stability in the soil, pollutants bioavailability and application rates of biochar are proposed topics for further research which is necessary to conduct a more thorough analysis.

Annexes

Table 4. PAHs concentrations found in the biomass prior to the pyrolysis and in the biochar after the pyrolysis including the biochar types and their pyrolysis conditions[8], [20].

Pollutant	Biomass category	Biochar type and pyrolysis conditions	Concentration of pollutants in the biomass prior to the pyrolysis, ppm	Concentration in the biochar after the pyrolysis, ppm	Reference
Sum of 16 PAHs	Non-Woody	Rice straw, 300°C		2.3	[27]
		Rice straw, 600°C		1.2	[27]
		Rice straw, 250-900°C		6.4	[81]
		Rice husk, 400°C		6.4	[19]
		Rice husk, 600°C		1.3	[19]
		Rice husk, 250-900°C		12.4	[81]
		Wheat straw, 450°C		1.8	[32]
		Wheat straw, 650°C		7.2	[20]
		Wheat straw, 250-900°C		6.4	[81]
		Wheat husk, 500°C		2.2	[19]
		Maize, 300°C		5.7	[27]
		Maize, 600°C		1.5	[27]
		Miscanthus (elephant grass), 650°C		28.3	[20]
		Miscanthus (elephant grass), 750°C		62.7	[22]
		Bamboo, 300°C		2.5	[27]
		Bamboo, 600°C		1.1	[27]
		Bamboo, 250-900°C		2.6	[81]
		Wicker, 650°C		1.1	[20]
		Coconut shell, 650°C		1.2	[20]
		Coconut shell, 650-700°C		0.2	[32]
		Coconut husk, 250-900°C		4	[81]
		Miscanthus (elephant grass), 350-650°C		28.3391	[20]
		Coconut shell, 350-650°C		1.2235	[20]
		Wicker, 350-650°C		1.1242	[20]
		Wheat straw, 350-650°C		7.1557	[20]
		Sewage sludge	32.7		[18]
		Rice husk, 400°C, 1h, batch		6.364	[19]
		Rice husk, 400°C, 4h, batch		5.653	[25]
		Rice husk, 500°C, 1h, batch		3.192	[25]

		Rice husk, 500°C, 4h, batch		2.749	[25]
		Rice husk, 600°C, 1h, batch		1.291	[25]
		Rice husk, 600°C, 4h, batch		0.923	[25]
		Sewage sludge, 600°C, 1h, batch		1.942	[25]
		Wood husk, 500°C, 20min, rotary reactor		2.169	[25]
		Sewage sludge, 600°C, 20min, rotary reactor		1.82	[25]
		Rice husk, 500°C, 20min, rotary reactor		1.395	[25]
		Rice husk, 600°C, 20min, rotary reactor		0.799	[25]
		Paper mill sludge, 500°C	0.073	16.916	[24]
	Woody	Coniferous residues, 750°C		355	[22]
		Sieved coniferous wood residues, 750°C		9.1	[22]
		Grapevine wood, 600°C		9.8	[22]
		Redwood, 300°C		4.5	[27]
		Redwood, 600°C		0.1	[27]
		Jujube wood, 250-900°C		4.4	[81]
		Pine wood, 350°C		0.2	[32]
		Pine wood, 500°C		2.7	[19]
		Pine wood, 350-600°C		16.9	[82]
		Pine wood, 600°C		0.1	[32]
		Pine wood, 250-900°C		2.4	[81]
		Pine wood, 900°C		0.1	[32]
		Vineyard wood, >4h in kiln reactor		5.33	[19]
		Wood chips, 500°C, 1h, batch		2.737	[19]
		Wood chips, 500°C, 20min, rotary reactor		2.404	[19]
		Sawdust, 250°C		0.19	[23]
		Sawdust, 300°C		0.4	[23]
		Sawdust, 400°C		0.86	[23]
		Sawdust, 500°C		0.65	[23]
		Sawdust, 700°C		0.59	[23]
		Landscape wood, 800-900°C		4.3	[12]
		Dry spruce tree, 2h, 650°C		1.2	[11]
	Mix	Sewage sludge, rice straw, wood chip, faecal sewage, inoculant	28.6		[18]
EBC-AgroOrganic limit				4±2	[9]
EBC-Agro limit				6±2.2	[9]

Table 5. Heavy metal concentrations found in the biomass prior to the pyrolysis and in the biochar after the pyrolysis including the biochar types and their pyrolysis conditions[8], [20].

