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# Contaminants in biochar and suggested mitigation measure - a review

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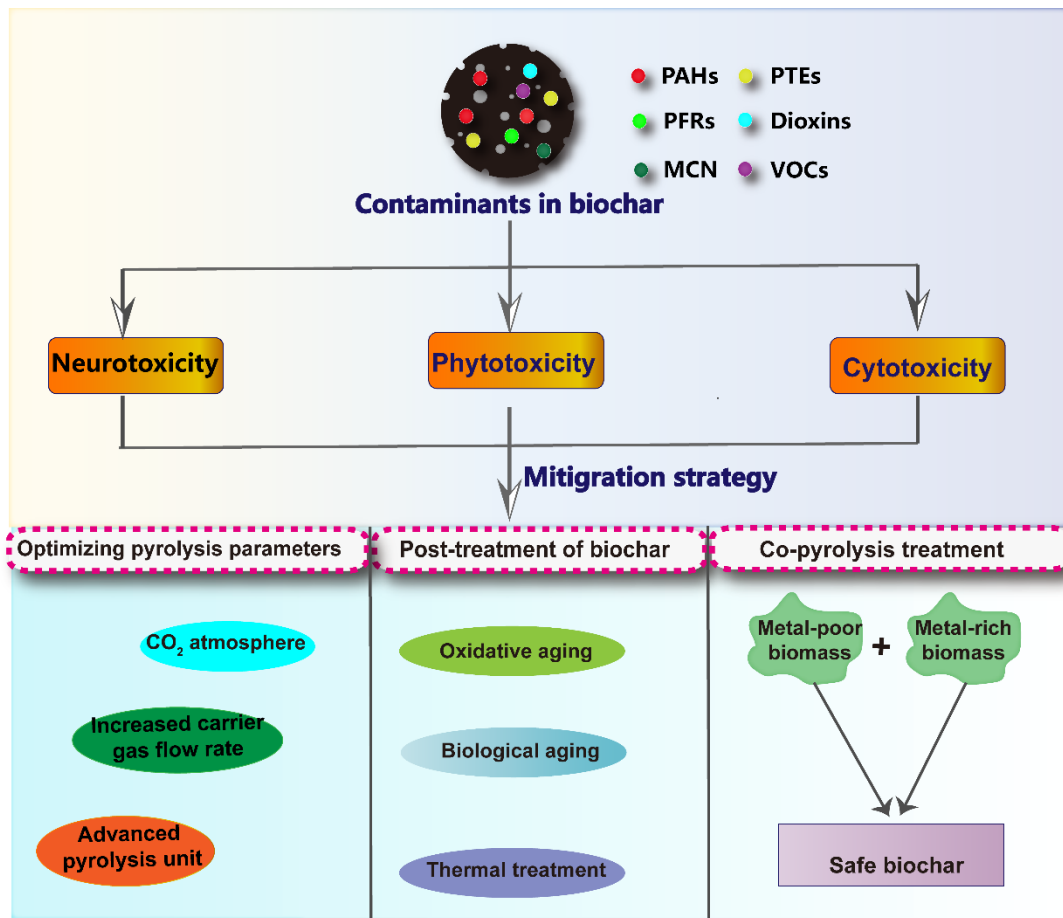
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Graphical abstract:



**Abstract:** Biochar produced by pyrolysis at elevated temperatures under oxygen limited conditions can contain both well-known contaminants (polycyclic aromatic hydrocarbons, potentially toxic elements, dioxins, and volatile organic compounds) and emerging contaminants (e.g., persistent free radicals, metal cyanide). Their potential to induce phytotoxicity, cytotoxicity, and neurotoxicity highlights the need to establish effective strategies to control and eliminate contaminants for sustainable biochar use. Although some articles have reviewed the ecotoxic potential of biochar in relation to some of these contaminants, strategies to mitigate the whole suite of contaminants potentially present in biochar have not been systematically reviewed so far. Thus, this review discusses (i) the formation mechanism of such contaminants and (ii) evaluates their potential risk to ecosystems, a prerequisite (iii) to understand and explore effective control strategies for producing biochar with minimum contamination. The pyrolysis unit design is of crucial importance to avoid biochar contamination with organic contaminants. Pyrolysis vapors need to be fully separated from biochar, which can be achieved by avoiding cold spots in the zone where vapors and biochar are separated and through optimization of pyrolysis parameters (e.g, carrier gas flow). Post-production treatments, such as thermal treatment or natural and artificial aging help organic contaminant removal and breakdown. Co-pyrolysis of metal-rich feedstock with metal-poor biomass is the main strategy to reduce total PTE levels, though levels of available PTEs are low in biochars and decrease further with pyrolysis temperature. With our proposed recommendations, biochars that pose minimum risk to the environment can be produced.

**Keywords:** Biochar; Contaminants; Toxicity; Potential risk; Control strategies; Ecosystems

## Abbreviations

PAHs: Polycyclic aromatic hydrocarbons

VOCs: Volatile organic compounds

PFRs: Persistent free radicals

MCN: Metal cyanide

PTEs: Potentially toxic elements

CNTs: Carbon nanotubes

NAP: Naphthalene

PHE: Phenanthrene

DahA: Dibenzo[a,h]anthracene

BghiP: Benzo[ghi]perylene

Ind: Indeno[1,2,3-cd]pyrene

EBC: European Biochar Certificate

IBI: International Biochar Initiative

ISO: International Organisation for Standardisation

ROS: Reactive oxygen species

SOD: Superoxide dismutase

PCBs: Polychlorinated biphenyls

DEP: Diethyl phthalate

PNP: *p*-nitrophenol

TC: Tetracycline

SMT: Sulfamethazine

SMX: Sulfamethoxazole

DCP: 2, 4-dichlorophenol

CIP: Ciprofloxacin

BPA: Bisphenol A

PNT: Phenacetin

AO7: Acid orange

*o*-NCB: Nitrochlorobenzene

PMS: Peroxymonosulfate

PS: Persulfate

RSBC-CuO: Copper oxide-modified rice straw biochar

PDS: Peroxydisulfate

PCDD: Polychlorinated dibenzo-*p*-dioxins

PCDF: Polychlorinated dibenzofurans

TEQ: Estimating 2,3,7,8-TCDD equivalents

DL-PCBs: Dioxin-like polychlorinated biphenyls

AhR: Aryl hydrocarbon receptors

MOCN: Metal oxy-cyanide

WSOCs: Water soluble organic compounds

DOM: Dissolved organic matter

# 1 Introduction

Biochar is derived from biomass, such as agricultural and industrial residues, including sewage sludge, that has been pyrolyzed in an oxygen-limited environment and per definition should be used for environmental management [1]. Due to its lower cost and simpler production process with better energy balance, biochar offers clear advantages over commercial activated carbon in many environmental management applications [2, 3], such as water treatment [4, 5]. Biochar can also play a key role for carbon sequestration [6], and soil and plant growth [7]. Further proposed applications of biochar are in catalysts for chemical synthesis, biorefinery, and biofuel production (syngas, liquid fuel and esters) [8-10]. The ability of biochar to sorb organic and inorganic compounds during wastewater treatment applications has accelerated the development of novel biochar-based materials, such as aluminum-biochar composites [6], biochar-clay composites [11], layered double hydroxides-biochar composites [12], nano-biochar composites [13], biochar-concrete composites [14], and  $\text{CuZnFe}_2\text{O}_4$ -biochar composites [15]. An essential consideration in all these applications is the potential of biochar to introduce potentially toxic contaminants to the environment following its application to soil or water.

One category of contaminants in biochar are potentially toxic elements (PTEs) that originate from the feedstock material and are enriched during pyrolysis [16]. While PTEs cannot be destroyed, organic contaminants in the feedstock material are typically decomposed during pyrolysis and subsequent combustion of pyrolysis vapors [17]. However, some organic contaminants are formed during pyrolysis and can be introduced into biochar. Pyrolysis generates polycyclic aromatic hydrocarbons (PAHs) [18, 19], dioxins (PCDD/DFs) [20], volatile organic compounds (VOCs) [21], persistent free radicals (PFRs) [22], and metal cyanide (MCN) [23]. These contaminants can pose a potential risk to human health and the environment [24, 25]. While many studies that investigated the effect of biochar on different organisms did not report negative effects, some observed phytotoxicity [25], ecotoxicity [26], cytotoxicity [27], and neurotoxicity [28] (Table 1). For instance, biochar promoted the formation of reactive oxygen species in animal and plant tissue, resulting in cytotoxicity and genotoxicity in human lung epithelial cells [29]. Therefore, it is essential to systematically evaluate the potential risk of biochar application and measures for their prevention.

Various strategies have been proposed to alleviate the formation of contaminants and eliminate potential risks to ensure the safe application of biochar [30-33], including elevated pyrolysis temperatures [34], co-pyrolysis with uncontaminated feedstocks [35, 36], thermal post-treatment, and aging [37]. Although several reviews have discussed the ecotoxicity of biochar related to PTEs [38, 39], PFRs [40, 41], VOCs [42], and PAHs [43], no reviews exist on formation and levels of MCN, and dioxins in biochar and their strategies to reduce contaminants in biochar. This review seeks to fill these gaps, and systematically summarizes the main types and formation mechanisms of contaminants in biochars and evaluates their potential risks to ecosystems. This is followed by highlighting the most effective strategies for mitigating contaminants in biochar, during production and using post-treatment measures. The overall aim is to give recommendations for production of biochar that is safe for use in a wide range of environmental applications.

## **2 Evaluating the risk of contaminants in biochars and their control strategies**

### **2.1 PAHs**

PAHs have attracted widespread attention owing to their mutagenic and carcinogenic properties. A large variety of PAHs can be generated during biomass pyrolysis, yet, typically only the PAH concentration based on a set of 16 PAHs ( $\Sigma_{16}$ PAHs) defined by the US EPA is reported for evaluating the risk to natural environments, such as rivers, sediments, and the atmosphere [44, 45]. Typical PAH concentrations in different biochars range from  $0.07 \text{ mg}\cdot\text{kg}^{-1}$  to  $100 \text{ mg}\cdot\text{kg}^{-1}$  (Table 2), and the threshold values of PAHs in ‘standard’ biochars, as suggested by the European Biochar Certificate (EBC, 2012) and International Biochar Initiative (IBI, 2015), are  $6 \text{ mg}\cdot\text{kg}^{-1}$  and  $300 \text{ mg}\cdot\text{kg}^{-1}$  [46, 47]. Therefore, it is essential to understand the formation mechanism of PAHs in biochar and its mitigating strategies.

#### ***2.1.1 Formation mechanism of PAHs***

Decomposition of biomass and subsequent recombination reactions (fusion of smaller hydrocarbons into larger) form PAHs during pyrolysis [48]. PAH formation is associated with successive ring buildup where the yields of PAHs with fewer rings is higher than the yield of higher-molecular weight PAHs and PAHs are fused to larger PAHs with increasing temperature [48]. An



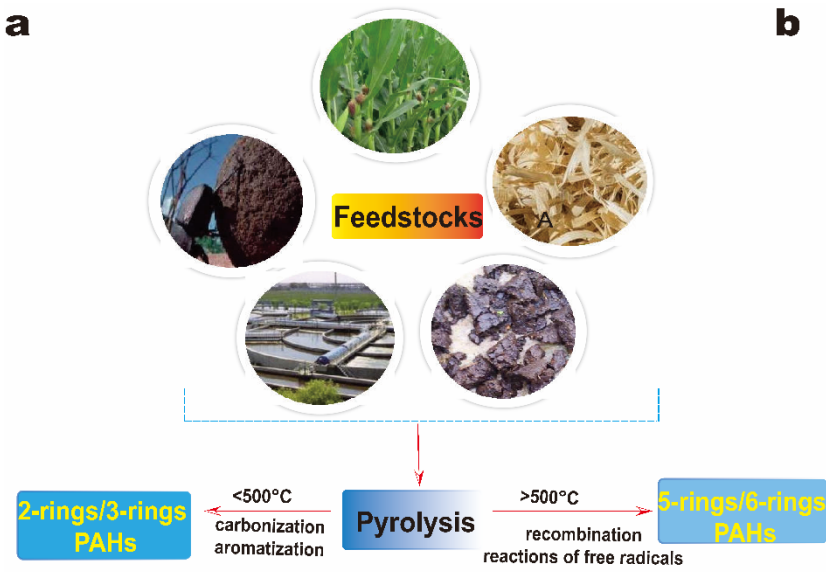
increase in the  $E_a$  (activation energy) values ranging from 50 to 110 kcal·mol<sup>-1</sup> resulted in increased ring numbers from one to five rings, along with decreased PAH yields [48]. Low-molecular-weight PAHs (2-rings or 3-rings) are formed already at temperatures < 500 °C [43], but the formation increases further until ~900 °C [48]. At temperatures of 500–950°C, higher molecular weight PAHs (4-, 5- and 6-rings) are pyro-synthesized through the recombination reaction of hydrocarbon radicals (Fig. 1a) [48, 49]. Overall, the PAH concentration accumulated over the three pyrolysis fractions (solids, liquids and gas) increases exponentially at ~700 °C [48, 49].

### **2.1.2 Factors responsible for PAHs formation**

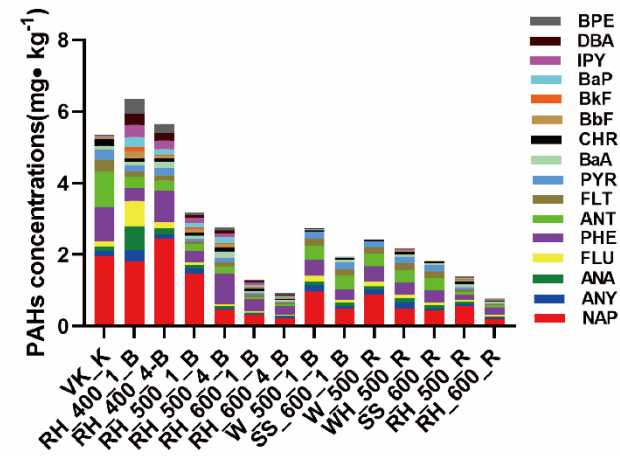
PAH formation during pyrolysis, however, must be distinguished from the PAH concentration in biochar since the distribution of PAHs within the different pyrolysis products is temperature-dependent [49]. Parameters, such as biomass type, pyrolysis temperature, and reactor type, influence the levels of PAHs in biochars [34, 50, 51]. Although the biomass type does influence the concentration in biochar, there is no clear consensus, whether lignin or cellulose preferentially form PAHs [52, 53]. The effect of temperature on the concentrations of PAHs in biochar was inconsistent in different studies [19, 54], e.g. Devi et al. found that the maximum concentration of PAHs in biochar was observed in the medium temperature range (400–500 °C) (Fig. 1c)[55]. This variable response is a result on the interaction of pyrolysis unit, feedstock type and other pyrolysis parameters [51]. PAHs are formed during pyrolysis, but feedstock-inherent PAHs can also be degraded and vaporized, e.g., the conversion of sewage sludge into biochar at 500-700 °C results in a decrease in the PAH content of sewage sludge by 8–25 times [56].

In most cases, naphthalene (NAP) and phenanthrene (PHE) account for the highest contribution of total PAHs in biochar (Fig. 1b) [25, 50, 55]. In some studies, no high molar weight PAHs with five and six rings, such as dibenz[a,h]anthracene (DahA), benzo[ghi]perylene BghiP, indeno[1,2,3-cd]pyrene (Ind), were detected due to their formation at the upper range of pyrolysis, and they need an optimized extraction technique for recovery from biochar [57, 58]. Levels of oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) and nitrogen-containing polycyclic aromatic compounds (N-PACs) in biochars were also very low, in many cases below the limit of detection [58].