Pollutant	Biomass / Biochar	Biomass category	Biomass or biochar type and pyrolysis conditions	Concentration of pollutants in the biomass prior to pyrolysis and in the biochar after the pyrolysis, ppm								Reference
				Cd	Cr	Cu	Ni	Pb	Zn	As	Hg	
PTEs (heavy metals)	Biomass	Non-Woody	Raw willow			25	3					[25]
			Ni contaminated willow			22	5632					[25]
			Cu contaminated willow			5156	3					[25]
			Phytoremediation willow stems	40.9		11.4		26.3	822			[29]
			Phytoremediation willow leaves	80		14.8		14.4	4636			[29]
	Biochar	Non-Woody	Plant biomass, manure (mangrove biomass, sugar cane straw, cow and pig manure), 300°C	0.2	144	343	17	66	1830			[8]
			Plant biomass, manure (mangrove biomass, sugar cane straw, cow and pig manure), 700°C	0.53	233	581	34	69	2371			[8]
			Waste (sewage sludge, textile dye sludge), 300°C	0.79	193	334	145	107	5775			[8]
			Waste (sewage sludge, textile dye sludge), 700°C	0.14	258	420	188	152	7790			[8]
			Sugarcane bagasse, 600°C		25	26			47.5			[83]
			Sugarcane bagasse, 500°C		7.2	93	9.5	8.8	133			[84]
			Pea straw, 500°C		3	20	2	3	29			[85]
			Compost, 600°C					2		1.3	10.8	[86]
			Pig manure, 600°C		477	902			5161			[87]
			Cow manure, 600°C	0.48	73.5	441	22.8	11.4	1040			[88]
			Cattle manure and silage digestate, 550°C	0.16	10.2	38.9	5.5	8.8	172			[89]
			Dry poulty litter, 550°C	0.23	16.2	138	10.7		772			[89]
			Municipal organic waste digestate, 550°C	1.1	64.2	269	83.4	30.7	691	6.8		[89]
			Textile dyeing sludge, 600°C	0.87	377	392	272		13080			[90]
			Sewage sludge, 500°C	2.5	3082	5266	648	110	3791			[90]
			Sewage sludge, 500°C		69	375	17	30	480			[84]
			Miscanthus (elephant grass), 350-650°C	0.87	18	2.22	9.95	22.3	102			[20]

			Coconut shell, 350-650°C	0.1	1.3	3.81		23.7	30.2			[20]
			Wicker, 350-650°C	0.2				20.6	97.9			[20]
			Wheat straw, 350-650°C	0.04				21.6	32.9			[20]
			Raw biomass, 350°C			1030						[25]
			Raw biomass, 550°C			120						[25]
			Raw biomass, 750°C			20						[25]
			Cu polluted biomass, 350°C			16290						[28]
			Cu polluted biomass, 550°C			19240						[28]
			Cu polluted biomass, 750°C			22110						[28]
			Phytoremediation residue, 350-750°C	33.8				41	36.2			[5]
		Woody	Eucalyptus bark, 500°C			64	9.7	4.3	363			[84]
			Pine sawdust, 500°C		180	880		2	10	410		[85]
			Molded wood pallet, 600°C					9.3		5.4	23.2	[86]
			Sawmill cut ends, 600°C					7.2		2.5	0.2	[86]
			Wastewood impregnated with Cu, Cr, boron salts and organic preservatives, 475°C		31561	22560						[16]
			Wastewood impregnated with Cu, Cr and boron salts, 475°C		19768	8257						[16]
			Cable drums, 475°C		14103	6921						[16]
			Fences, 475°C		4748	1628						[16]
			Railway sleepers, 475°C		267	932						[16]
			Particle boards, 475°C		527	270						[16]
			Window frames, 475°C		465	681						[16]
			Forest wood chip, up to 850°C	0.2	6	11	4	2	63	0.8	0.07	[13]
			Landscape wood, 800-900°C	0.2	17	39	12	11	80	12	0.07	[12]
			Dry spruce tree, 2h, 650°C	0.2	3	3	3	2	38	0.8	0.07	[11]
EBC-AgroBio limit				0.7	70	70	25	45	200	13	0.4	[9]
EBC-Agro limit				1.5	90	100	50	120	400	13	1	[9]

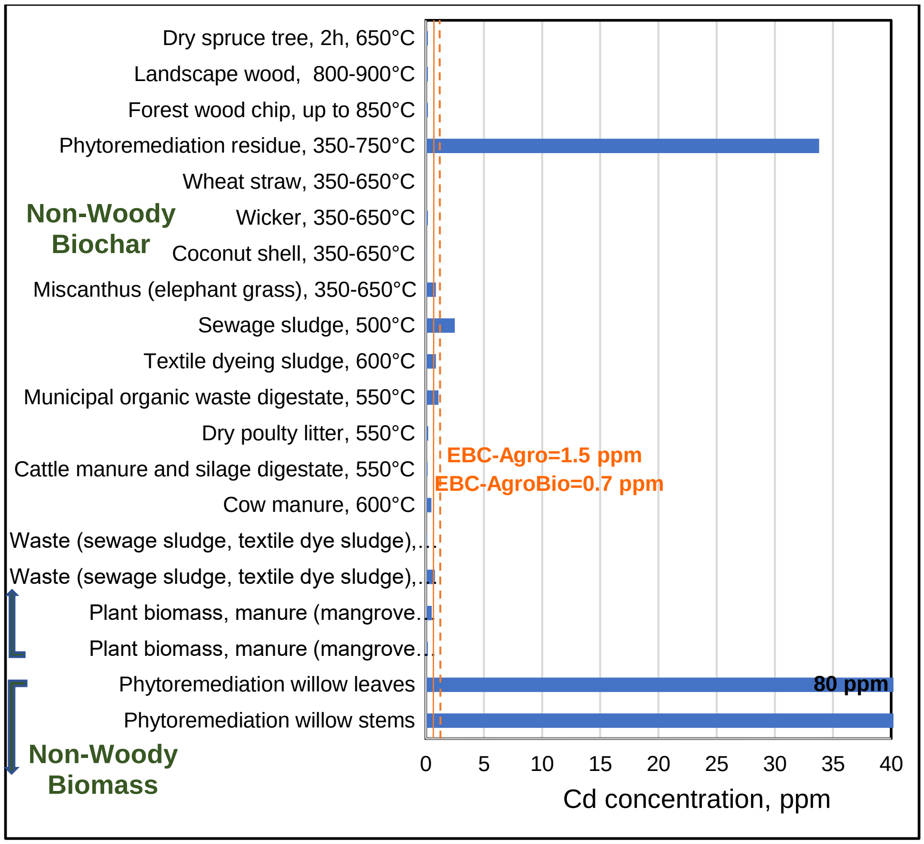

Figure 5. Cd concentrations of various biochars and EBC limits for Cd. The graph is limited at 40 ppm on x-axis so lower concentrations can be seen better, however there is one Cd concentration of 80 ppm (phytoremediation willow biomass) as marked on the graph.