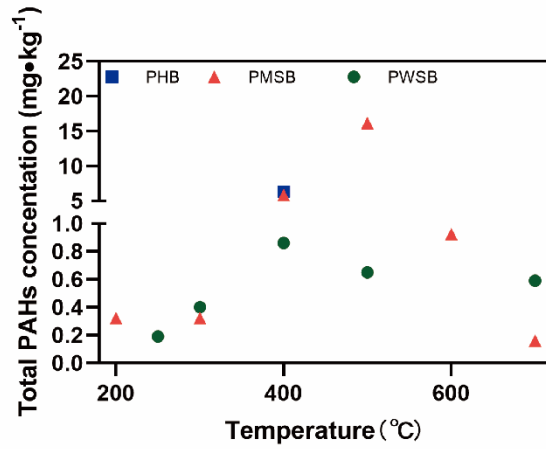
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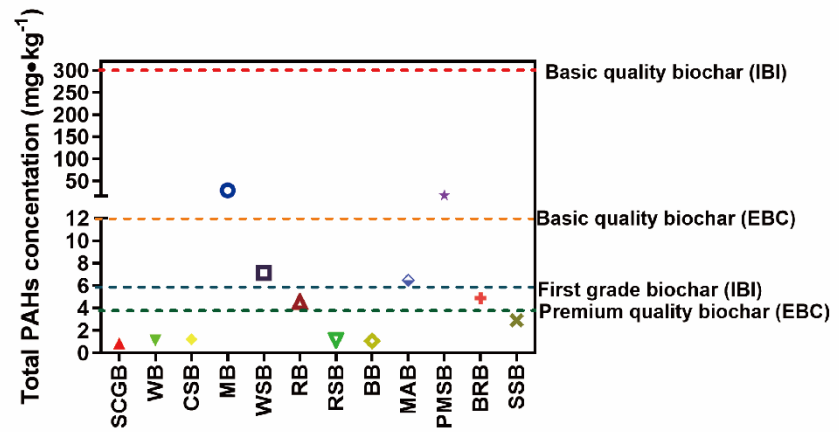
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**d**



**Fig. 1. Fate and contents of polycyclic aromatic hydrocarbons (PAHs) in biochar. a, Formation mechanism of PAHs from various feedstock-based biochars [43]; b, PAH composition in biochars produced under a variety of pyrolysis conditions [34]; c, Effect of pyrolysis temperature on the PAH content of biochars from three feedstocks [20, 34, 50, 55]; d, Concentrations of sum of 16 US EPA PAHs in biochars with threshold values for biochars according to IBI and EBC guidelines [46, 51]. WB: wicker biochar; CSB: coconut shell biochar; MB: miscanthus biochar; WSB: wheat straw biochar; RB: redwood biochar; RSB: rice straw biochar; BB: bamboo biochar; MAB: maize biochar; PMSB: paper mill sludge biochar; BRB: biogas residue biochar; SSB: sewage sludge biochar; RHB, rice husk biochar; PWSB, pine wood sawdust biochar; SCGB, spent coffee ground biochar.**

**Table 1. Examples from the literature on the effects of biochar on microbial communities, plants, soil fauna, and human health**

Toxicity	Biochar feedstock	Experiment media	Effect	Ref.
Ecotoxicity	Wheat straw	soil	No negative impact on soil microbial communities	[59]
Ecotoxicity	Pine wood	soil	Change of microbial metabolic activity but not community structure	[60]
Cytotoxicity	Wood chips	extract	Change surface morphology of <i>E.coli</i> and metabolites content associated with tricarboxylic acid cycle and glycolysis	[61]
Cytotoxicity	Maize silage, Food leftovers, Digestates, Grass cut, Sewage sludge	extract	Caused chromosomal aberrations of pollen cells in <i>Tradescantia</i> , inhibiting its germination	[62]
Phytotoxicity	Argan shell	extract	Stimulated the germination and fresh biomass of salad and barley	[63]
Cytotoxicity	Miscanthus, Wheat straw	extract	Inhibited the growth of alga <i>Selenastrum capricornutum</i>	[25]
Cytotoxicity	Pine needle	extract	Upregulated the ROS and SOD level in <i>Scenedesmus obliquus</i> and decreased chlorophyll-a concentration	[64]
Cytotoxicity	Cotton leaf and Cu(II)	extract	Inhibited the growth of <i>M. aeruginosa</i>	[24]
Cytotoxicity	Apple wood	soil	Caused weight loss of earthworms without influencing its reproduction	[65]
Neurotoxicity	Rice straw	agar	Caused neurotoxic effect on model organism <i>Caenorhabditis elegans</i> ,	[28]
Ecotoxicity	Urban pruning wood	soil	Had no effect on soil invertebrates	[66]
Cytotoxicity	Softwood pellets	extract	Inhibited the growth of NIH 3T3 mouse fibroblast cell line	[27]
Cytotoxicity	Nano-sized carbon black	extract	Increased the level of TNF- $\alpha$ , IL-6 and IL-8 of human monocytes	[67]
Cytotoxicity	Tobacco stem	extract	Caused adverse oxidative responses in normal human lung BEAS-2B cells.	[29]

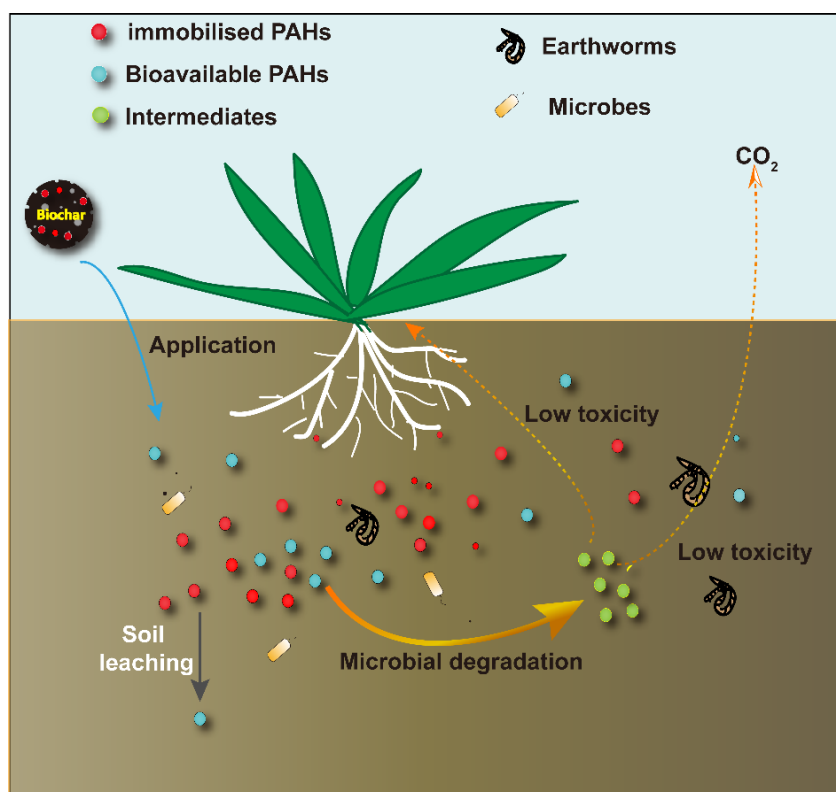
**Note:** ROS: reactive oxygen species; SOD: superoxide dismutase.

### 2.1.3 PAHs in biochars exhibit low risk to organisms

Elevated PAH uptake by the earthworm *E. fetida* has been observed when present in biochar-amended soil [68]. Yet, Oleszczuk et al. evaluated the PAH content in four commercial biochars and their eco-toxicological properties in a battery of biotests (plants, bacteria, alga, protozoa and crustaceans) [25] and a correlation between content of PAHs and toxicity was noted only in the case of crustaceans (*Daphnia magna*). Rombolà et al. proposed that water-soluble components (e.g., organic acids) are responsible for the high phytotoxicity of poultry litter biochar, rather than PAHs [69]. Biochars can also pose mutagenic effects, yet no clear relationship between biochar mutagenicity in plants and PAH levels could be established [62]. The cancer risk of biochar is

assumed to be low due to human exposure [70]. Due to coexistence of other organic contaminants with PAHs in biochars, it is difficult to establish a direct relationship between PAHs levels and biochar toxicity, but the evidence indicates that PAHs toxicity is a minor concern [21].

Application of wood- and wheat straw-derived biochar to soil resulted in PAH contents in soil ranging from  $0.1 \text{ mg}\cdot\text{kg}^{-1}$  to  $1.5 \text{ mg}\cdot\text{kg}^{-1}$ , which are below the agricultural soil limit [44, 71]. The concentration of bioavailable PAHs in biochar are very low, levels of water-extractable PAHs were  $\leq 162 \text{ ng}\cdot\text{L}^{-1}$  in biochars produced under various conditions [72]. Long-term (851 days) field experiments on soil amended with commercial biochar further confirmed that the available content of PAHs ( $\Sigma_{13}\text{C}_{\text{free}} \text{ PAHs } 5 \text{ ng}\cdot\text{L}^{-1}$ ) was 42% lower than in the control soil [73]. Moreover, PAHs in biochar-amended soil can be degraded and removed from soil to background soil levels in a few months (105 days in this particular experiment) due to microbial degradation and leaching (Fig. 2) [71]. Although the formation of PAHs is inevitable as a result of biochar production, levels of bioavailable PAHs are low, resulting in a low risk to soil.



**Fig. 2. Fate of PAHs in biochar after soil application. Low risk of PAHs soil due to low bioavailability and microbial degradation of the accessible PAHs. PAHs: Polycyclic aromatic hydrocarbons**

**Table 2. Examples from the literature on concentrations of contaminants in biochar**

Biochar feedstock	HTT (°C)	RT (min)	Pyrolysis reactor	Extraction method	Contaminant concentration (mg·kg <sup>-1</sup> )	Ref.
Spent coffee ground	300-900	120	Tubular	acetone/n-hexane mixture	0.56-0.85 PAHs	[50]
Wood chips, Paper sludge, Sewage sludge	200-620	20	Rotary	toluene	0.9-15.4 PAHs	[44]
Straw pellets, Soft pellets, Miscanthus chips, Demolition wood, Arundo donax, Willow chips, Sewage sludge	350-750	10-40	Tube furnace, Rotary kiln	toluene	1.2-100 PAHs	[51]
Rice husk, Wheat, Wood Sewage sludge	400-600	20-240	Rotary kiln	toluene	0.80-6.36 PAHs	[34]
Miscanthus, Wheat straw, Coconut shell Wicker,	350-650	-	Rotary kiln	toluene	1.12-28.3 PAHs; 0.04-0.87 Cd; 0.00-3.81 Cu; 0-9.95 Ni; 0-18 Cr; 30.2-102.2 Zn	[25]
Redwood, Rice straw, Maize, Bamboo	300-600	150-720	Muffle furnace	hexane, toluene, dichloromethane	0.08-8.7 PAHs; 0.02-0.94 Cd; 0.12-6.48 Cr; 0.04-13.2 Cu; 0.1-1.37 Ni; 0.06-3.87 Pb; 0.94-207 Zn; 0.03-0.27 As	[74]
Softwood pellets	550	20	Rotary kiln	toluene	6-53 PAHs; 37.1-771.9 LMW aliphatic acids;	[21]
Paper mill sludge	200-700	-	-	toluene	0.32-16.92 PAHs	[55]
50 different feedstocks	250-900	30	-	toluene	0.07-45 PAHs; 0-92 pg g <sup>-1</sup> doxins	[75]
Solid residue from biogas production	400-800	300	Rotary kiln	toluene	1.47-4.87 PAHs; 1.9-8.7 Cd; 20.4-77.7 Cu; 6.6-33.6 Ni; 4.2-38.9 Cr; 22-301 Zn; 128-484 Mn; 3.3-25.9 Pb	[76]
Sewage sludge	400-900	-	Microwave	toluene	2.946 PAHs; 0.02-0.25 TEQ	[77]
Miscanthus, Willow, Wheat straw	350-650	-	Rotary kiln	hexane, toluene, dichloromethane	3.8-40 PAHs	[37]
Softwood pellets	550	20	Rotary kiln	-	1.79-2.79 PAHs	[78]
Dried raw sludge	400-600	60	Muffle furnace	-	1551-1697 Cu; 147.4-218.6 Ni; 665-1374.4 Cr; 2572-3368 Zn; 731.2-1382.7 Mn; 84.7-110.7 Pb	[79]
Ten marginal biomass-derived feedstocks	350-750	21.5	Rotary kiln	-	0.72-1.96 As; 0.04-44.86 Cd; 0.08-9.81 Co; 0.49-176.4 Cr; 2.17-118.6 Cu; 0.23 Hg; 0.21-9.48 Mo; 0.48-110.6 Ni; 0.74-149.5 Pb; 2.65-1404.3 Zn	[80]
Sawdust	250-700	180	Muffle furnace	toluene	0.59-0.86 PAHs; 50-270 pg g <sup>-1</sup> doxins	[20]
Softwood, Wheat straw	550-700	5-10	Auger, Rotary kiln	toluene	0.82-19.6 PAHs; 0.6-0.9 pg g <sup>-1</sup> doxins	[58]
Pine needles, Wheat straw, Maize straw	300-500	360	Muffle furnace	-	(1.25-22.3)×10 <sup>18</sup> spins g <sup>-1</sup> PFRs	[81]
Pine needles	200-600	120-1440	Muffle furnace	-	(0.06-37.1)×10 <sup>18</sup> spins g <sup>-1</sup> PFRs	[64]
Phytoremediation	350-	35-75	Muffle	-	36.2 Zn, 41.0 Pb, 33.8 Cd	[82]

residue	750		furnace			
Phyllostachys pubescens	400-700	120	Tube furnace	toluene	8.59-14.67 PAHs, 1.82-3.26 Cu, 1.17-3.53 Pb, 8.76-16.47 Zn	[83]
Pig manure	300-700	60	Tube furnace	-	513-819 Cr, 1390-1920 Mn, 673-1080 Cu, 4310-7720 Zn	[84]
Cow manure	300-700	60	Tube furnace	-	0.02-0.42 Cd; 20.37-40.62 Cr; 71.13-415.92 Cu; 3.62-12.07 Ni; 1.52-6.56 Pb; 15.37-559.21 Zn	[85]
18 different feedstocks	800	60	Tube furnace	-	23,251-85,870 MCN	[23]

**Note: HTT, highest treatment temperature; RT, residence time**

#### 2.1.4 Strategies to minimize and mitigate PAHs in biochar

PAHs in biochar pose little risk for the environment mainly due to low bioavailability (section 2.1.2 and Fig. 2). However, some biochars still exceed threshold values for total levels of PAHs (Fig. 1d). Total PAHs are the traditional way of assessing contaminants in environmental samples and although not always appropriate, biochars still require to meet these threshold values. Therefore, there is a need to evaluate measures to reduce the total PAH concentrations in biochar, which is done in the following section.

The PAH content in biochar is primarily affected by feedstock type and pyrolysis conditions [43]. In a systematic study using over 50 biochars, fast pyrolysis and gasification biochar exhibited higher total PAHs levels ( $23 \text{ mg}\cdot\text{kg}^{-1}$  and  $45 \text{ mg}\cdot\text{kg}^{-1}$ , respectively) compared to slow pyrolysis biochar ( $0.07\text{-}3.27 \text{ mg}\cdot\text{kg}^{-1}$ ) [72]. Further, wood-derived biochar produced in a traditional kiln showed 6-fold higher PAHs than that produced by fast pyrolysis [44]. Pyrolysis in a Kon Tiki kiln, a simple, open flame-curtain pyrolysis kiln, demonstrated low levels of PAHs in the resulting biochar [86]. It highlights that modern high-tech pyrolysis units, but also simple kilns can produce biochars with low PAH levels. With respect to the operating parameters of batch pyrolysis reactors, increasing the carrier gas flow ( $0.67 \text{ L}\cdot\text{min}^{-1}$  in this particular study) resulted in a 92% reduction in PAH concentrations in straw-based biochar compared to the absence of a carrier gas [51, 87], whereas the change in residence time (10–40 min) had no impact on PAH concentrations in wood- and straw-based biochar [88]. The use of carbon dioxide as gas carrier further reduced PAH concentrations in biochar compared to nitrogen (Fig. 3a) [89].

Increasing the pyrolysis temperature accelerates the formation of PAHs, including the concentrations in PAHs across pyrolysis solids (biochar), liquids and gases [49]. However, PAHs

are also increasingly evaporated from the pyrolysis solids (biochar) with higher pyrolysis temperatures and therefore, the concentration of PAHs in biochar is not directly linked to its production temperature [51]. Even at medium pyrolysis temperatures (e.g., 450 °C), > 99% of PAHs are evaporated and ended up in pyrolysis liquids and gases, resulting in clean and low-PAH biochar after the separation of the liquids from biochar. In contrast, cold spots in pyrolysis reactors can result in high PAH concentrations in biochar because of PAH condensation and deposition on the biochar. Under normal production conditions in a well-designed unit, the availability of PAHs in resulting biochar is very low [75], but this condensation effect increases the availability of PAHs substantially, which subsequently could pose a risk for the environment [21, 90]. Therefore, a suitable pyrolysis unit is vital for controlling PAH concentrations in biochar. The design of the part of the pyrolysis unit where vapors and biochar are separated seems to have the largest influence on PAH concentration in biochar. This area needs to be kept at the same temperatures as the pyrolysis area through insulation and/or active heating. This prevents vapor condensation and subsequent contamination of the biochar [91].

In addition to controlling the pyrolysis process itself, thermal post-treatment of biochar can reduce total ( $C_{\text{tot}}$ ) and available ( $C_{\text{free}}$ ) PAHs in biochar [37]. Post-treatment of biochar at 100-300 °C caused a 33.8%-100% reduction in PAHs content within 24 h (Fig. 3b) [78, 92]. Thermal treatment below the actual biochar production temperature can be effective when the biochar was contaminated by condensation of pyrolysis vapors and PAHs within the cooler areas outside the main pyrolysis zone. Subsequent heating of biochar even to temperatures lower than the pyrolysis temperatures results in weight loss in biochars that were contaminated by pyrolysis vapors, though not in “uncontaminated biochar” as shown previously via thermogravimetric analysis [90].

Microbial degradation and abiotic oxidation are natural processes that reduce PAH concentrations in the environment and hence also reduce the concentrations in biochar [93]. Aging process increases organic functional groups in biochar along with decreasing surface area owing to the dissolution and re-precipitation of minerals [94]. Oleszczuk et al. found that aging for 420 days in airtight stainless steel at different temperatures (-20 to 70 °C) effectively decreased the  $C_{\text{tot}}$  and  $C_{\text{free}}$  PAH content of wheat straw- and elephant grass-derived biochars by 25–50.2% [95]. Aging in the presence of microorganisms and nutrients caused a 12–100% reduction in  $C_{\text{free}}$  PAH content and



a 30–100% reduction in the  $C_{\text{tot}}$  PAH content (Fig. 3b). These observations correspond to the results of previous studies, in which aging of biochar using biological and chemical methods clearly decreased the content of pyrene [96] and phenanthrene [97]. Additionally, after artificial aging via  $\text{H}_2\text{O}_2$  oxidation and horseradish peroxidase enzymatic oxidation, total and bio-accessible levels of PAHs in biochar were reduced, indicating that the highest risk is at initial biochar application [31]. Natural aging of biochar occurs because of microbial degradation and oxidation. This is confirmed by a field study where the application of biochar at  $16 \text{ t ha}^{-1}$  resulted in soil PAH levels below the limits established by Brazilian regulations and the concentrations after 6 years were comparable to the control [98].

Overall, around 99% of the produced PAHs are separated and vaporized from the biochar during production, and subsequently are transferred into the pyrolysis liquid fraction. Optimized pyrolysis unit design and increased carrier gas flow rate can decrease PAH concentrations in biochar for safe environmental applications, as well as aging and thermal treatment. Of the 16 PAHs, naphthalene (NAP) is the least toxic with the lowest boiling point[99], but also is the most abundant PAH in biochar; As for rotary kiln biochars, NAP constituted 30-80% of total PAHs content [100]. It seems advisable to separate NAP from the other PAHs due to its very low toxicity to plants and animals [101]. Yet, this separation and independent evaluation of different groups of PAHs is rarely done. More importantly, it is essential for designing specific experiment to elucidate the direct relationship between PAHs in biochar and its toxicity.

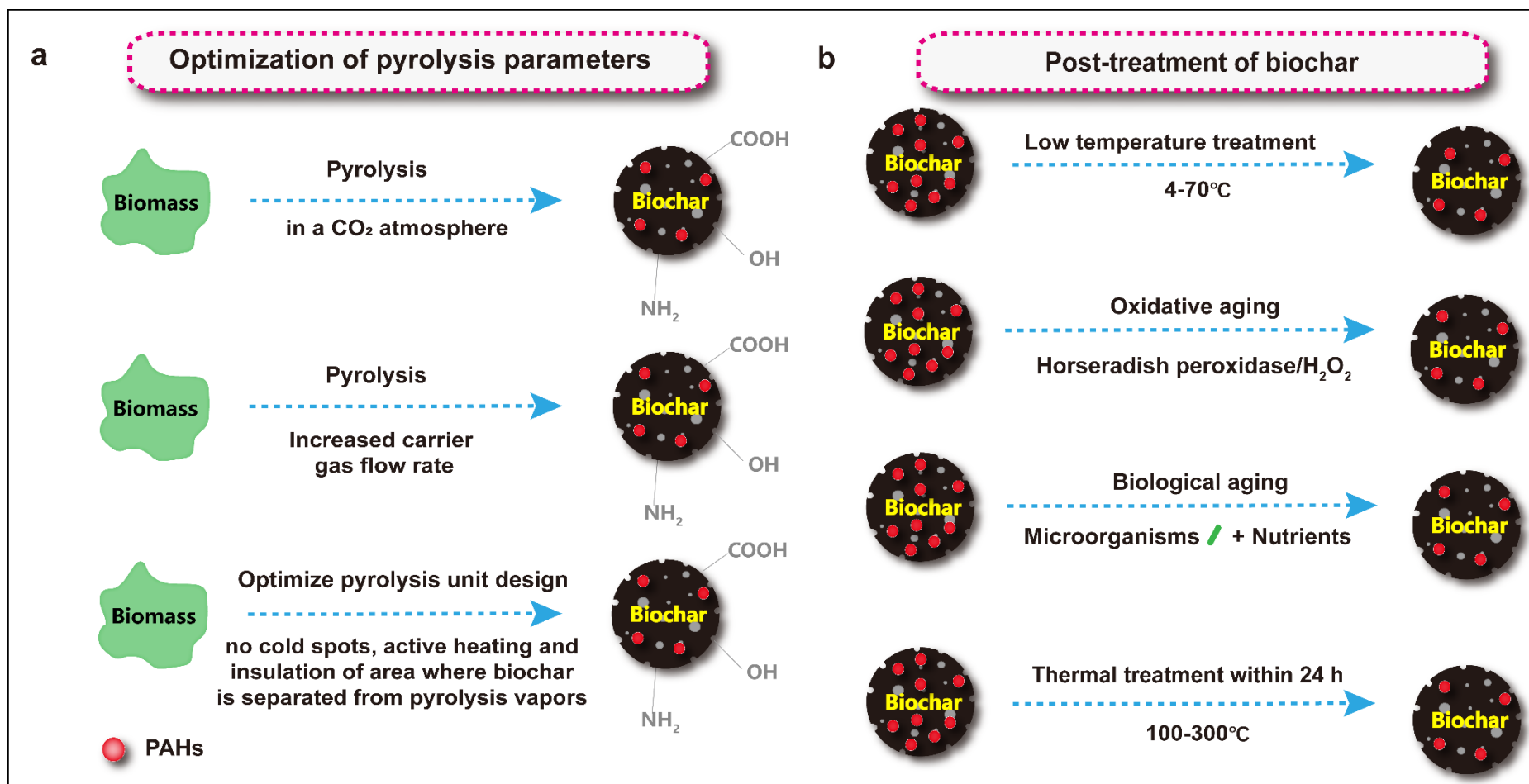


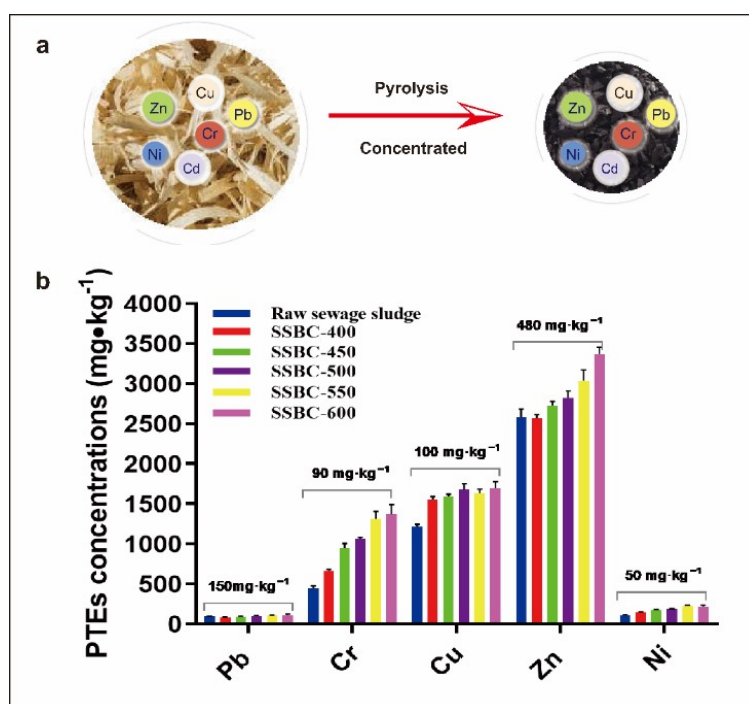
Fig. 3. Strategies for the production of biochar with low-PAH levels through (a) optimization of pyrolysis parameters and (b) post-treatment of biochar [37, 51, 95, 102]. PAHs: Polycyclic aromatic hydrocarbons.

## 2.2 PTEs: Metals and metalloids

PTEs, such as As, Cd, Cr, Co, Cu, Pb, Hg, Ni, Zn, and Mo, are another class of contaminants in biochar that raises concerns [103]. The enrichment of PTEs within biochars could pose a threat to soil microorganisms and plants [82]. The International Biochar Initiative (IBI, 2015) proposed guideline values for Cd, Zn, Ni, Pb, Cr, and Cu at  $1.5 \text{ mg}\cdot\text{kg}^{-1}$ ,  $480 \text{ mg}\cdot\text{kg}^{-1}$ ,  $50 \text{ mg}\cdot\text{kg}^{-1}$ ,  $150 \text{ mg}\cdot\text{kg}^{-1}$ ,  $90 \text{ mg}\cdot\text{kg}^{-1}$ , and  $100 \text{ mg}\cdot\text{kg}^{-1}$ , respectively [46], based on data on acceptable limits for other soil amendments, such as compost [103].

### 2.2.1 PTE levels in biochar

During pyrolysis, the majority of PTEs present in biomass are concentrated in biochars due to the loss of organic matter (Fig. 4a), resulting in elevated PTE levels compared to the feedstock material [24, 84]. Initial PTE concentrations in the feedstock primarily determine the PTE contents in the resulting biochar: PTE levels (e.g., Cd, Cu, Ni, Cr, Zn, Pb, As) in biochar derived from biomass containing low PTE levels, such as redwood, rice straw, maize, and bamboo, were lower than ambient background soil concentrations ( $89 \text{ mg}\cdot\text{kg}^{-1}$ ) [74], as published by the International Organisation for Standardisation (ISO, 2005). However, some marginal biomass-derived biochars, such as sewage sludge, biomass grown on contaminated soil or demolition waste, contained PTE concentrations above the recommended threshold values for soils and biochars (Fig. 4b) [79, 80].



**Fig. 4. Fate and contents of potentially toxic elements (PTEs) in biochar. a, Pyrolysis enriches the PTEs present in the feedstock material; b, PTEs concentrations of sewage sludge (SS) and sewage sludge biochar (SSBC) under different pyrolysis temperature conditions. The value represents the guideline values of PTEs within biochars from IBI [79].**

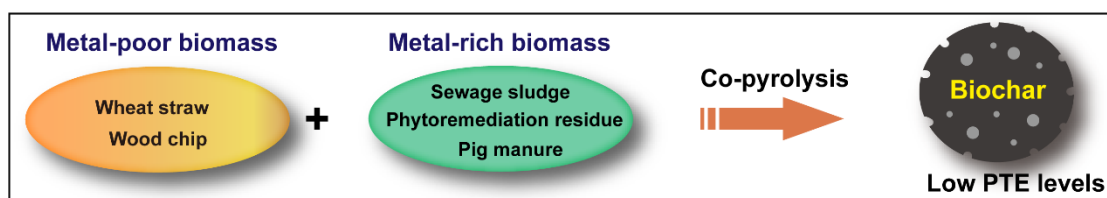
### ***2.2.2 Potentially toxic effects of PTEs in biochar***

Buss et al. did not find a relationship between phytotoxicity of biochar with total or available PTEs levels in biochar after investigating a set of 19 biochars that originated from PTE-contaminated feedstocks [16]. Some of the biochars significantly exceeded threshold values of total and available PTE levels, yet the toxic effects that were observed could instead be attributed to high pH and salinity of biochars [83]. Available fractions of heavy metals are converted into stable fractions with low risk of leaching or plant uptake following pyrolysis [16, 85, 104]. Although PTEs are non-destructible and will accumulate in soil after repeated soil application, the release of heavy metals during aging in soil was low, in particular when high temperature biochar was applied to soil of  $\text{pH} < 7$ , the typical pH of agricultural soils [105]. Therefore, PTEs in biochar will also unlikely pose risk for leaching or plant uptake in the future. The low bioavailability of PTEs means that biochar use is safer than the application of un-pyrolysed biomass and there is little environment risk at typical application rates even if threshold values are exceeded [16, 106, 107].

### ***2.2.3 Strategies to reduce total and available PTE levels in biochar***

Pyrolysis does evaporate some feedstock-inherent PTEs with low boiling point, such as As and hence, can reduce total levels of some PTEs [80]. Still, the type of feedstock is the key factor that determines PTE concentrations in biochars. Among these feedstocks, phytoremediation residue [82], sewage sludge [108], and pig manure [35] contain high levels PTEs, resulting in high PTE concentrations in their corresponding biochars. Co-pyrolysis of high-PTE with low-PTE biomass is an option to reduce the PTE burden in biochar (Fig. 5) [109]. For instance, the co-pyrolysis of pig manure with rice straw resulted in lower levels of Cu and Zn when compared to biochar produced from only pig manure [35]. A similar finding was also observed following the co-pyrolysis of sewage sludge with various biomass feedstocks low in PTEs (e.g., bamboo sawdust, rice straw) [36]. Furthermore, the blending ratio of metal-poor biomass and metal-rich biomass has significant

impact on the PTE level in biochar, e.g. co-pyrolysis of straw and manure at a ratio of 3:1 was optimal to reduce environmental risks of PTE [35, 109]. Another way of reducing total PTE levels in biochar is pretreatment of biomass through acid washing, which removes some of the PTEs prior to pyrolysis [110]. This can be achieved using acids produced by the pyrolysis process itself, increasing circularity of the system. To some extent, operational parameters such as retention time, heating rate, gas flow rate, and particle size also control the availability/mobility of PTEs in biochars. Using a metal-accumulator invasive plant species, increasing pyrolysis temperature and heating rate decreased the ecological risk of biochar [111]. Mineral addition, such as phosphate or calcium minerals, can also decrease the availability of PTEs [112, 113].



**Fig. 5. Illustration highlighting the possibility of co-pyrolysis of metal-rich biomass and metal-poor biomass for mitigating PTE levels in biochars [76, 109]**

Overall, PTEs in biochars are enriched during pyrolysis, but the availability is reduced compared to the feedstock material, making soil application generally safe. To comply with legislation threshold values, which are typically based on concentrations of total PTEs, feedstock material with low PTE levels needs to be selected for biochar production. As for PTE-rich biomass, co-pyrolysis or pretreatment of biomass is feasible for the producing biochars with PTE levels below threshold values. Pyrolysis temperature has a profound impact on plant availability and leachability of PTEs, higher temperatures reduce the ecological risk of biochars [16, 82, 111]. Yet, there is not always a clear relationship between pyrolysis temperature and available of total PTE content [16]. This is likely related to two effects that occur simultaneously with increasing pyrolysis temperature and that have opposite influences on PTE mobility: (i) the increase in biochar pH decreases mobility of most PTEs, while (ii) the loss of surface functionality reduces sorption of PTEs and hence increases PTE availability.

## 2.3 PFRs

PFRs are emerging contaminants in biochar with the potential to cause toxicity [114, 115].

PFRs induce the formation of reactive oxygen species (ROS) in water, which can cause cardiovascular and respiratory diseases by attacking DNA [116]. In contrast to traditional toxins (e.g., metals and PAHs), low doses of PFRs in biochar (corn stalks, rice, and wheat straw biochar tested) showed considerable cytotoxicity and phytotoxicity [117].

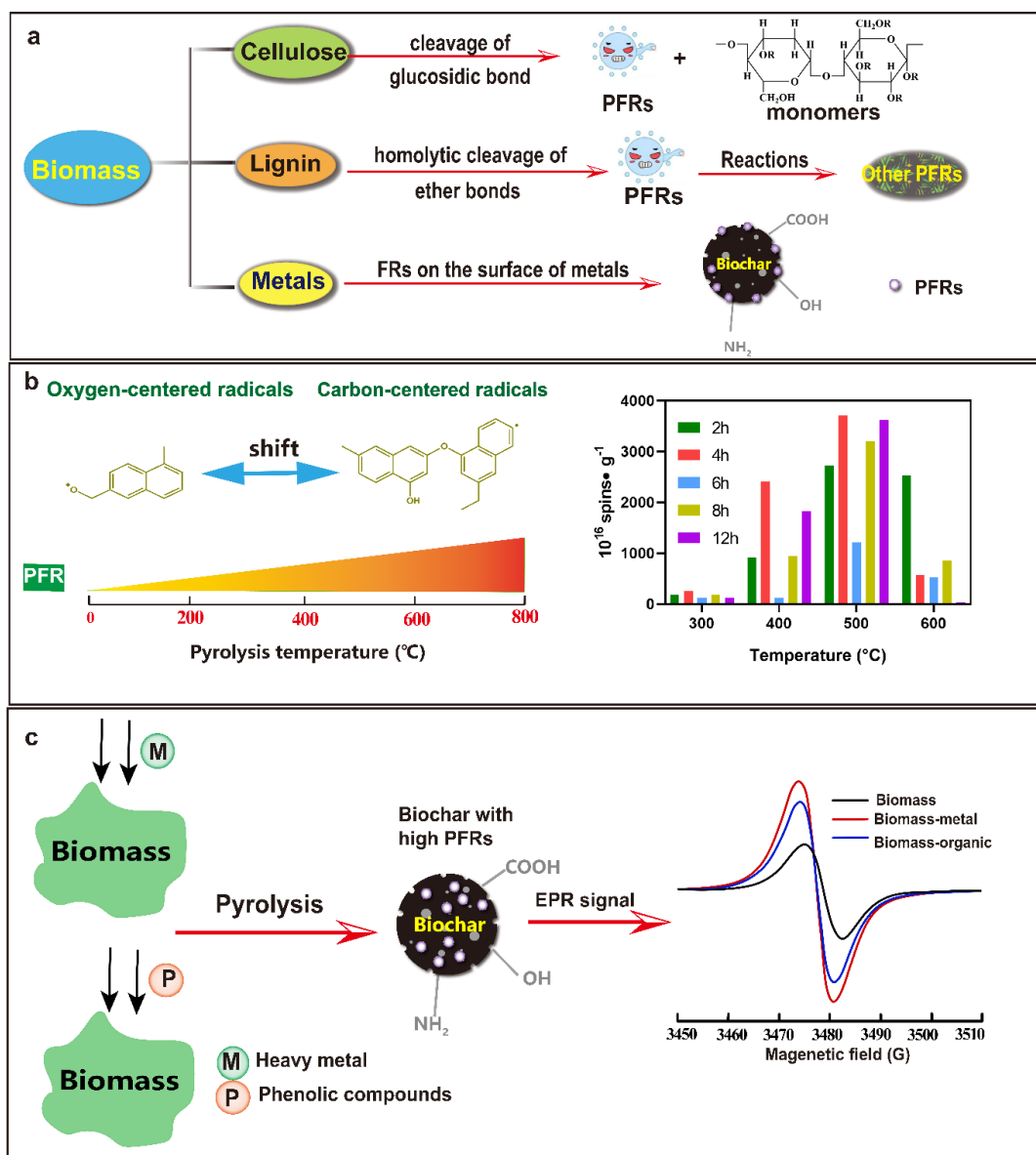
### **2.3.1 Formation mechanism of PFRs**

Regardless of type of feedstock and their major components (cellulose and lignin), PFRs are ubiquitous in biochar [117]. Pyrolysis of cellulose and hemicellulose is accompanied by the formation of their own monomers and monomeric radicals for the cleavage of glucosidic bonds [118]. During lignin pyrolysis, the homolytic cleavage of the  $\alpha$ - and  $\beta$ -alkyl-aryl ether bonds, C-C and C-O linkages firstly generates radicals, and further forms radical coupling products (Fig. 6a) [119]. Steric hindrance caused by the strong interaction between PFRs in biochar surface and adjacent solid particles reduce diffusion and hence interaction with compounds present in solution surrounding the biochar particle as the pore diameter drops below the minimum critical molecular diameter [120]. Such steric effect not only led to low adsorption affinity towards solutes, but also made PFRs more stable because PFRs cannot react with other molecules [41]. The half-lives of PFRs in biochars are on the order of hours to months [41], which is distinct from atmospheric gas-phase free radicals that exist for mere seconds. PFRs can be detected by electron paramagnetic resonance (EPR), for which the  $g$ -factor values are used for distinguishing carbon-centered radicals ( $g < 2.003$ ), carbon-centered radicals with an adjacent oxygen atom ( $g = 2.003 - 2.004$ ), and oxygen-centered radicals ( $g > 2.004$ ) [41]. At elevated temperatures, the PFR types shifted from oxygen-centered radicals to carbon-centered ones (Fig. 6b) [64].