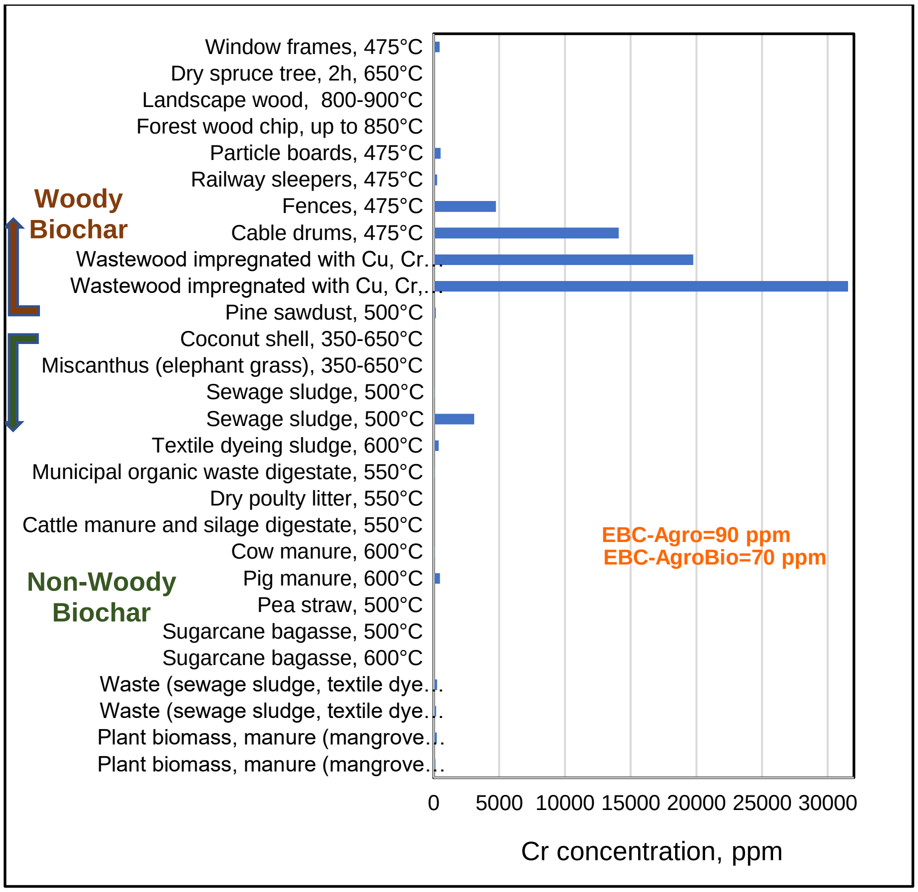

Figure 6. Cr concentrations of various biochars and EBC limits for Cr.

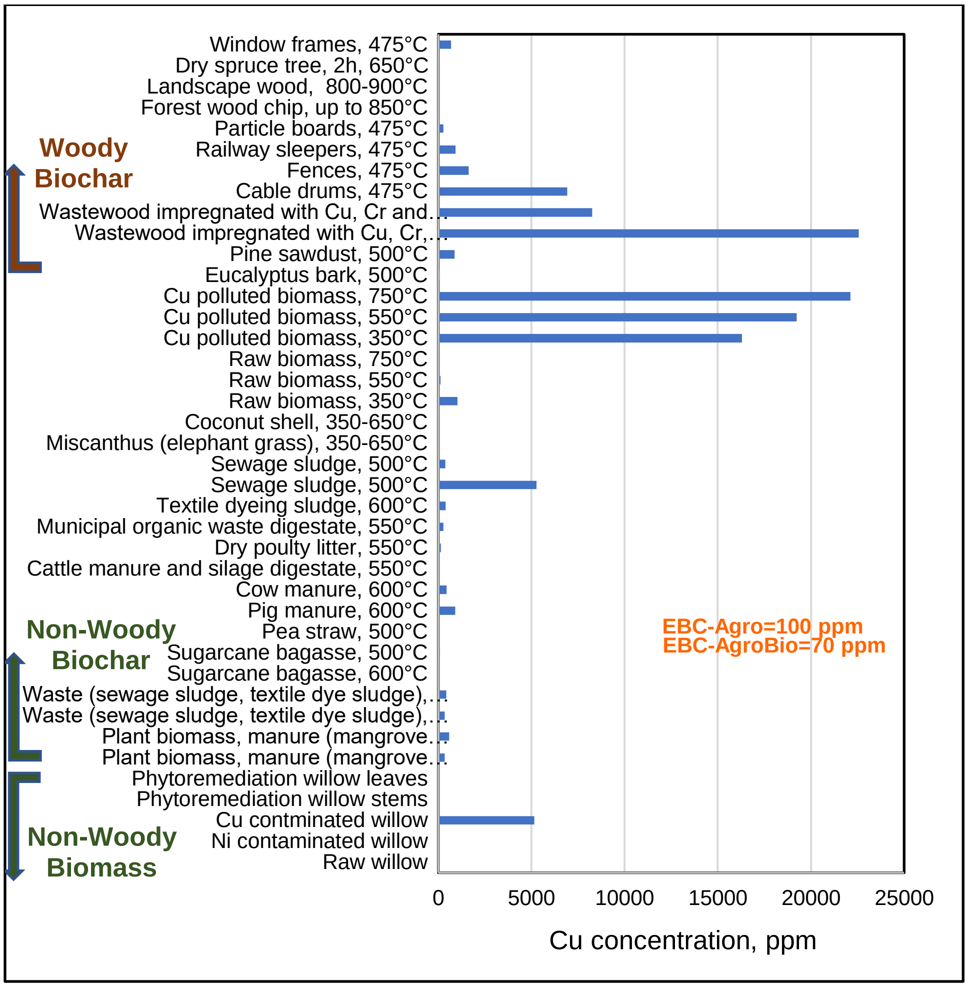

Figure 7.Cu concentrations of various biochars and EBC limits for Cu.

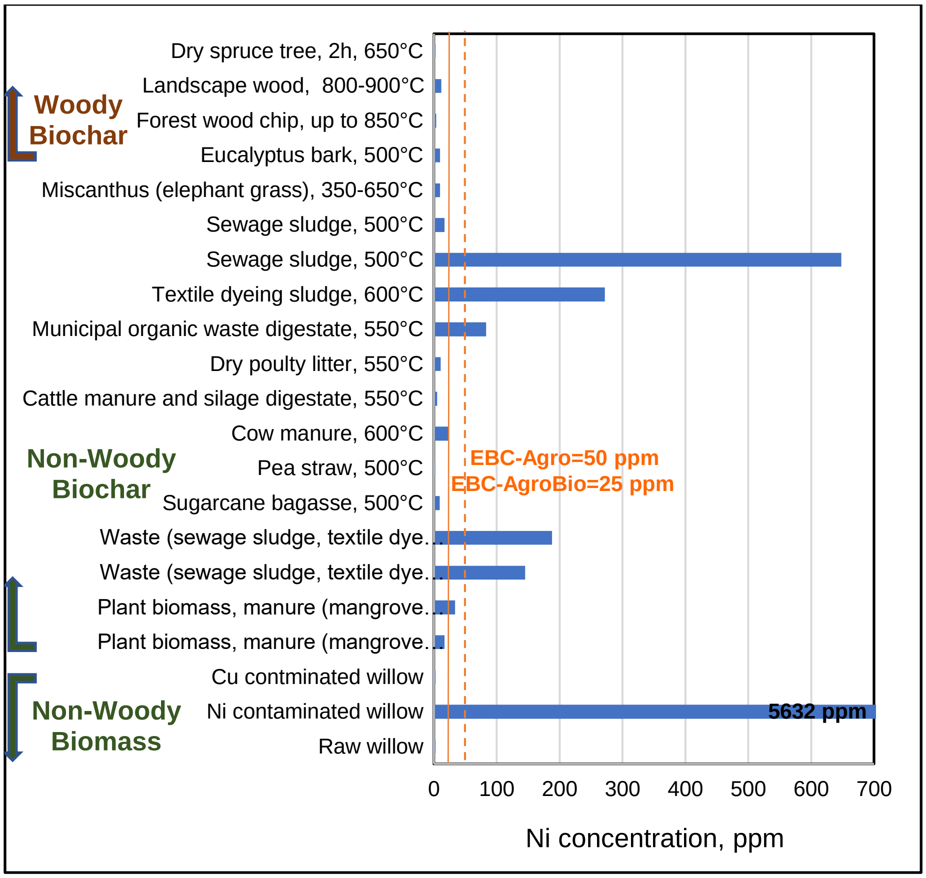

Figure 8. Ni concentrations of various biochars and EBC limits for Ni. The graph is limited at 700 ppm on x-axis so lower concentrations can be seen better, however there is one Ni concentration of 5632 ppm (Ni contaminated willow) as marked on the graph.