### **2.3.2 Factors responsible for the formation of PFRs**

Lignin in biomass is the main contributor of PFRs in biochars [121]. Abundant phenol or quinone moieties in biomass can induce the formation of surface-bound PFRs in biochar via transferring the electron to transition metals (Fig. 6a) [122]. In general, the contents of PFRs in biochar increased with elevated pyrolysis temperatures (300-600 °C) and then decreased sharply at 700 °C [121]. In contrast, biochar derived from rice straw and pine wood produced below 300°C showed weak EPR signal [117, 121, 123], suggesting biochars produced at temperatures below the typical pyrolysis range (torrefaction range) contain rather low levels of PFRs. High production

temperatures (e.g., 700 °C) destroyed the radical structures and resulted in the disappearance of PFRs [124]. Low concentrations of transition metals ( $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$   $< 0.1 \text{ mM}\cdot\text{L}^{-1}$ ) or phenolic compounds (PCs,  $< 5 \text{ mM}\cdot\text{L}^{-1}$ ) loaded in biomass increased the concentration of PFRs (Fig. 6c) [22]. In this respect, transition metals and substituted aromatics are key factors in PFR formation of biochar.



**Fig. 6.** Fate and contents of persistent free radicals (PFRs) in biochar. **a**, Formation mechanism of PFR in biochars; **b**, the PFRs concentrations of pine needles biochar increased with pyrolysis temperature, along with a change of PFR types from oxygen-centered radicals to carbon-centered ones [64]; **c**, effect of metal and organic loading on the concentration of PFRs in biochar and their EPR spectra [22].

### 2.3.3 The risk of PFRs in biochar-a double-edged sword

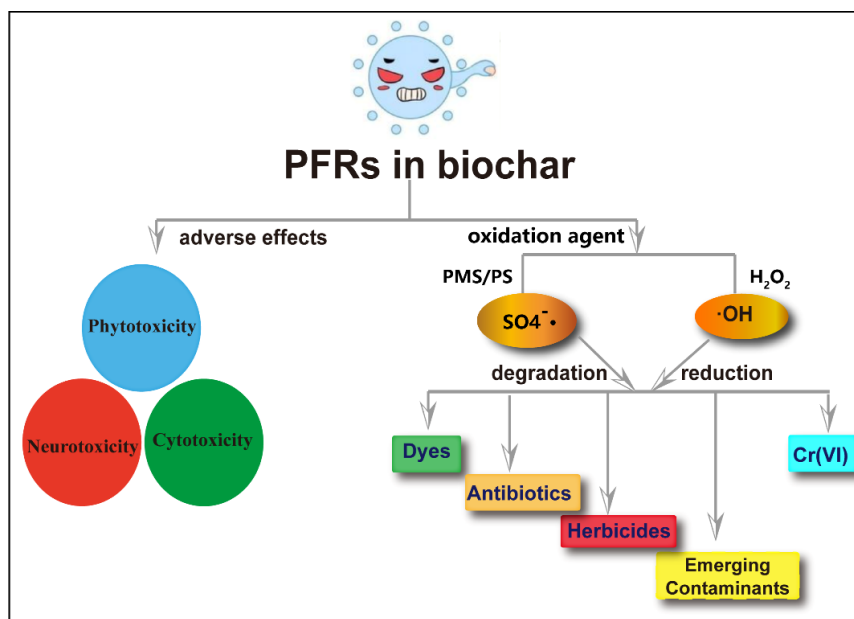
PFR-containing biochars induced the upregulation of ROS and superoxide dismutase in the aquatic organism *Scenedesmus obliquus* [64]. In addition, the toxicity of *S. obliquus* showed a positive correlation ( $R^2$ , 0.807) with PFR concentration in pine needle biochar [64]. Recent studies have revealed the neurotoxic effects of straw biochar on model organism *Caenorhabditis elegans*, e.g., impairing defecation and recognition obstacles to chemical attractants (Fig. 7) [28]. Moreover, the application of corn cob biochars also inhibited urease activity of soil because of oxidative reactions with free radicals on the biochar surface or oxidative reactions with reactive oxygen species promoted by free radicals [125]. This suggests that some risks of specific types of biochars may have been overlooked.

Extensive studies indicated that PFRs in biochar can also be beneficial by activating persulfate (PS) or  $H_2O_2$  to produce  $SO_4^{\cdot-}$  and  $\cdot OH$ , respectively [22, 41]. These radicals can degrade refractory organic pollutants, such as polychlorinated biphenyls (PCBs) [22], diethyl phthalate (DEP) [81], *p*-nitrophenol (PNP) [123], tetracycline (TC) [126], sulfamethazine (SMT) [127], sulfamethoxazole (SMX) [128], acetaminophen (ACT) [129], 2, 4-dichlorophenol (DCP), ciprofloxacin (CIP) [130], bisphenol A (BPA) [131], phenacetin (PNT) [132], acid orange (AO7) [133], phenol [134], atrazine [135], nitrochlorobenzene (*o*-NCB) [136], from water environments (Fig. 7). For instance, PFRs catalyzed the removal of  $30\text{ mg}\cdot\text{L}^{-1}$  TC with 87–100% efficacy in a biochar/ $H_2O_2$  systems [126], and exhibited excellent TC removal efficiency in river water (95.4%) and municipal wastewater (83.7%). A similar SMT degradation rate in swine manure biochar/ $H_2O_2$  systems was over 85% in 30 min [127].

PMS (peroxymonosulfate)- or PS-activated  $SO_4^{\cdot-}$  was found to possess higher oxidation reduction potential (2.5–3.1 V) than that observed in  $\cdot OH$  (1.8–2.7 V) and sustained a longer half-time of 30–40  $\mu\text{s}$  than the 20 ns of  $\cdot OH$  in solution [131]. These features offer an unprecedented advantage in the degradation of organic pollutants (e.g., BPAs). Li et al. confirmed that copper oxide-modified rice straw biochar (RSBC-CuO) contains four reaction oxygen species, namely  $SO_4^{\cdot-}$ ,  $\cdot OH$ ,  $O_2^{\cdot-}$ , and  $^1O_2$  in a PDS (peroxydisulfate)/RSBC-CuO system [132], thus possessing a range of 86–100% degradation potential toward PNT, SMT, paracetamol, aniline, *p*-chlorobenzoic acid, and 2,4,6-Trichlorophenol. Metal-modified biochar/PS systems, including Fe, N co-doped



biochar, and  $\text{CuFe}_2\text{O}_4@\text{BC}$  showed a significant advantage in the removal of AO7 and *o*-NCB degradation compared to that of a raw biochar/PS system [133, 136]. Chemically-modified (e.g., HCl,  $\text{NH}_4\text{OH}$ , and KOH) sludge biochars were also efficient in dye degradation by means of PMS activation, including AO7, methylene blue, and methyl orange [137]. In this respect, metal-modified biochars, such as Fe-Mg oxide/biochar displayed negligible inhibition on the growth of gram-negative strain *E. coli* due to SMT degradation by biochar-supported bimetallic oxide/PS systems [138]. Apart from the degradation of organic pollutants, PFRs in corn straw biochar can also serve as an electron shuttle to mediate Cr(VI) reduction [139], and approximately 90% of Cr(VI) adsorbed in biochars can be reduced to Cr(III) by the consumption of PFRs on the surface of biochar. More importantly, PFR possesses excellent potential for degradation of organic compounds, such as atrazine (herbicide), including its intermediate products, reducing environmental toxicity [135, 140]. Nonetheless, the weak neurotoxicity of soil organisms caused by PFRs in biochars should be addressed for safe environmental applications [141].

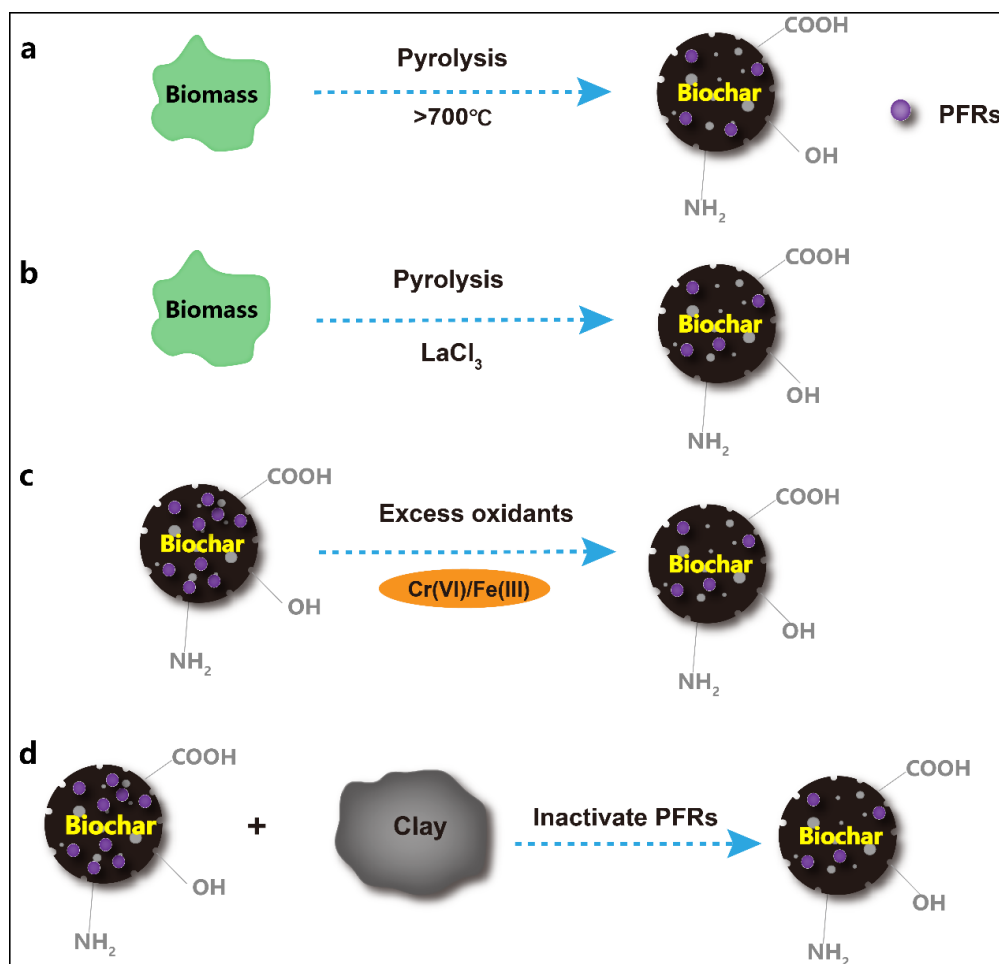


**Fig. 7. The risks and benefits of PFRs in biochar. PFRs: persistent free radicals; PMS: Peroxymonosulfate; PS: Persulfate**

#### 2.3.4 Strategies to reduce PFRs levels in biochar

As shown by existing studies [121, 123], high pyrolysis temperatures ( $>700\text{ }^\circ\text{C}$ ) yielded biochar with low content of PFRs, as many PFRs and their precursors were destroyed under such

conditions (Fig. 8a). High levels of oxidants [e.g., Cr(VI), Fe(III)] decreased PFRs in rice husk-derived biochar (Fig. 8b), because the resultant PFRs can be consumed for Cr(VI) [142] or Fe(III) reduction [139]. In addition, the involvement of lanthanum in pyrolysis significantly mitigated the phytotoxicity of oak sawdust biochar by reducing organic compounds and PFRs (Fig. 8c) [143].



**Fig. 8 Strategies for mitigating PFRs in biochar. Avoiding PFR in biochar through (a) pyrolysis temperatures of >700°C or (b) LaCl<sub>3</sub> addition prior to pyrolysis. Removing PFR from biochar through (c) mixing biochar with excess oxidants or (d) clay. PFRs: persistent free radicals**

PFR stability and persistence in biochars depends on the metals they are bound to. Among transition metals, the PFRs in ZnO nanoparticles can be persistent over years [115]. Even after natural aging in a glass desiccator for one month, PFR concentrations in pine needle biochar decreased by less than 10% [64]. In addition to suppression of PFRs during production, natural process in soil, such as interactions with organic matter and/or clay particles can inactivate the PFRs in biochars (Fig. 8d) [144], indicating clay-biochar composites could be good candidates for

soil amendments owing to synergies between the constituents [145].

Overall, PFRs from biochar production are stabilized on the surfaces of transition metals and can also persist in the atmospheric environment [30]. Although metals can significantly increase the PFRs concentration, the underlying mechanism remains unclear. Up until now, no research studies reported the impact of biochar-related PFRs on higher-level organisms such as animals and humans. Moreover, the roles of PAHs, clay surface properties, soil organic carbon and ultraviolet radiation should not be underestimated in the formation of PFRs in the environment.

## 2.4 Dioxins

Dioxins, a class of structurally and chemically related polyhalogenated aromatic hydrocarbons, have been classified as a “probable” carcinogen in human and other vertebrates [146]. Its high affinity towards cellular aryl hydrocarbon receptors protein (AhR) disrupts normal hormone signaling pathways, as well as reproductive and developmental defects [147]. Among of dioxins, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) was the most toxic dioxin. Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and the ‘dioxin-like’ biphenyls (DL-PCBs) have been assigned dioxin toxic equivalency factors (TEFs) based upon their relative potency [148].

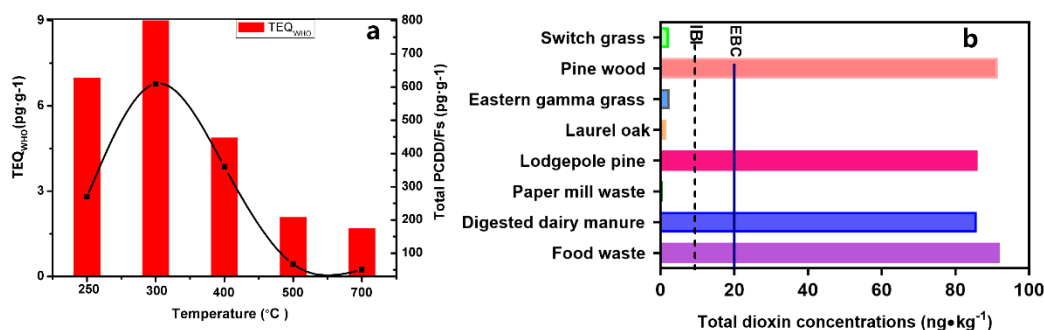
### 2.4.1 Formation mechanism of dioxins

The incomplete combustion of biomass generally produces dioxin-like substances, including PCDD, PCDF, and DL-PCBs [149]. These dioxins have been detected in various biochars formed at pyrolysis temperatures of 250–900 °C [150, 151]. Physical transformation from the feedstock via volatilization, followed by re-condensation or adsorption, is another mechanism of PCDDs and PCDFs formation [152].

### 2.4.2 The potential risks of dioxins

Hale et al. tested the toxic dioxin levels in 14 biochars and their TEQ varied from 0.008 to 1.2  $\text{pg}\cdot\text{g}^{-1}$ , which is below the Swedish guideline values for dioxin contamination of soil (250  $\text{pg}\cdot\text{g}^{-1}$  TEQ) [72]. In sawdust biochar, a TEQ of 7  $\text{ng}\cdot\text{kg}^{-1}$  was observed, which is lower than the threshold value for dioxins established by the IBI (9  $\text{ng}\cdot\text{kg}^{-1}$ ) and the EBC (20  $\text{ng}\cdot\text{kg}^{-1}$ ) (Fig. 9) [46, 47]. Weidemann et al. were unable to detect any quantifiable dioxins in wood-, straw- and sewage sludge biochars produced in different pyrolysis units [58]. A hepatoma cell line H4IIE-*luc* test showed that

biochar produced at  $>400^{\circ}\text{C}$  exhibited lower AhR-mediated potency [20]. Overall, dioxins in biochars represent a low risk to the environment [58].