Table 6. Dioxins concentrations found in the biochar after the pyrolysis including the biochar types and their pyrolysis conditions.

Pollutant	Biomass category	Biochar type and pyrolysis conditions	Concentration in the biochar after the pyrolysis, ppm	Reference
Dioxins	Woody	Pine tree sawdust, 300°C	6.1×10^{-4}	[23]
		Pine tree sawdust, 400°C	3.6×10^{-4}	[23]
		Pine tree sawdust, 500°C	6.7×10^{-5}	[23]
		Pine tree sawdust, 700°C	5×10^{-5}	[23]
		Softwood, wheat straw, 550-700°C	9×10^{-7}	[5]
		Sawdust, 250-700°C	2.7×10^{-4}	[5]
		Sawdust, 250°C	2.7×10^{-4}	[23]
		Sawdust, 300°C	6.1×10^{-4}	[23]
		Sawdust, 400°C	3.6×10^{-4}	[23]
		Sawdust, 500°C	6.7×10^{-5}	[23]
		Sawdust, 700°C	5×10^{-5}	[23]
		Dry spruce tree, 2h, 650°C	5×10^{-7}	[11]
		Forest wood chip, up to 850°C	3.44×10^{-7}	[13]
	Mix	50 different feedstocks, 250-900°C	9.2×10^{-5}	[5]
EBC-PCB limit			0.2	[9]
EBC-PCDD/F limit			2×10^{-5}	[9]

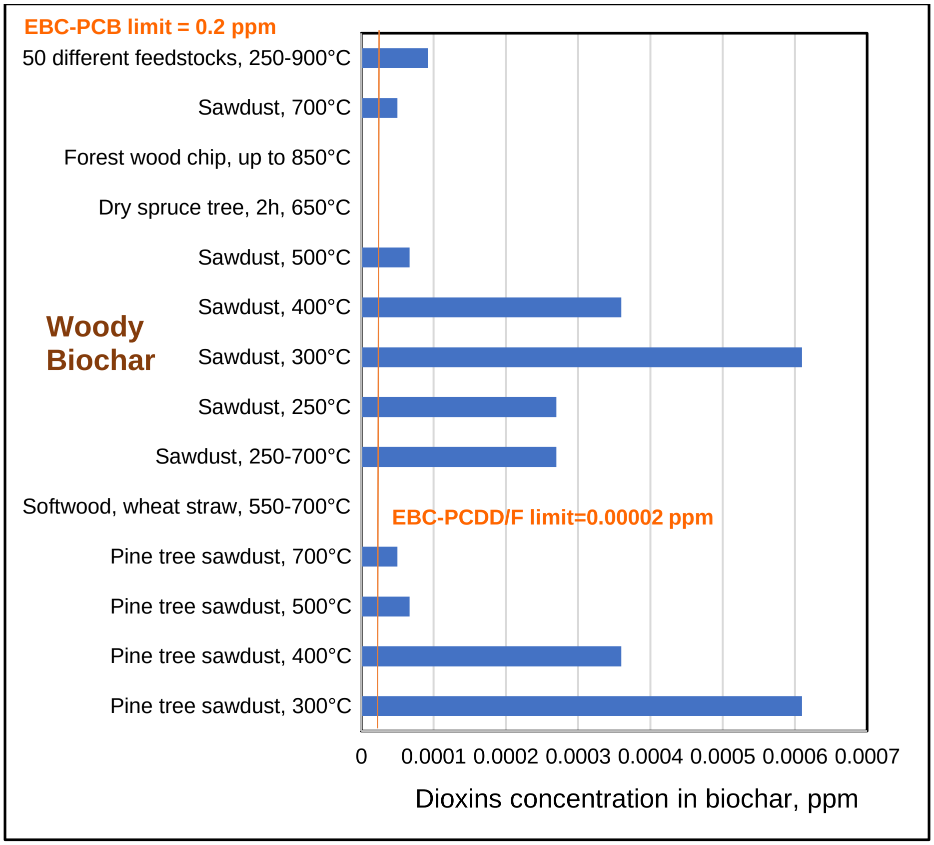

Figure 9. Dioxins concentrations in various biochar types and EBC limits for dioxins.