**Fig. 9** PCDD/DF contents in biochar. **a**, Total PCDD/DFs and TEQ of sawdust biochar produced at pyrolysis temperatures of 250–700 °C [20]; **b**, Total dioxin concentrations in biochars produced from 8 different feedstocks and PCDD/DFs threshold values for biochars suggested by the IBI and EBC [72]. PCDD: polychlorinated dibenzo-*p*-dioxins; PCDF: polychlorinated dibenzofurans; TEQ: estimating 2,3,7,8-TCDD equivalents.

#### 2.4.3 Strategies to reduce dioxins levels in biochar

Suitable precursors present in feedstock (e.g. chlorine compounds) are the main source of PCDD/Fs formation in biochar during pyrolysis[153]. Some municipal solid waste contaminated with chlorine-containing plastic materials is another source of dioxin formation in biochar [72, 154]. Generally, more than 1% chlorine concentrations (e.g.,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) in biomass promoted the formation of PCDD/DFs and PCBs [155]. Such chlorine-mediated high PCDD/DFs levels can be counteracted by low-catalytic metals (chromated copper arsenate) and organic contaminants (e.g. pentachlorophenol) [152, 156]. Dioxins levels in biochar are feedstock-dependent (Fig. 9b), thus biomass with considerable amounts of chlorine and heavy metals (e.g., copper) should be avoided for biochar production.

Several studies observed the highest concentration of PCDD/DFs in biochar due to pyrolysis at 300 °C [20, 72]. Another study conducted by Lyu et al. reported pyrolysis at 700 °C significantly decreased the concentration of total PCDD/DFs in sawdust biochar [20]. During sewage sludge pyrolysis, the dioxin concentration accumulated in all three pyrolysis fractions also significantly decreased at temperatures  $>700^{\circ}\text{C}$ , which was attributed to gas phase decomposition reactions [157]. Under controlled pyrolysis condition, the restriction of oxygen supply can avoid the formation of

dioxins in biochar [158]. Furthermore, organic contaminants are present in much higher quantities in the pyrolysis liquid fraction than in biochar [21, 58] and therefore, pyrolysis unit design optimized for complete separation of pyrolysis liquids from biochar is essential for the production of dioxins-free biochar.

Overall, the toxicity of PCDD/DFs in biochar still rather limited, but the bioavailability of PCDD/Fs in biochar is lower than that observed in soil due to strong sorption of biochar. Dioxins levels in biochar are feedstock-dependent (Fig. 9b), thus we cannot give a clear recommendation about the most suitable temperature for producing biochar with minimum dioxin levels. Previous studies showed that the formation of MoCDF (Monochlorinated dibenzofuran) occurred preferentially pyrolysis units of larger-scale, yet this effect needs further investigation [58].

## 2.5 MCNs

Cyanides are carbon-nitrogen radicals that are naturally produced by various organisms as a defensive mechanism, such as bacteria, fungi and algae, but MCNs are also detected in biochar [23]. Elevated levels of cyanides in the environment are a serious concern due to their toxicity to human, animal, and aquatic life [159]. Long-term human exposure to cyanides causes weight loss, thyroid effects, nerve damage and death [160]. The toxicity of MCNs are based on inactivating metalloenzymes (e.g. cytochrome c oxidase) and blocking the mitochondrial electron transport chain due to binding with metals, resulting in depression of the central nervous system and myocardial activity [161].

### 2.5.1 Formation mechanism of cyanide

The interactive reaction between organic nitrogen and metals can form new N-containing metal substances such as MCN [162]. A recent study by Luo et al. reported that MCN existed in biochars from food wastes, sludge, fungi residues, and algae, with the maximum concentration of  $85 \text{ g}\cdot\text{kg}^{-1}$  detected in phycocyanin-derived biochar [23]. In contrast, biochars from sawdust, wheat straw, and livestock manure exhibited only small amounts of cyanide ions ( $\text{CN}^-$ ). The complexation reaction of unstable O-containing alkali salts (e.g.,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{SO}_4$ ) and organic nitrogen is a prerequisite to the formation of MOCN (metal oxycyanide, sole precursor of MCN), which then converts into MCN via carbothermal reduction (Fig. 10 a).

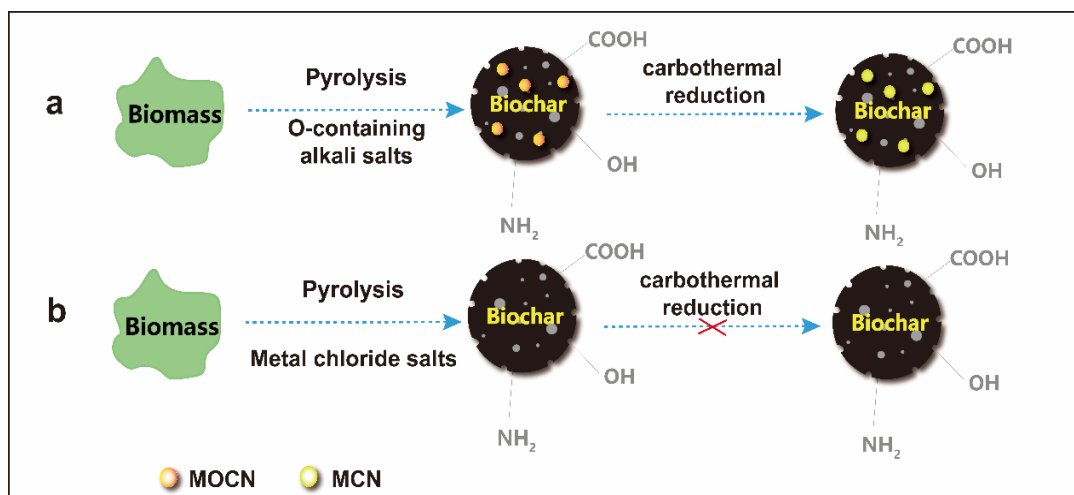


Fig. 10. Formation mechanism (a) and strategies to control (b) metal cyanide (MCN) in biochar [23]. MCN: metal cyanide; MOCN: metal oxycyanide.

### 2.5.2 Strategies to reduce MCNs levels in biochar

Pearson analysis revealed a positive correlation between Na content and  $\text{CN}^-$  content in biochar, along with a negative correlation between  $\text{CN}^-$  content and the content of Ca, Mg and Fe, suggesting that the alkali metals (e.g. Na) in biomass may provide sites to support  $\text{CN}^-$  formation. Taking consideration of the fact that oxygen atoms from metal salts are important to form  $\text{OCN}^-$ , metal chloride salts (e.g., KCl,  $\text{FeCl}_3$ , and  $\text{MgCl}_2$ ) in biomass inhibited the formation of MOCN and hence MCNs (Fig. 10b) [23]. Moreover, pyrolysis temperatures  $< 500\text{ }^\circ\text{C}$  also effectively decreased the content of  $\text{CN}^-$  due to slow carbothermal reduction reaction [23], while biochar produced at  $900\text{ }^\circ\text{C}$  exhibited low  $\text{CN}^-$  level because of  $\text{CN}^-$  volatilization.

Overall, avoiding biomass with O-containing alkali salts can effectively prevent the formation of MCN in biochar. To date, there has been a lack of information on the ecological risk of MCN from biochar. We now know that MCNs can be present in biochar, but it is very difficult and, in some cases, impossible to relate biochar ecotoxicity to specific contaminants present in biochar as pointed out in the manuscript when discussing the effects of PAHs. Therefore, some specific experiments should be designed to investigate MCN toxicity in biochar, e.g., by spiking a biochar with MCN and comparing its effect to an identical, non-spiked biochar. Although the availability of MCN in biochar is not still fully understood, existing studies revealed that cyanide seldom remains biologically available because of complexation reaction or volatilization [159].

## 2.6 VOCs

Volatile organic compounds are hydrocarbons with boiling points of  $\leq 250^{\circ}\text{C}$  that due to their volatility can be a human health risk [163]. Individual VOCs are not routinely assessed in biochar due to the diversity of compounds present in this group. Yet, the EBC recommends investigating total VOC levels in biochar via weight loss through TGA at first use of a pyrolysis unit [47].

### ***2.6.1 Formation mechanism of VOCs and their potential risks***

During slow pyrolysis, VOCs evaporate from biochar at standard temperatures ( $>350^{\circ}\text{C}$ ) and become part of the pyrolysis liquids [90, 164]. In contrast to hydrochar and fast pyrolysis biochars, slow pyrolysis biochars typically contain lower, yet highly variable levels of VOCs. This high variability is caused by the different extent of devolatilization as well as condensation of pyrolysis vapors onto biochar during biomass pyrolysis and in the zone after the pyrolysis reactor. Both vapors (VOCs) and leachates (WSOCs) from high-VOC biochar fully inhibited seed germination of cress, demonstrating potential risk for the environment [90]. Spokas et al. firstly identified over 140 volatile organic compounds (VOCs) sorbed to biochar via gas chromatographic-mass spectrometry [165]. The compounds identified as the same typically present in pyrolysis liquids and primarily organic acids, aldehydes, furans, ketones, alcohols, phenols, o-, m-, and p-cresol, and 2,4-dimethylphenol [21]. Their concentrations can exceed  $100 \mu\text{g}\cdot\text{g}^{-1}$  in biochars that were in contact with pyrolysis vapors as a result of cold spots in the pyrolysis unit and subsequent vapor condensation [21].

### ***2.6.2 Strategies to reduce VOCs levels in biochar***

The levels of VOCs in biochars are feedstock-independent [165], with production conditions and post-production handling being the key factors that determine VOC levels in biochar [78, 165]. Unlike for dioxins, pyrolysis in the presence of small amounts of oxygen reduced the content of VOCs in biochar [165]. Carbonized biochars (typically  $\text{H/C} < 0.70$ ) obtainable at relatively high pyrolysis temperatures ( $>400^{\circ}\text{C}$ ) can't release any VOCs [166]. Post-treatment of VOC-rich biochar (e.g., storage in aluminum trays and rinsing with deionized water) is an alternative strategy to alleviate their phytotoxicity [164], although this presents other contamination challenges related to air emissions and water contamination. Thermal post-treatment at  $200^{\circ}\text{C}$  is another viable option for reducing VOC concentrations in softwood pellet biochar by  $>95\%$  [78, 165]. Blending of high- and low-VOC biochars (ratio of 1:9) also demonstrated to be effective in reducing VOC emissions

and toxicity, which is a result of VOC sorption by the low-VOC biochar rather than just simple dilution [90].

Overall, the largest impact on VOC levels in biochar from slow pyrolysis is condensation and deposition of pyrolysis vapors on biochar [21, 90]. Therefore, the best way to avoid unwanted VOC contamination is the use of production units where pyrolysis vapors are fully separated from biochar without contact in areas of the unit that have lower temperatures than the actual pyrolysis treatment temperature [90].

### **3 Conclusions and future perspectives**

The application of biochars can be considered a ‘win-win-win scenario’ in terms of energy, carbon storage, and ecosystem functions. Yet, under some circumstances, biochars can introduce organic (e.g., PAHs, PFRs, dioxins, and VOCs) and inorganic contaminants (PTEs and MCN) into the environment with the potential to cause phytotoxicity, cytotoxicity, and neurotoxicity. It is therefore important to have a very good understanding of mechanisms resulting in biochar contamination, and how to use this information to produce safe biochar. Most of the research on contaminants in biochar and their effects on the ecosystem focusses on pristine biochar, yet functionalized biochars, doped with minerals and activated via different processes are the focus of current biochar development. Therefore, there is a need to investigate contaminant levels in these novel biochar-based composites and their potential toxic effects. Another area of research is the potential re-release of PTEs and organic contaminants into the environment from biochars used for contaminant remediation due to aging. Because of the co-existence of different contaminants in biochar, it is challenging to obtain correlation analysis between biochar toxicity and specific contaminants. Thus, it is essential to expand standardized research on biochar toxicity, and further investigate the relationships with biochar toxicity via meta-analysis or regression analysis.

The levels of contaminants in biochar are to a large extent feedstock- and pyrolysis temperature-dependent, but appropriate pyrolysis unit design can minimize the content of PAHs, VOCs, dioxins and PFRs for safe biochar production from a variety of materials and under a wide range of temperatures. Overall, wood and crop residue biochar produced under controlled pyrolysis conditions does not pose a risk to soil and plant health at any application rate. Biomass pyrolysis in a well-designed pyrolysis unit at the higher pyrolysis temperature range (e.g., 550–700 °C) can



decrease the majority of organic contaminants in biochar. In addition, aging and thermal post-treatment of biochars offers significant potential to reduce content or completely remove PAHs and VOCs even from biochar produced under sub-optimal conditions (vapor condensation onto biochar). As for PTE-rich biomass, such as food waste, sewage sludge, pig manure, and phytoremediation residues, the co-pyrolysis with feedstocks low in PTEs (e.g., bamboo sawdust, rice straw) decreases the levels of PTEs and PFRs of the resulting biochars. Avoiding biomass with unstable, O-containing alkali salts is effective in producing biochar with low levels of MCN [23]. In this respect, the fabrication of functionalized biochar composites should avoid the introduction of  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{K}_2\text{SO}_4$  in practical applications. Among these recommended measures, pyrolysis temperature, for example, has a direct impact on adsorption ability of biochar and therefore, contaminant mitigation could go hand-in hand with higher performance of biochar for adsorption applications [167]. Yet, whether measures we recommend here affect the application performance of biochar needs further study on a case-by-case basis taking into account the large diversity of biochar uses.

Recognizing the diversity of biochar properties, we cannot recommend the introduction of a particular threshold value that limits the per hectare application of biochar as a soil amendment. In fact, some of the most fertile soils globally contain biochar at up to 40-50% of their soil organic carbon contents [168]. Considering that some biochars are used as amendments to improve soil properties or for contaminant sorption, where large amounts of biochars are used, and others are used as high-efficiency fertilizers (low application rates), simple use of threshold values based on concentration of contaminants might also be inappropriate. Instead, maximum dosages per year could be introduced taking into account contaminant concentrations and biochar application rates as for example previously used for sewage sludge application in the EU[169]. Collectively, the environmental risk of contaminants in biochar can be considered low if recommendations for feedstock selection and biochar production are followed and contaminants should not hinder the large-scale application of biochar.

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## References

- [1] J. Lehmann, S. Joseph, Biochar for environmental management: science, technology and implementation, Routledge 2015.
- [2] D. Kołodyńska, J. Krukowska, P. Thomas, Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon, Chemical Engineering Journal 307 (2017) 353-363. <https://doi.org/10.1016/j.cej.2016.08.088>.
- [3] T. Chen, Y. Zhang, H. Wang, W. Lu, Z. Zhou, Y. Zhang, L. Ren, Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge, Bioresource technology 164 (2014) 47-54. <https://doi.org/10.1016/j.biortech.2014.04.048>.
- [4] D. O'Connor, T. Peng, J. Zhang, D.C.W. Tsang, D.S. Alessi, Z. Shen, N.S. Bolan, D. Hou, Biochar application for the remediation of heavy metal polluted land: A review of in situ field trials, The Science of the total environment 619-620 (2018) 815-826. <https://doi.org/10.1016/j.scitotenv.2017.11.132>.
- [5] C. Nzediegwu, M.A. Naeth, S.X. Chang, Lead(II) adsorption on microwave-pyrolyzed biochars and hydrochars depends on feedstock type and production temperature, Journal of hazardous materials 412 (2021) 125255. <https://doi.org/10.1016/j.jhazmat.2021.125255>.
- [6] A.E. Creamer, B. Gao, S. Wang, Carbon dioxide capture using various metal oxyhydroxide–biochar composites, Chemical Engineering Journal 283 (2016) 826-832. <https://doi.org/10.1016/j.cej.2015.08.037>.
- [7] C. Nzediegwu, S. Prasher, E. Elsayed, J. Dhiman, A. Mawof, R. Patel, Effect of Biochar on the Yield of Potatoes Cultivated Under Wastewater Irrigation for Two Seasons, Journal of Soil Science and Plant Nutrition 19(4) (2019) 865-877. <https://doi.org/10.1007/s42729-019-00085-0>.
- [8] A.L. Ido, M.D.G. de Luna, D.C. Ong, S.C. Capareda, Upgrading of Scenedesmus obliquus oil to high-quality liquid-phase biofuel by nickel-impregnated biochar catalyst, Journal of Cleaner Production 209 (2019) 1052-1060. <https://doi.org/10.1016/j.jclepro.2018.10.028>.
- [9] Z. Liu, G. Han, Production of solid fuel biochar from waste biomass by low temperature pyrolysis, Fuel 158 (2015) 159-165. <https://doi.org/10.1016/j.fuel.2015.05.032>.
- [10] I.K.M. Yu, X. Xiong, D.C.W. Tsang, L. Wang, A.J. Hunt, H. Song, J. Shang, Y.S. Ok, C.S. Poon, Aluminium-biochar composites as sustainable heterogeneous catalysts for glucose isomerisation in a