Table 7. Positive, negative, neutral and overall effect of various biochar types when applied to specific soil types including various application rates[8], [20], [37].

Biomass category	Biochar type	Type of soil	Application rate, ppm	Positive effects	Negative effects	Neutral effects	Overall positive effect	Overall negative effect	Reference
Non-Woody	Wheat straw, 350-550°C	Silt loam	50, 10	Mitigation or even elimination of stress effects of salt on okra plant. Soil bulk density decreased and water content increased.			Significantly positive		[56]
	Spent coffee grounds, 450°C	Anthrosol	10, 25	Significant increase in digestive enzyme activities of earthworms with no apparent detrimental effect.			Significantly positive		[76]
	Rainbow eucalyptus, 350°C	Clay soil with humus accumulation	26	Rice root biomass increase of 1-10%. Above-ground biomass increased by 1-152%. Shoot-to-root ratio increased by 2-200%.			Significantly positive		[78]
	Maize straw, 450°C	Fluvo-aquic loamy soil	5, 10, 25, 50		Fungi and bacteria content significantly reduced with increasing biochar addition rate. Microbial biomass negatively correlated with SOC and total N.			Significantly negative	[66]
	Corn stover, 600°C	Agricultural loamy soil	20, 50		Significant weight loss in earthworms.			Significantly negative	[68]
	Rice husk, 550°C	Loamy soil	200		Significant reduction in earthworm mean mass after 2 weeks.			Significantly negative	[70]
	Wheat straw, 500°C	Artificial soil	100		Significantly decreased earthworm growth and DNA damage.			Significantly negative	[8]
	Rice husk, >480°C	Pristine agricultural soil	5-500		Significant weight loss of the earthworms. Increase in biochar addition results in increased earthworm's mortality.			Significantly negative	[72]

	Miscanthus (elephant grass), 350-650°C	Heavy clay soil	10, 50, 100	Slight growth stimulating effect on microorganisms.	5% dose causes plant root growth inhibition by 48% and increased toxicity is observed. 10% dose causes inhibition of 92%. Bacterial luminescence inhibited by 99%. Causes crustaceans mortality rate of 100%.	No negative effect observed in protozoa and alga.	Positive	Significantly negative	[20]
	Coconut shell, 350-650°C	Heavy clay soil	10, 50, 100		Highest dose inhibits plant root growth by 4%. Bacterial luminescence inhibited by 12%. Causes alga mortality rate of 26.5%. Causes protozoa mortality rate of 16.8%. Causes crustaceans mortality rate of 10%.	No significant relationship between does and the effect observed.		Significantly negative	[20]
	Wicker, 350-650°C	Heavy clay soil	10, 50, 100	Stimulated plant root growth by 12-41%. Growth stimulating effect on microorganisms.	Bacterial luminescence inhibited by 40%. Causes alga mortality rate of 21%. Causes crustaceans mortality rate of 100%.	No significant relationship between does and the effect observed.	Positive	Significantly negative	[20]
	Wheat straw, 350-650°C	Heavy clay soil	10, 50, 100	Slight growth stimulating effect on microorganisms.	5% dose causes plant root growth inhibition by 33% and increased toxicity is observed. 10% dose causes inhibition of 58%. Bacterial luminescence inhibited by 85%. Causes alga mortality rate of 2%. Causes protozoa mortality rate of 15.1%. Causes crustaceans mortality rate of 100%.		Positive	Significantly negative	[20]
	Straw, 525°C	Sandy loam	30	Decrease in soil bulk density by 8.6% after 3	Decrease in soil electrical conductivity by		Significantly positive	Significantly negative	[40]