- biorefinery, *Green Chemistry* 21(6) (2019) 1267-1281. <https://doi.org/10.1039/c8gc02466a>.
- [11] L. Chen, X.L. Chen, C.H. Zhou, H.M. Yang, S.F. Ji, D.S. Tong, Z.K. Zhong, W.H. Yu, M.Q. Chu, Environmental-friendly montmorillonite-biochar composites: Facile production and tunable adsorption-release of ammonium and phosphate, *Journal of Cleaner Production* 156 (2017) 648-659. <https://doi.org/10.1016/j.jclepro.2017.04.050>.
- [12] S. Wang, B. Gao, Y. Li, A.R. Zimmerman, X. Cao, Sorption of arsenic onto Ni/Fe layered double hydroxide (LDH)-biochar composites, *RSC Advances* 6(22) (2016) 17792-17799. <https://doi.org/10.1039/c5ra17490b>.
- [13] H. Lyu, J. Tang, Y. Huang, L. Gai, E.Y. Zeng, K. Liber, Y. Gong, Removal of hexavalent chromium from aqueous solutions by a novel biochar supported nanoscale iron sulfide composite, *Chemical Engineering Journal* 322 (2017) 516-524. <https://doi.org/10.1016/j.cej.2017.04.058>.
- [14] A. Akhtar, A.K. Sarmah, Novel biochar-concrete composites: Manufacturing, characterization and evaluation of the mechanical properties, *The Science of the total environment* 616-617 (2018) 408-416. <https://doi.org/10.1016/j.scitotenv.2017.10.319>.
- [15] J. Heo, Y. Yoon, G. Lee, Y. Kim, J. Han, C.M. Park, Enhanced adsorption of bisphenol A and sulfamethoxazole by a novel magnetic CuZnFe<sub>2</sub>O<sub>4</sub>-biochar composite, *Bioresource technology* 281 (2019) 179-187. <https://doi.org/10.1016/j.biortech.2019.02.091>.
- [16] W. Buss, M.C. Graham, J.G. Shepherd, O. Masek, Risks and benefits of marginal biomass-derived biochars for plant growth, *The Science of the total environment* 569-570 (2016) 496-506. <https://doi.org/10.1016/j.scitotenv.2016.06.129>.
- [17] W. Buss, Pyrolysis Solves the Issue of Organic Contaminants in Sewage Sludge while Retaining Carbon—Making the Case for Sewage Sludge Treatment via Pyrolysis, *ACS Sustainable Chemistry & Engineering* (2021). <https://doi.org/10.1021/acssuschemeng.1c03651>.
- [18] Y. Li, Y. Liao, Y. He, K. Xia, S. Qiao, Q. Zhang, Polycyclic Aromatic Hydrocarbons Concentration in Straw Biochar with different Particle Size, *Procedia Environmental Sciences* 31 (2016) 91-97. <https://doi.org/10.1016/j.proenv.2016.02.012>.
- [19] L. Dunnigan, B.J. Morton, P.J. van Eyk, P.J. Ashman, X. Zhang, P.A. Hall, C.W. Kwong, Polycyclic aromatic hydrocarbons on particulate matter emitted during the co-generation of bioenergy and biochar from rice husk, *Bioresource technology* 244(Pt 1) (2017) 1015-1023. <https://doi.org/10.1016/j.biortech.2017.08.091>.

- [20] H. Lyu, Y. He, J. Tang, M. Hecker, Q. Liu, P.D. Jones, G. Codling, J.P. Giesy, Effect of pyrolysis temperature on potential toxicity of biochar if applied to the environment, *Environmental pollution* 218 (2016) 1-7. <https://doi.org/10.1016/j.envpol.2016.08.014>.
- [21] W. Buss, O. Masek, M. Graham, D. Wust, Inherent organic compounds in biochar--Their content, composition and potential toxic effects, *Journal of environmental management* 156 (2015) 150-7. <https://doi.org/10.1016/j.jenvman.2015.03.035>.
- [22] G. Fang, C. Liu, J. Gao, D.D. Dionysiou, D. Zhou, Manipulation of persistent free radicals in biochar to activate persulfate for contaminant degradation, *Environmental science & technology* 49(9) (2015) 5645-53. <https://doi.org/10.1021/es5061512>.
- [23] J. Luo, L. Lin, C. Liu, C. Jia, T. Chen, Y. Yang, M. Shen, H. Shang, S. Zhou, M. Huang, Y. Wang, D. Zhou, J. Fan, J.H. Clark, S. Zhang, X. Zhu, Reveal a hidden highly toxic substance in biochar to support its effective elimination strategy, *Journal of hazardous materials* 399 (2020) 123055. <https://doi.org/10.1016/j.jhazmat.2020.123055>.
- [24] R. Li, H. Huang, J.J. Wang, W. Liang, P. Gao, Z. Zhang, R. Xiao, B. Zhou, X. Zhang, Conversion of Cu(II)-polluted biomass into an environmentally benign Cu nanoparticles-embedded biochar composite and its potential use on cyanobacteria inhibition, *Journal of Cleaner Production* 216 (2019) 25-32. <https://doi.org/10.1016/j.jclepro.2019.01.186>.
- [25] P. Oleszczuk, I. Josko, M. Kusmierz, Biochar properties regarding to contaminants content and ecotoxicological assessment, *Journal of hazardous materials* 260 (2013) 375-82. <https://doi.org/10.1016/j.jhazmat.2013.05.044>.
- [26] P. Oleszczuk, I. Joško, M. Kuśmierz, B. Futa, E. Wielgosz, S. Ligęza, J. Pranagal, Microbiological, biochemical and ecotoxicological evaluation of soils in the area of biochar production in relation to polycyclic aromatic hydrocarbon content, *Geoderma* 213 (2014) 502-511. <https://doi.org/10.1016/j.geoderma.2013.08.027>.
- [27] G. Sigmund, D. Huber, T.D. Bucheli, M. Baumann, N. Borth, G.M. Guebitz, T. Hofmann, Cytotoxicity of Biochar: A Workplace Safety Concern?, *Environmental Science & Technology Letters* 4(9) (2017) 362-366. <https://doi.org/10.1021/acs.estlett.7b00267>.
- [28] T. Lieke, X. Zhang, C.E.W. Steinberg, B. Pan, Overlooked Risks of Biochars: Persistent Free Radicals trigger Neurotoxicity in *Caenorhabditis elegans*, *Environmental science & technology* 52(14) (2018) 7981-7987. <https://doi.org/10.1021/acs.est.8b01338>.

- [29] Y.-C. Chen, K.-F. Chen, J.-H. Lin, S.-W. Huang, H.-H. Chen, K.-Y.A. Lin, C.-H. Lin, The impact of pyrolysis temperature on physicochemical properties and pulmonary toxicity of tobacco stem micro-biochar, *Chemosphere* 263 (2021) 128349.
- [30] E.S. Odinga, M.G. Waigi, F.O. Gudda, J. Wang, B. Yang, X. Hu, S. Li, Y. Gao, Occurrence, formation, environmental fate and risks of environmentally persistent free radicals in biochars, *Environment international* 134 (2020) 105172. <https://doi.org/10.1016/j.envint.2019.105172>.
- [31] G. Sigmund, T.D. Bucheli, I. Hilber, V. Micic, M. Kah, T. Hofmann, Effect of ageing on the properties and polycyclic aromatic hydrocarbon composition of biochar, *Environmental science. Processes & impacts* 19(5) (2017) 768-774. <https://doi.org/10.1039/c7em00116a>.
- [32] M. Stefaniuk, P. Oleszczuk, K. Różyło, Co-application of sewage sludge with biochar increases disappearance of polycyclic aromatic hydrocarbons from fertilized soil in long term field experiment, *Science of The Total Environment* 599-600 (2017) 854-862. <https://doi.org/https://doi.org/10.1016/j.scitotenv.2017.05.024>.
- [33] X. Wang, Q. Chi, X. Liu, Y. Wang, Influence of pyrolysis temperature on characteristics and environmental risk of heavy metals in pyrolyzed biochar made from hydrothermally treated sewage sludge, *Chemosphere* 216 (2019) 698-706. <https://doi.org/10.1016/j.chemosphere.2018.10.189>.
- [34] J.M. De la Rosa, A.M. Sanchez-Martin, P. Campos, A.Z. Miller, Effect of pyrolysis conditions on the total contents of polycyclic aromatic hydrocarbons in biochars produced from organic residues: Assessment of their hazard potential, *The Science of the total environment* 667 (2019) 578-585. <https://doi.org/10.1016/j.scitotenv.2019.02.421>.
- [35] J. Meng, S. Liang, M. Tao, X. Liu, P.C. Brookes, J. Xu, Chemical speciation and risk assessment of Cu and Zn in biochars derived from co-pyrolysis of pig manure with rice straw, *Chemosphere* 200 (2018) 344-350. <https://doi.org/10.1016/j.chemosphere.2018.02.138>.
- [36] J. Jin, M. Wang, Y. Cao, S. Wu, P. Liang, Y. Li, J. Zhang, J. Zhang, M.H. Wong, S. Shan, P. Christie, Cumulative effects of bamboo sawdust addition on pyrolysis of sewage sludge: Biochar properties and environmental risk from metals, *Bioresource technology* 228 (2017) 218-226. <https://doi.org/10.1016/j.biortech.2016.12.103>.
- [37] M. Kołtowski, P. Oleszczuk, Toxicity of biochars after polycyclic aromatic hydrocarbons removal by thermal treatment, *Ecological Engineering* 75 (2015) 79-85. <https://doi.org/10.1016/j.ecoleng.2014.11.004>.

- [38] J.Y. Kim, S. Oh, Y.K. Park, Overview of biochar production from preservative-treated wood with detailed analysis of biochar characteristics, heavy metals behaviors, and their ecotoxicity, *Journal of hazardous materials* 384 (2020) 121356. <https://doi.org/10.1016/j.jhazmat.2019.121356>.
- [39] Z. Liu, L.A. Wang, H. Xiao, X. Guo, O. Urbanovich, L. Nagorskaya, X. Li, A review on control factors of pyrolysis technology for plants containing heavy metals, *Ecotoxicology and environmental safety* 191 (2020) 110181. <https://doi.org/10.1016/j.ecoenv.2020.110181>.
- [40] B. Pan, H. Li, D. Lang, B. Xing, Environmentally persistent free radicals: Occurrence, formation mechanisms and implications, *Environmental pollution* 248 (2019) 320-331.
- [41] X. Ruan, Y. Sun, W. Du, Y. Tang, Q. Liu, Z. Zhang, W. Doherty, R.L. Frost, G. Qian, D.C.W. Tsang, Formation, characteristics, and applications of environmentally persistent free radicals in biochars: A review, *Bioresource technology* 281 (2019) 457-468. <https://doi.org/10.1016/j.biortech.2019.02.105>.
- [42] T. Dutta, E. Kwon, S.S. Bhattacharya, B.H. Jeon, A. Deep, M. Uchimiya, K.H.J.G.B. Kim, Polycyclic aromatic hydrocarbons and volatile organic compounds in biochar and biochar-amended soil: a review, 9(6) (2017) 990-1004.
- [43] C. Wang, Y. Wang, H.M.S.K. Herath, Polycyclic aromatic hydrocarbons (PAHs) in biochar – Their formation, occurrence and analysis: A review, *Organic Geochemistry* 114 (2017) 1-11. <https://doi.org/10.1016/j.orggeochem.2017.09.001>.
- [44] J.M. De la Rosa, M. Paneque, I. Hilber, F. Blum, H.E. Knicker, T.D. Bucheli, Assessment of polycyclic aromatic hydrocarbons in biochar and biochar-amended agricultural soil from Southern Spain, *Journal of Soils and Sediments* 16(2) (2015) 557-565. <https://doi.org/10.1007/s11368-015-1250-z>.
- [45] M. Stefaniuk, D.C.W. Tsang, Y.S. Ok, P. Oleszczuk, A field study of bioavailable polycyclic aromatic hydrocarbons (PAHs) in sewage sludge and biochar amended soils, *Journal of hazardous materials* 349 (2018) 27-34. <https://doi.org/10.1016/j.jhazmat.2018.01.045>.
- [46] S.P. Definition, Product Testing Guidelines for Biochar that is used in Soil, International Biochar Initiative. Version, 2 (2015).
- [47] H. EBC, European Biochar Certificate–Guidelines for a Sustainable Production of Biochar, European Biochar Foundation (EBC), Arbaz, Switzerland., (2012).
- [48] E.B. Ledesma, N.D. Marsh, A.K. Sandrowitz, M.J. Wornat, Global kinetic rate parameters for the formation of polycyclic aromatic hydrocarbons from the pyrolysis of catechol, a model compound representative of solid fuel moieties, *Energy & Fuels* 16(1331-1336)

(2002).

[49] Q. Dai, X. Jiang, Y. Jiang, Y. Jin, F. Wang, Y. Chi, J. Yan, Formation of PAHs during the pyrolysis of dry sewage sludge, *Fuel* 130 (2014) 92-99. <https://doi.org/10.1016/j.fuel.2014.04.017>.

[50] V.T. Nguyen, T.B. Nguyen, C.W. Chen, C.M. Hung, T.D. Vo, J.H. Chang, C.D. Dong, Influence of pyrolysis temperature on polycyclic aromatic hydrocarbons production and tetracycline adsorption behavior of biochar derived from spent coffee ground, *Bioresource technology* 284 (2019) 197-203. <https://doi.org/10.1016/j.biortech.2019.03.096>.

[51] W. Buss, M.C. Graham, G. MacKinnon, O. Mašek, Strategies for producing biochars with minimum PAH contamination, *Journal of Analytical and Applied Pyrolysis* 119 (2016) 24-30. <https://doi.org/10.1016/j.jaap.2016.04.001>.

[52] R.K. Sharma, J.B. Wooten, V.L. Baliga, X. Lin, W.G. Chan, M.R.J.F. Hajaligol, Characterization of chars from pyrolysis of lignin, *83(11-12)* (2004) 1469-1482.

[53] H. Zhou, C. Wu, A. Meng, Y. Zhang, P.T. Williams, Effect of interactions of biomass constituents on polycyclic aromatic hydrocarbons (PAH) formation during fast pyrolysis, *Journal of Analytical and Applied Pyrolysis* 110 (2014) 264-269. <https://doi.org/10.1016/j.jaap.2014.09.007>.

[54] O. Mašek, M. Konno, S. Hosokai, N. Sonoyama, K. Norinaga, J.-i. Hayashi, A study on pyrolytic gasification of coffee grounds and implications to allothermal gasification, *Biomass and Bioenergy* 32(1) (2008) 78-89. <https://doi.org/10.1016/j.biombioe.2007.07.007>.

[55] P. Devi, A.K. Saroha, Effect of pyrolysis temperature on polycyclic aromatic hydrocarbons toxicity and sorption behaviour of biochars prepared by pyrolysis of paper mill effluent treatment plant sludge, *Bioresource technology* 192 (2015) 312-20. <https://doi.org/10.1016/j.biortech.2015.05.084>.

[56] A. Ziełńska, P. Oleszczuk, The conversion of sewage sludge into biochar reduces polycyclic aromatic hydrocarbon content and ecotoxicity but increases trace metal content, *Biomass and Bioenergy* 75 (2015) 235-244. <https://doi.org/10.1016/j.biombioe.2015.02.019>.

[57] I. Hilber, F. Blum, J. Leifeld, H.P. Schmidt, T.D. Bucheli, Quantitative determination of PAHs in biochar: a prerequisite to ensure its quality and safe application, *Journal of agricultural and food chemistry* 60(12) (2012) 3042-50. <https://doi.org/10.1021/jf205278v>.

[58] E. Weidemann, W. Buss, M. Edo, O. Masek, S. Jansson, Influence of pyrolysis temperature and production unit on formation of selected PAHs, oxy-PAHs, N-PACs, PCDDs, and PCDFs in biochar-a screening study, *Environmental science and pollution research international* 25(4) (2018) 3933-3940.

<https://doi.org/10.1007/s11356-017-0612-z>.

[59] A. Maienza, S. Baronti, A. Cincinelli, T. Martellini, A. Grisolia, F. Miglietta, G. Renella, S.R. Stazi, F.P. Vaccari, L. Genesio, Biochar improves the fertility of a Mediterranean vineyard without toxic impact on the microbial community, *Agronomy for Sustainable Development* 37(5) (2017).

<https://doi.org/10.1007/s13593-017-0458-2>.

[60] J. Tian, J. Wang, M. Dippold, Y. Gao, E. Blagodatskaya, Y. Kuzyakov, Biochar affects soil organic matter cycling and microbial functions but does not alter microbial community structure in a paddy soil, *Science of The Total Environment* 556 (2016) 89-97.

<https://doi.org/https://doi.org/10.1016/j.scitotenv.2016.03.010>.

[61] R. Hill, J. Hunt, E. Sanders, M. Tran, G.A. Burk, T.E. Mlsna, N.C. Fitzkee, Effect of biochar on microbial growth: a metabolomics and bacteriological investigation in *E. coli.*, *Environmental science & technology* (2019).

[62] D. Busch, A. Stark, C.I. Kammann, B. Glaser, Genotoxic and phytotoxic risk assessment of fresh and treated hydrochar from hydrothermal carbonization compared to biochar from pyrolysis, *Ecotoxicology and environmental safety* 97 (2013) 59-66. <https://doi.org/10.1016/j.ecoenv.2013.07.003>.