				years. Increase in soil aggregate stability. Increase in plant available water.	70.9% after 3 years.				
	Vineyard, 400°C	Sandy loam	30	Decrease in soil bulk density by 1.6% after 3 years.	Decrease in soil electrical conductivity by 20.9% after 3 years.		Positive	Significantly negative	[40]
	Rice husk, >480°C	Pristine agricultural soil	5-500	Significantly increased microbiota abundance (biomass increased by >25%) and composition over time.	The abundance of fungi significantly negatively influenced.		Significantly positive	Significantly negative	[72]
	Oryza sativa l. straw, husk and bran, 500°C	Contaminated soil from farmer fields	50	Increase in pH resulting in decrease in Cd, Pb and Zn concentrations in pore water and bioaccumulation in rice shoot.	Increase in pH resulting in increase in As bioaccumulation in rice shoot by up to 327%.		Positive	Negative	[77]
	Corn stover, 600°C	Agricultural loamy soil	5, 20, 50			No significant effect on the number of springtail offspring.		Neutral	[68]
	Cattle manure, 600°C	Silty clay	50		Excessive soil salinity resulting in adverse effects on plants.	No influence on water use efficiency by plant.		Negative	[41]
	Poultry litter manure, 700°C	Acidic sandy loam	20000		Excessively raised soil pH resulting in concerns about availability of important plant nutrients. Excessive soil P concentrations and leachate enriched with dissolved P.			Negative	[62]
	Corn stover, 600°C	Loamy temperate soil	2, 5, 20, 70, 140		Decreased basal soil respiration and bacteria-to-fungi ratio.	Microbial biomass doesn't change or increased by at most 15% with the different biochar rates over the incubation time.		Negative	[91]
	Wheat straw, 550°C	Loamy soil	200		Reduced mean mass in earthworms.	No significant impact on		Negative	[70]

						earthworm survival.			
	Vineyard, 525°C	Sandy loam	30	Decrease in soil bulk density by 3.1% after 3 years.	Decrease in soil electrical conductivity by 42.1% after 3 years.		Positive	Significantly negative	[40]
	Leucaena leucocephala (Lam.) de Wit wood, 700°C	Loamy	25, 50	Significantly reduced soil loss by 50% and 64%. Increased mean weight diameter of soil aggregates.	Improved soil erosion potential.		Significantly positive	Negative	[49]
Woody	Woodchip, 525°C	Clay loam	30	Increase in soil electrical conductivity by 22.8% after 3 years.	Increase in soil bulk density by 6.3% after 3 years.	No effect on plant available water.	Significantly positive	Negative	[40]
	Apple wood sawdust, 525°C	Artificial soil	100000, 200000		Significant weight loss in earthworms.	No significant effect on earthworm reproduction.		Significantly negative	[69]
	Woodchip, 525°C	Sandy loam	30	Decrease in soil bulk density by 6.1% after 3 years.	Decrease in soil electrical conductivity by 6.6% after 3 years.	No effect on plant available water.	Significantly positive	Significantly negative	[40]
	Acer pseudoplatanus l. Residues, 560°C	Silty loam	100, 200	Salinity-induced oxidative stress alleviated, osmotic substances accumulation in seedlings reduced, enhanced shoot and root dry weight under increased salinity.			Significantly positive		[59]
	Woodchip, 525°C	Silt loam	30	Increase in soil electrical conductivity by 11% and decrease in soil bulk density by 0.8% after 3 years.		No effect on plant available water.	Significantly positive		[40]
	Pinus radiate D.Don woodchips, 700°C	Market garden soil	10, 20, 40	Increased soil moisture content and water holding capacity.	Plant biomass decreased with increasing rate of biochar addition.		Positive	Negative	[45]
	Apple branch, 550°C	Silt loam loess	10, 30, 50, 70	Total erosion decreased with an increase in biochar particle size.	Total erosion increased with an increase in biochar application rate.		Positive	Negative	[52]
	Fir woodchip, 1200 °C	Loam	20			No effect on water drainage and solute leaching. Saturated		Neutral	[46]

						hydraulic conductivity may be affected.			
Mix	Wood, 700°C and rice husk, 600°C	Sandy loam	100		Reproduction rates of springtail reduced by 38% and 27% in comparison to unamended soil.			Significantly negative	[74]

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