[63] L. Bouqbis, S. Daoud, H.W. Koyro, C.I. Kammann, F.Z. Ainhout, M.C. Harrouni, Phytotoxic effects of argan shell biochar on salad and barley germination, *Agriculture and Natural Resources* 51(4) (2017) 247-252. <https://doi.org/10.1016/j.anres.2017.04.001>.

[64] Y. Zhang, R. Yang, X. Si, X. Duan, X. Quan, The adverse effect of biochar to aquatic algae- the role of free radicals, *Environmental pollution* 248 (2019) 429-437. <https://doi.org/10.1016/j.envpol.2019.02.055>.

[65] A.M. Liesch, S.L. Weyers, J.W. Gaskin, K.C. Das, Impact of two different biochars on earthworm growth and survival, *Annals of environmental science* 2010 v.4 (2010) pp. 1-0.

[66] M. Simón, I. García, M. Díez-Ortiz, V. González, Biochar from Different Carbonaceous Waste Materials: Ecotoxicity and Effectiveness in the Sorption of Metal(loid)s, *Water, Air, & Soil Pollution* 229(7) (2018). <https://doi.org/10.1007/s11270-018-3860-8>.

[67] D. Sahu, G.M. Kannan, R. Vijayaraghavan, Carbon black particle exhibits size dependent toxicity in human monocytes, *International journal of inflammation* 2014 (2014) 827019. <https://doi.org/10.1155/2014/827019>.

[68] O. Malev, M. Contin, S. Licen, P. Barbieri, M. De Nobili, Bioaccumulation of polycyclic aromatic



hydrocarbons and survival of earthworms (*Eisenia andrei*) exposed to biochar amended soils, *Environmental science and pollution research international* 23(4) (2016) 3491-502. <https://doi.org/10.1007/s11356-015-5568-2>.

[69] A.G. Rombolà, G. Marisi, C. Torri, D. Fabbri, A. Buscaroli, M. Ghidotti, A. Hornung, Relationships between Chemical Characteristics and Phytotoxicity of Biochar from Poultry Litter Pyrolysis, *Journal of agricultural and food chemistry* 63(30) (2015) 6660-6667. <https://doi.org/10.1021/acs.jafc.5b01540>.

[70] J. Wang, E.S. Odinga, W. Zhang, X. Zhou, B. Yang, M.G. Waigi, Y. Gao, Polyaromatic hydrocarbons in biochars and human health risks of food crops grown in biochar-amended soils: A synthesis study, *Environment international* 130 (2019) 104899. <https://doi.org/10.1016/j.envint.2019.06.009>.

[71] M. Kusmierz, P. Oleszczuk, P. Kraska, E. Palys, S. Andruszczak, Persistence of polycyclic aromatic hydrocarbons (PAHs) in biochar-amended soil, *Chemosphere* 146 (2016) 272-9. <https://doi.org/10.1016/j.chemosphere.2015.12.010>.

[72] S.E. Hale, J. Lehmann, D. Rutherford, A.R. Zimmerman, R.T. Bachmann, V. Shitumbanuma, A. O'Toole, K.L. Sundqvist, H.P. Arp, G. Cornelissen, Quantifying the total and bioavailable polycyclic aromatic hydrocarbons and dioxins in biochars, *Environmental science & technology* 46(5) (2012) 2830-8. <https://doi.org/10.1021/es203984k>.

[73] P. Oleszczuk, M. Kusmierz, P. Godlewska, P. Kraska, E. Palys, The concentration and changes in freely dissolved polycyclic aromatic hydrocarbons in biochar-amended soil, *Environmental pollution* 214 (2016) 748-755. <https://doi.org/10.1016/j.envpol.2016.04.064>.

[74] A. Freddo, C. Cai, B.J. Reid, Environmental contextualisation of potential toxic elements and polycyclic aromatic hydrocarbons in biochar, *Environmental pollution* 171 (2012) 18-24. <https://doi.org/10.1016/j.envpol.2012.07.009>.

[75] S.E. Hale, J. Lehmann, D. Rutherford, A.R. Zimmerman, R.T. Bachmann, V. Shitumbanuma, A. O'Toole, K.L. Sundqvist, H.P.H. Arp, G. Cornelissen, Quantifying the Total and Bioavailable Polycyclic Aromatic Hydrocarbons and Dioxins in Biochars, *Environmental science & technology* 46(5) (2012) 2830-2838. <https://doi.org/10.1021/es203984k>.

[76] M. Stefaniuk, P. Oleszczuk, P. Bartminski, Chemical and ecotoxicological evaluation of biochar produced from residues of biogas production, *Journal of hazardous materials* 318 (2016) 417-424. <https://doi.org/10.1016/j.jhazmat.2016.06.013>.

[77] Q. Dai, X. Jiang, Y. Jiang, Y. Jin, F. Wang, Y. Chi, J. Yan, A. Xu, Temperature Influence and

Distribution in Three Phases of PAHs in Wet Sewage Sludge Pyrolysis Using Conventional and Microwave Heating, *Energy & Fuels* 28(5) (2014) 3317-3325. <https://doi.org/10.1021/ef5003638>.

[78] W. Buss, O. Mašek, High-VOC biochar—effectiveness of post-treatment measures and potential health risks related to handling and storage, *Environmental Science and Pollution Research* 23(19) (2016) 19580-19589. <https://doi.org/10.1007/s11356-016-7112-4>.

[79] J. Jin, Y. Li, J. Zhang, S. Wu, Y. Cao, P. Liang, J. Zhang, M.H. Wong, M. Wang, S. Shan, P. Christie, Influence of pyrolysis temperature on properties and environmental safety of heavy metals in biochars derived from municipal sewage sludge, *Journal of hazardous materials* 320 (2016) 417-426. <https://doi.org/10.1016/j.jhazmat.2016.08.050>.

[80] W. Buss, M.C. Graham, J.G. Shepherd, O. Masek, Suitability of marginal biomass-derived biochars for soil amendment, *The Science of the total environment* 547 (2016) 314-322. <https://doi.org/10.1016/j.scitotenv.2015.11.148>.

[81] G. Fang, C. Zhu, D.D. Dionysiou, J. Gao, D. Zhou, Mechanism of hydroxyl radical generation from biochar suspensions: Implications to diethyl phthalate degradation, *Bioresource technology* 176 (2015) 210-7. <https://doi.org/10.1016/j.biortech.2014.11.032>.

[82] H. Huang, W. Yao, R. Li, A. Ali, J. Du, D. Guo, R. Xiao, Z. Guo, Z. Zhang, M.K. Awasthi, Effect of pyrolysis temperature on chemical form, behavior and environmental risk of Zn, Pb and Cd in biochar produced from phytoremediation residue, *Bioresource technology* 249 (2018) 487-493. <https://doi.org/10.1016/j.biortech.2017.10.020>.

[83] C. Zhang, B. Shan, S. Jiang, W. Tang, Effects of the pyrolysis temperature on the biotoxicity of *Phyllostachys pubescens* biochar in the aquatic environment, *Journal of hazardous materials* 376 (2019) 48-57. <https://doi.org/10.1016/j.jhazmat.2019.05.010>.

[84] X. Shen, J. Zeng, D. Zhang, F. Wang, Y. Li, W. Yi, Effect of pyrolysis temperature on characteristics, chemical speciation and environmental risk of Cr, Mn, Cu, and Zn in biochars derived from pig manure, *The Science of the total environment* 704 (2020) 135283. <https://doi.org/10.1016/j.scitotenv.2019.135283>.

[85] P. Zhang, X. Zhang, Y. Li, L. Han, Influence of pyrolysis temperature on chemical speciation, leaching ability, and environmental risk of heavy metals in biochar derived from cow manure, *Bioresource technology* 302 (2020) 122850. <https://doi.org/10.1016/j.biortech.2020.122850>.

[86] G. Cornelissen, N.R. Pandit, P. Taylor, B.H. Pandit, M. Sparrevik, H.P.J.P.o. Schmidt, Emissions

and char quality of flame-curtain" Kon Tiki" Kilns for Farmer-Scale charcoal/biochar production, 11(5) (2016) e0154617.

[87] D. Fabbri, A.G. Rombolà, C. Torri, K.A. Spokas, Determination of polycyclic aromatic hydrocarbons in biochar and biochar amended soil, *Journal of Analytical and Applied Pyrolysis* 103 (2013) 60-67. <https://doi.org/https://doi.org/10.1016/j.jaap.2012.10.003>.

[88] H. Zhou, C. Wu, J.A. Onwudili, A. Meng, Y. Zhang, P.T. Williams, Polycyclic Aromatic Hydrocarbon Formation from the Pyrolysis/Gasification of Lignin at Different Reaction Conditions, *Energy & Fuels* 28(10) (2014) 6371-6379. <https://doi.org/10.1021/ef5013769>.

[89] M. Koneczak, B. Pan, Y.S. Ok, P. Oleszczuk, Carbon dioxide as a carrier gas and mixed feedstock pyrolysis decreased toxicity of sewage sludge biochar, *The Science of the total environment* 723 (2020) 137796. <https://doi.org/10.1016/j.scitotenv.2020.137796>.

[90] W. Buss, O. Masek, Mobile organic compounds in biochar - a potential source of contamination - phytotoxic effects on cress seed (*Lepidium sativum*) germination, *Journal of environmental management* 137 (2014) 111-9. <https://doi.org/10.1016/j.jenvman.2014.01.045>.

[91] W. Buss, Contaminant issues in production and application of biochar-Chapter 6: Composition of PAHs in biochar and implications for recommendations for biochar production, (2016). <https://doi.org/doi:10.13140/RG.2.2.20139.44328>.

[92] J. Madej, I. Hilber, T.D. Bucheli, P. Oleszczuk, Biochars with low polycyclic aromatic hydrocarbon concentrations achievable by pyrolysis under high carrier gas flows irrespective of oxygen content or feedstock, *Journal of Analytical and Applied Pyrolysis* 122 (2016) 365-369. <https://doi.org/10.1016/j.jaap.2016.09.005>.

[93] B.T. Nguyen, J. Lehmann, Black carbon decomposition under varying water regimes, *Organic Geochemistry* 40(8) (2009) 846-853. <https://doi.org/https://doi.org/10.1016/j.orggeochem.2009.05.004>.

[94] Sumaraj, L.P. Padhye, Influence of surface chemistry of carbon materials on their interactions with inorganic nitrogen contaminants in soil and water, *Chemosphere* 184 (2017) 532-547. <https://doi.org/10.1016/j.chemosphere.2017.06.021>.

[95] P. Oleszczuk, M. Koltowski, Changes of total and freely dissolved polycyclic aromatic hydrocarbons and toxicity of biochars treated with various aging processes, *Environmental pollution* 237 (2018) 65-73. <https://doi.org/10.1016/j.envpol.2018.01.073>.

[96] S. Hale, K. Hanley, J. Lehmann, A. Zimmerman, G. Cornelissen, Effects of Chemical, Biological,

and Physical Aging As Well As Soil Addition on the Sorption of Pyrene to Activated Carbon and Biochar, *Environmental science & technology* 45(24) (2011) 10445-10453. <https://doi.org/10.1021/es202970x>.

[97] K.G.I.D. Kumari, P. Moldrup, M. Paradelo, L.W. de Jonge, Phenanthrene Sorption on Biochar-Amended Soils: Application Rate, Aging, and Physicochemical Properties of Soil, *Water, Air, & Soil Pollution* 225(9) (2014). <https://doi.org/10.1007/s11270-014-2105-8>.

[98] M.F. de Resende, T.F. Brasil, B.E. Madari, A.D. Pereira Netto, E.H. Novotny, Polycyclic aromatic hydrocarbons in biochar amended soils: Long-term experiments in Brazilian tropical areas, *Chemosphere* 200 (2018) 641-648. <https://doi.org/10.1016/j.chemosphere.2018.02.139>.

[99] D. Delistraty, Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons, *Toxicological & Environmental Chemistry* 64(1-4) (1997) 81-108. <https://doi.org/10.1080/02772249709358542>.

[100] T.D. Bucheli, I. Hilber, H.-P.J.B.f.E.M.S. Schmidt, Technology, Implementation, Polycyclic aromatic hydrocarbons and polychlorinated aromatic compounds in biochar, (2015) 595-624.

[101] E.E. Commission), Opinion of the Scientific Committee on food on the risk to human health of polycyclic aromatic hydrocarbons in food, Health Consumer Protection Directorate-General SCF/CS/CNTM/PAH/29 Final Report 1-65 (2002).

[102] M. Koltowski, I. Hilber, T.D. Bucheli, P. Oleszczuk, Effect of steam activated biochar application to industrially contaminated soils on bioavailability of polycyclic aromatic hydrocarbons and ecotoxicity of soils, *The Science of the total environment* 566-567 (2016) 1023-1031. <https://doi.org/10.1016/j.scitotenv.2016.05.114>.

[103] S.M. Shaheen, N.K. Niazi, N.E.E. Hassan, I. Bibi, H. Wang, Daniel C.W. Tsang, Y.S. Ok, N. Bolan, J. Rinklebe, Wood-based biochar for the removal of potentially toxic elements in water and wastewater: a critical review, *International Materials Reviews* 64(4) (2018) 216-247. <https://doi.org/10.1080/09506608.2018.1473096>.

[104] A. Méndez, A. Gómez, J. Paz-Ferreiro, G. Gascó, Effects of sewage sludge biochar on plant metal availability after application to a Mediterranean soil, *Chemosphere* 89(11) (2012) 1354-1359. <https://doi.org/https://doi.org/10.1016/j.chemosphere.2012.05.092>.

[105] Y. Yuan, J. Li, C. Wang, G. An, Contrasting microcystin-LR sorption and desorption capability of different farmland soils amended with biochar: Effects of biochar dose and aging time, *Environmental pollution* 286 (2021) 117364. <https://doi.org/10.1016/j.envpol.2021.117364>.

- [106] V. Frišták, M. Pipiška, G. Soja, Pyrolysis treatment of sewage sludge: a promising way to produce phosphorus fertilizer, *Journal of Cleaner Production* 172 (2018) 1772-1778.
- [107] D.A. Roberts, A.J. Cole, A. Whelan, R. de Nys, N.A. Paul, Slow pyrolysis enhances the recovery and reuse of phosphorus and reduces metal leaching from biosolids, *Waste Management* 64 (2017) 133-139.
- [108] Y.F. Huang, Y.Y. Huang, P.T. Chiueh, S.L. Lo, Heterogeneous Fenton oxidation of trichloroethylene catalyzed by sewage sludge biochar: Experimental study and life cycle assessment, *Chemosphere* 249 (2020) 126139. <https://doi.org/10.1016/j.chemosphere.2020.126139>.
- [109] Y. Xu, F. Qi, T. Bai, Y. Yan, C. Wu, Z. An, S. Luo, Z. Huang, P. Xie, A further inquiry into co-pyrolysis of straws with manures for heavy metal immobilization in manure-derived biochars, *Journal of hazardous materials* 380 (2019) 120870. <https://doi.org/10.1016/j.jhazmat.2019.120870>.
- [110] M.S. Islam, J.H. Kwak, C. Nzediegwu, S. Wang, K. Palansuriya, E.E. Kwon, M.A. Naeth, M.G. El-Din, Y.S. Ok, S.X. Chang, Biochar heavy metal removal in aqueous solution depends on feedstock type and pyrolysis purging gas, *Environmental pollution* 281 (2021) 117094. <https://doi.org/10.1016/j.envpol.2021.117094>.
- [111] B. Yousaf, G. Liu, Q. Abbas, M.U. Ali, R. Wang, R. Ahmed, C. Wang, M.I. Al-Wabel, A.R.A. Usman, Operational control on environmental safety of potentially toxic elements during thermal conversion of metal-accumulator invasive ragweed to biochar, *Journal of Cleaner Production* 195 (2018) 458-469. <https://doi.org/10.1016/j.jclepro.2018.05.246>.
- [112] L. Shi, L. Wang, T. Zhang, J. Li, X. Huang, J. Cai, J. Lu, Y. Wang, Reducing the bioavailability and leaching potential of lead in contaminated water hyacinth biomass by phosphate-assisted pyrolysis, *Bioresource technology* 241 (2017) 908-914. <https://doi.org/10.1016/j.biortech.2017.06.025>.
- [113] Q. Liu, Z. Fang, Y. Liu, Y. Liu, Y. Xu, X. Ruan, X. Zhang, W. Cao, Phosphorus speciation and bioavailability of sewage sludge derived biochar amended with CaO, *Waste Manag* 87 (2019) 71-77. <https://doi.org/10.1016/j.wasman.2019.01.045>.
- [114] L.W. Kiruri, L. Khachatryan, B. Dellinger, S. Lomnicki, Effect of Copper Oxide Concentration on the Formation and Persistency of Environmentally Persistent Free Radicals (EPFRs) in Particulates, *Environmental science & technology* 48(4) (2014) 2212-2217. <https://doi.org/10.1021/es404013g>.
- [115] E.P. Vejerano, G. Rao, L. Khachatryan, S.A. Cormier, S. Lomnicki, Environmentally Persistent Free Radicals: Insights on a New Class of Pollutants, *Environmental science & technology* 52(5) (2018)

2468-2481. <https://doi.org/10.1021/acs.est.7b04439>.

[116] R.T. Dugas, S. Lomnicki, A.S. Cormier, B. Dellinger, M. Reams, Addressing Emerging Risks: Scientific and Regulatory Challenges Associated with Environmentally Persistent Free Radicals, *International Journal of Environmental Research and Public Health* 13(6) (2016). <https://doi.org/10.3390/ijerph13060573>.

[117] S. Liao, B. Pan, H. Li, D. Zhang, B. Xing, Detecting free radicals in biochars and determining their ability to inhibit the germination and growth of corn, wheat and rice seedlings, *Environmental science & technology* 48(15) (2014) 8581-7. <https://doi.org/10.1021/es404250a>.

[118] A. Nzihou, B. Stanmore, P. Sharrock, A review of catalysts for the gasification of biomass char, with some reference to coal, *Energy* 58 (2013) 305-317. <https://doi.org/10.1016/j.energy.2013.05.057>.

[119] J. Kibet, L. Khachatryan, B. Dellinger, Molecular products and radicals from pyrolysis of lignin, *Environmental science & technology* 46(23) (2012) 12994-3001. <https://doi.org/10.1021/es302942c>.

[120] F. Xiao, J.J. Pignatello, Interactions of triazine herbicides with biochar: Steric and electronic effects, *Water research* 80 (2015) 179-88. <https://doi.org/10.1016/j.watres.2015.04.040>.

[121] W. Tao, W. Duan, C. Liu, D. Zhu, X. Si, R. Zhu, P. Oleszczuk, B. Pan, Formation of persistent free radicals in biochar derived from rice straw based on a detailed analysis of pyrolysis kinetics, *The Science of the total environment* 715 (2020) 136575. <https://doi.org/10.1016/j.scitotenv.2020.136575>.

[122] G. Fang, J. Gao, C. Liu, D.D. Dionysiou, Y. Wang, D. Zhou, Key Role of Persistent Free Radicals in Hydrogen Peroxide Activation by Biochar: Implications to Organic Contaminant Degradation, *Environmental science & technology* 48(3) (2014) 1902-1910. <https://doi.org/10.1021/es4048126>.

[123] J. Yang, B. Pan, H. Li, S. Liao, D. Zhang, M. Wu, B. Xing, Degradation of p-Nitrophenol on Biochars: Role of Persistent Free Radicals, *Environmental science & technology* 50(2) (2016) 694-700. <https://doi.org/10.1021/acs.est.5b04042>.

[124] J. Qin, Q. Chen, M. Sun, P. Sun, G. Shen, Pyrolysis temperature-induced changes in the catalytic characteristics of rice husk-derived biochar during 1,3-dichloropropene degradation, *Chemical Engineering Journal* 330 (2017) 804-812. <https://doi.org/10.1016/j.cej.2017.08.013>.

[125] Y. Liu, Q. Dai, X. Jin, X. Dong, J. Peng, M. Wu, N. Liang, B. Pan, B. Xing, Negative Impacts of Biochars on Urease Activity: High pH, Heavy Metals, Polycyclic Aromatic Hydrocarbons, or Free Radicals?, *Environmental science & technology* 52(21) (2018) 12740-12747. <https://doi.org/10.1021/acs.est.8b00672>.

- [126] D. Huang, H. Luo, C. Zhang, G. Zeng, C. Lai, M. Cheng, R. Wang, R. Deng, W. Xue, X. Gong, X. Guo, T. Li, Nonnegligible role of biomass types and its compositions on the formation of persistent free radicals in biochar: Insight into the influences on Fenton-like process, *Chemical Engineering Journal* 361 (2019) 353-363. <https://doi.org/10.1016/j.cej.2018.12.098>.
- [127] R. Deng, H. Luo, D. Huang, C. Zhang, Biochar-mediated Fenton-like reaction for the degradation of sulfamethazine: Role of environmentally persistent free radicals, *Chemosphere* 255 (2020) 126975. <https://doi.org/10.1016/j.chemosphere.2020.126975>.
- [128] Y. Qi, B. Ge, Y. Zhang, B. Jiang, C. Wang, M. Akram, X. Xu, Three-dimensional porous graphene-like biochar derived from *Enteromorpha* as a persulfate activator for sulfamethoxazole degradation: Role of graphitic N and radicals transformation, *Journal of hazardous materials* 399 (2020) 123039. <https://doi.org/10.1016/j.jhazmat.2020.123039>.
- [129] D.-G. Kim, S.-O. Ko, Effects of thermal modification of a biochar on persulfate activation and mechanisms of catalytic degradation of a pharmaceutical, *Chemical Engineering Journal* 399 (2020) 125377. <https://doi.org/10.1016/j.cej.2020.125377>.
- [130] J. Zou, J. Yu, L. Tang, X. Ren, Y. Pang, H. Zhang, Q. Xie, Y. Liu, H. Liu, T. Luo, Analysis of reaction pathways and catalytic sites on metal-free porous biochar for persulfate activation process, *Chemosphere* (2020) 127747. <https://doi.org/10.1016/j.chemosphere.2020.127747>.
- [131] Y. Li, S. Ma, S. Xu, H. Fu, Z. Li, K. Li, K. Sheng, J. Du, X. Lu, X. Li, S. Liu, Novel magnetic biochar as an activator for peroxymonosulfate to degrade bisphenol A: Emphasizing the synergistic effect between graphitized structure and CoFe<sub>2</sub>O<sub>4</sub>, *Chemical Engineering Journal* 387 (2020) 124094. <https://doi.org/10.1016/j.cej.2020.124094>.
- [132] W. Li, B. Liu, Z. Wang, K. Wang, Y. Lan, L. Zhou, Efficient activation of peroxydisulfate (PDS) by rice straw biochar modified by copper oxide (RSBC-CuO) for the degradation of phenacetin (PNT), *Chemical Engineering Journal* 395 (2020) 125094. <https://doi.org/10.1016/j.cej.2020.125094>.
- [133] X. Li, Y. Jia, M. Zhou, X. Su, J. Sun, High-efficiency degradation of organic pollutants with Fe, N co-doped biochar catalysts via persulfate activation, *Journal of hazardous materials* 397 (2020) 122764. <https://doi.org/10.1016/j.jhazmat.2020.122764>.
- [134] J. Liang, X. Xu, Q. Zhong, Z. Xu, L. Zhao, H. Qiu, X. Cao, Roles of the mineral constituents in sludge-derived biochar in persulfate activation for phenol degradation, *Journal of hazardous materials* 398 (2020) 122861. <https://doi.org/10.1016/j.jhazmat.2020.122861>.

- [135] B. Liu, W. Guo, H. Wang, Q. Si, Q. Zhao, H. Luo, N. Ren, Activation of peroxymonosulfate by cobalt-impregnated biochar for atrazine degradation: The pivotal roles of persistent free radicals and ecotoxicity assessment, *Journal of hazardous materials* 398 (2020) 122768. <https://doi.org/10.1016/j.jhazmat.2020.122768>.
- [136] Y. Zhao, M. Song, Q. Cao, P. Sun, Y. Chen, F. Meng, The superoxide radicals' production via persulfate activated with CuFe<sub>2</sub>O<sub>4</sub>@Biochar composites to promote the redox pairs cycling for efficient degradation of o-nitrochlorobenzene in soil, *Journal of hazardous materials* (2020) 122887. <https://doi.org/10.1016/j.jhazmat.2020.122887>.
- [137] M.M. Mian, G. Liu, Activation of peroxymonosulfate by chemically modified sludge biochar for the removal of organic pollutants: Understanding the role of active sites and mechanism, *Chemical Engineering Journal* 392 (2020) 123681. <https://doi.org/10.1016/j.cej.2019.123681>.
- [138] F. Qin, Y. Peng, G. Song, Q. Fang, R. Wang, C. Zhang, G. Zeng, D. Huang, C. Lai, Y. Zhou, X. Tan, M. Cheng, S. Liu, Degradation of sulfamethazine by biochar-supported bimetallic oxide/persulfate system in natural water: Performance and reaction mechanism, *Journal of hazardous materials* 398 (2020) 122816. <https://doi.org/10.1016/j.jhazmat.2020.122816>.
- [139] N. Zhao, Z. Yin, F. Liu, M. Zhang, Y. Lv, Z. Hao, G. Pan, J. Zhang, Environmentally persistent free radicals mediated removal of Cr(VI) from highly saline water by corn straw biochars, *Bioresource technology* 260 (2018) 294-301. <https://doi.org/10.1016/j.biortech.2018.03.116>.
- [140] J. Yu, L. Tang, Y. Pang, G. Zeng, J. Wang, Y. Deng, Y. Liu, H. Feng, S. Chen, X. Ren, Magnetic nitrogen-doped sludge-derived biochar catalysts for persulfate activation: Internal electron transfer mechanism, *Chemical Engineering Journal* 364 (2019) 146-159. <https://doi.org/10.1016/j.cej.2019.01.163>.
- [141] J. Yu, L. Tang, Y. Pang, G. Zeng, J. Wang, Y. Deng, Y. Liu, H. Feng, S. Chen, X.J.C.E.J. Ren, Magnetic nitrogen-doped sludge-derived biochar catalysts for persulfate activation: internal electron transfer mechanism, 364 (2019) 146-159.
- [142] K. Zhang, P. Sun, Y. Zhang, Decontamination of Cr(VI) facilitated formation of persistent free radicals on rice husk derived biochar, *Frontiers of Environmental Science & Engineering* 13(2) (2019). <https://doi.org/10.1007/s11783-019-1106-7>.
- [143] Y. Li, Y. Yang, F. Shen, G. Yang, Y. Zhang, S. Deng, J. Zhang, Y. Zeng, Y. Hu, Mitigating biochar phytotoxicity via lanthanum (La) participation in pyrolysis, *Environmental science and pollution*



- research international 24(11) (2017) 10267-10278. <https://doi.org/10.1007/s11356-017-8653-x>.
- [144] H. Jia, S. Zhao, G. Nulaji, K. Tao, F. Wang, V.K. Sharma, C. Wang, Environmentally Persistent Free Radicals in Soils of Past Coking Sites: Distribution and Stabilization, *Environmental science & technology* 51(11) (2017) 6000-6008. <https://doi.org/10.1021/acs.est.7b00599>.
- [145] H. Han, M.K. Rafiq, T. Zhou, R. Xu, O. Masek, X. Li, A critical review of clay-based composites with enhanced adsorption performance for metal and organic pollutants, *Journal of hazardous materials* 369 (2019) 780-796. <https://doi.org/10.1016/j.jhazmat.2019.02.003>.
- [146] K. Eichbaum, M. Brinkmann, S. Buchinger, G. Reifferscheid, M. Hecker, J.P. Giesy, M. Engwall, B. van Bavel, H. Hollert, In vitro bioassays for detecting dioxin-like activity — Application potentials and limits of detection, a review, *Science of The Total Environment* 487 (2014) 37-48. <https://doi.org/10.1016/j.scitotenv.2014.03.057>.
- [147] P.S. Kulkarni, J.G. Crespo, C.A.M. Afonso, Dioxins sources and current remediation technologies — A review, *Environment international* 34(1) (2008) 139-153. <https://doi.org/https://doi.org/10.1016/j.envint.2007.07.009>.
- [148] P.S. Kulkarni, J.G. Crespo, C.A. Afonso, Dioxins sources and current remediation technologies--a review, *Environment international* 34(1) (2008) 139-53. <https://doi.org/10.1016/j.envint.2007.07.009>.
- [149] B.R. Stanmore, The formation of dioxins in combustion systems, *Combustion and Flame* 136(3) (2004) 398-427. <https://doi.org/10.1016/j.combustflame.2003.11.004>.
- [150] J.L. Wu, F. Ji, H. Zhang, C. Hu, M.H. Wong, D. Hu, Z. Cai, Formation of dioxins from triclosan with active chlorine: A potential risk assessment, *Journal of hazardous materials* 367 (2019) 128-136. <https://doi.org/10.1016/j.jhazmat.2018.12.088>.
- [151] M. Zhang, A. Buekens, X. Li, Brominated flame retardants and the formation of dioxins and furans in fires and combustion, *Journal of hazardous materials* 304 (2016) 26-39. <https://doi.org/10.1016/j.jhazmat.2015.10.014>.
- [152] Q. Gao, M. Edo, S.H. Larsson, E. Collina, M. Rudolfsson, M. Gallina, I. Oluwoye, M. Altarawneh, B.Z. Dlugogorski, S. Jansson, Formation of PCDDs and PCDFs in the torrefaction of biomass with different chemical composition, *Journal of Analytical and Applied Pyrolysis* 123 (2017) 126-133. <https://doi.org/10.1016/j.jaap.2016.12.015>.
- [153] T.D. Bucheli, I. Hilber, H.-P. Schmidt, Polycyclic aromatic hydrocarbons and polychlorinated aromatic compounds in biochar, *Biochar for environmental management*, Routledge2015, pp. 627-656.

- [154] K. Wilson, D.J.I.W.P. Reed, Implications and risks of potential dioxin presence in biochar, (2012).
- [155] E. Wikström, G. Löfvenius, C. Rappe, S. Marklund, Influence of Level and Form of Chlorine on the Formation of Chlorinated Dioxins, Dibenzofurans, and Benzenes during Combustion of an Artificial Fuel in a Laboratory Reactor, *Environmental science & technology* 30(5) (1996) 1637-1644. <https://doi.org/10.1021/es9506364>.
- [156] T. Zhang, J. Huang, S. Deng, G. Yu, Influence of pesticides contamination on the emission of PCDD/PCDF to the land from open burning of corn straws, *Environmental pollution* 159(6) (2011) 1744-1748. <https://doi.org/https://doi.org/10.1016/j.envpol.2011.01.042>.
- [157] Q. Dai, J. Wen, X. Jiang, L. Dai, Y. Jin, F. Wang, Y. Chi, J. Yan, Distribution of PCDD/Fs over the three product phases in wet sewage sludge pyrolysis, *Journal of Analytical and Applied Pyrolysis* 133 (2018) 169-175. <https://doi.org/10.1016/j.jaap.2018.04.005>.
- [158] A.L. Cowie, A.E. Downie, B.H. George, B.-P. Singh, L. Van Zwieten, D. O'Connell, Is sustainability certification for biochar the answer to environmental risks? , *Pesquisa Agropecuária Brasileira* 47 (2012) 637-648.
- [159] R. Kumar, S. Saha, S. Dhaka, M.B. Kurade, C.U. Kang, S.H. Baek, B.-H. Jeon, Remediation of cyanide-contaminated environments through microbes and plants: a review of current knowledge and future perspectives, *Geosystem Engineering* 20(1) (2016) 28-40. <https://doi.org/10.1080/12269328.2016.1218303>.
- [160] R.R. Dash, A. Gaur, C. Balomajumder, Cyanide in industrial wastewaters and its removal: a review on biotreatment, *Journal of hazardous materials* 163(1) (2009) 1-11. <https://doi.org/10.1016/j.jhazmat.2008.06.051>.
- [161] V.M. Luque-Almagro, C. Moreno-Vivian, M.D. Roldan, Biodegradation of cyanide wastes from mining and jewellery industries, *Curr Opin Biotechnol* 38 (2016) 9-13. <https://doi.org/10.1016/j.copbio.2015.12.004>.
- [162] J. Luo, C. Jia, M. Shen, S. Zhang, X. Zhu, Enhancement of adsorption and energy storage capacity of biomass-based N-doped porous carbon via cyclic carbothermal reduction triggered by nitrogen dopants, *Carbon* 155 (2019) 403-409. <https://doi.org/https://doi.org/10.1016/j.carbon.2019.08.075>.
- [163] E. Parliament, DIRECTIVE 2004/42/CE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 april 2004 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes and vehicle refinishing products and amending

directive 1999/13/EC, 2004.

[164] I. Bargmann, M.C. Rillig, W. Buss, A. Kruse, M. Kuecke, Hydrochar and Biochar Effects on Germination of Spring Barley, *Journal of Agronomy and Crop Science* 199(5) (2013) 360-373. <https://doi.org/10.1111/jac.12024>.

[165] K.A. Spokas, J.M. Novak, C.E. Stewart, K.B. Cantrell, M. Uchimiya, M.G. Dusaire, K.S. Ro, Qualitative analysis of volatile organic compounds on biochar, *Chemosphere* 85(5) (2011) 869-82. <https://doi.org/10.1016/j.chemosphere.2011.06.108>.

[166] M. Ghidotti, D. Fabbri, A. Hornung, Profiles of Volatile Organic Compounds in Biochar: Insights into Process Conditions and Quality Assessment, *ACS Sustainable Chemistry & Engineering* 5(1) (2016) 510-517. <https://doi.org/10.1021/acssuschemeng.6b01869>.

[167] Y. Yi, G. Tu, P. Eric Tsang, Z. Fang, Insight into the influence of pyrolysis temperature on Fenton-like catalytic performance of magnetic biochar, *Chemical Engineering Journal* 380 (2020). <https://doi.org/10.1016/j.cej.2019.122518>.

[168] J.D. Mao, R.L. Johnson, J. Lehmann, D.C. Olk, E.G. Neves, M.L. Thompson, K. Schmidt-Rohr, Abundant and stable char residues in soils: implications for soil fertility and carbon sequestration, *Environmental science & technology* 46(17) (2012) 9571-6. <https://doi.org/10.1021/es301107c>.

[169] C.J.J.E.C. Directive, Council Directive on the Protection of the Environment, and in Particular of the Soil, When Sewage Sludge Is Used in Agriculture. *Offic*, 181 (1986) 0006-0012.