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Occurrence, formation, environmental fate and risks of environmentally persistent free radicals in biochars

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ABSTRACT

Biochars are used globally in agricultural crop production and environmental remediation. However, environmentally persistent free radicals (EPFRs), which are stable emerging pollutants, are generated as a characteristic feature during biomass pyrolysis. EPFRs can induce the formation of reactive oxygen species, which poses huge agro-environmental and human health risks. Their half-lives and persistence in both biochar residues and in the atmosphere may lead to potentially adverse risks in the environment. This review highlights the comprehensive research into these bioreactive radicals, as well as the bottlenecks of biochar production leading up to the formation and persistence of EPFRs. Additionally, a way forward has been proposed, based on two main recommendations. A global joint initiative to create an all-encompassing regulations policy document that will improve both the technological and the quality control aspects of biochars to reduce EPFR generation at the production level. Furthermore, environmental impact and risk assessment studies should be conducted in the extensive applications of biochars in order to protect the environmental and human health. The highlighted key research directions proposed herein will shape the production, research, and adoption aspects of biochars, which will mitigate the considerable concerns raised on EPFRs.

1. Introduction

Biochar (also known as char or black carbon) is a predominantly stable, carboniferous by-product, formed through the pyrolysis of low-cost biomass residues (from plant and/or animal) at charring temperatures over 250 °C in oxygen-limiting conditions (Lehmann and Joseph, 2015). Due to its well-defined and quality-controlled process under reductive thermal conditions, this carbonaceous compound has recently been widely considered as an organic amendment of beneficial importance in agriculture and environment (Lehmann et al., 2006). For example, biochar can improve agricultural soil performance by enhancing soil fertility and fostering plant growth while contributing to the maintenance of cation exchange capacity (CEC) in soils (Ding et al., 2016). Moreover, it contributes to the amelioration of soil acidity, enhancing soil hydrological properties and soil nutrients (thus, increasing crop yield), sequestration of greenhouse gases (by creating a permanent 'carbon sink' for climate change mitigation), and adsorption of pollutants, e.g., polycyclic aromatic hydrocarbons (PAHs) and heavy metals from soil matrices (Beesley et al., 2011; Jeffery et al., 2011; Kinney et al., 2012; McElligott et al., 2011; Omondi et al., 2016; Qin et al., 2018; Zhang et al., 2018). These amendments have been applied in the degradation of contaminants in soils and water from various ecosystems (Fang et al., 2015a; Huang et al., 2019; Oliveira et al., 2017; Qin et al., 2017, 2018). Due to these benefits, biochars play a huge role in environmental remediation and agricultural applications globally.

Despite their previously mentioned advantages, biochars may also contain highly heterogeneous composite lattice structures comprised of organic (labile and recalcitrant organic molecules such as polycyclic aromatic hydrocarbons, furans, dioxins), as well as inorganic fractions, which contain oxides, cations, anions and free radicals (Chintala et al., 2016). The latter type of inorganic fractions may gradually form as environmentally persistent free radicals (EPFRs), which are surface stabilized metal-radical complexes that are formed from the so-called "products of incomplete combustion" (dela Cruz et al., 2011; Dellinger et al., 2001; Lomnicki et al., 2008b; Stephenson et al., 2016). Also known as persistent free radicals, biologically persistent free radicals, environmentally significant surface radicals, combustion-generated radicals, surface-stabilized EPFRs, stable bioreactive radicals or stable

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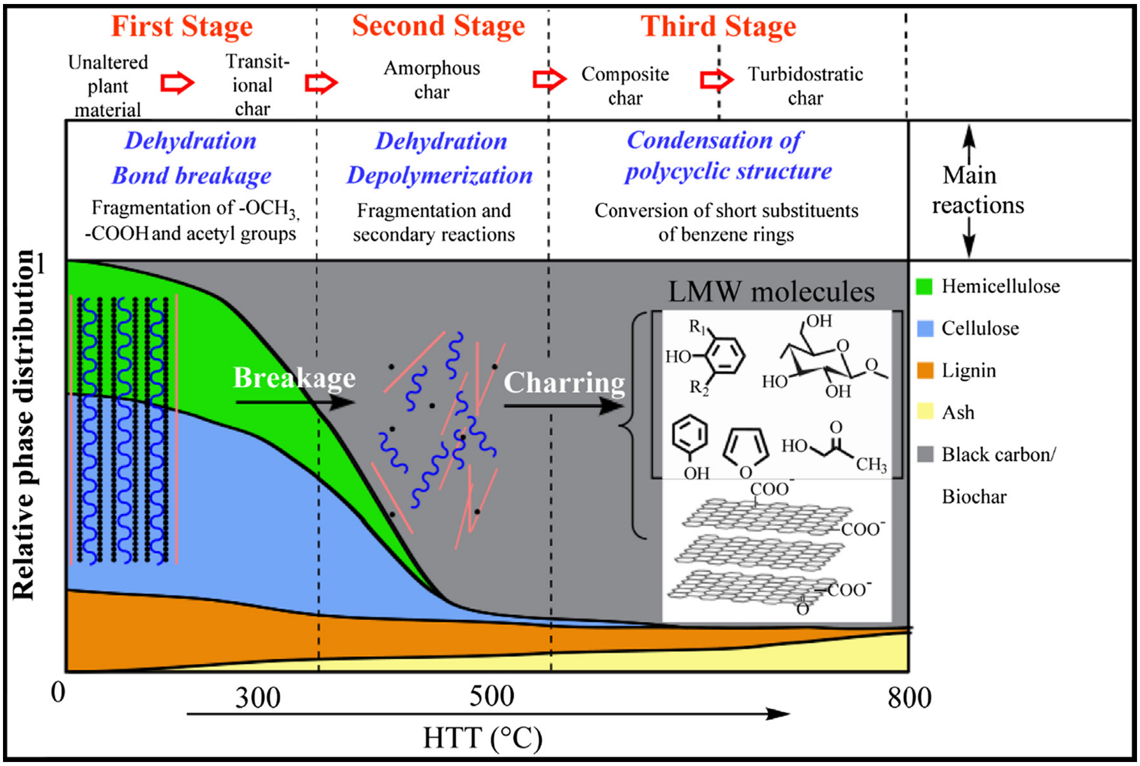


Fig. 1. The impact of increasing HTT (100–700 °C) during biomass pyrolysis on the various types of reactions. The reactions in stage one of biomass pyrolysis detail the mass loss due to water elimination, bond breakage, appearance of free radicals, and formation of carbonyl and carboxyl groups (Collard and Blin, 2014; Demirbas and Arin, 2002). The second stage entails the depolymerization, fragmentation, and secondary reactions (Van de Velden et al., 2010), which leads to maximum weight loss of the biomass feedstock (Collard and Blin, 2014). The final stage of biomass pyrolysis (i.e., very high HTT) involves the charring process, where the slow decomposition of biochar solid residues is attributable to the condensation of the polycyclic structure (i.e., benzene rings) (Collard and Blin, 2014). These structures become larger and more condensed with increasing HTT. The figure is adapted from the following references (Keiluweit et al., 2010; Lian and Xing, 2017).

free radicals (Dellinger et al., 2009), due to their persistent and stable nature in various environmental matrices (Vejerano et al., 2018). The free radicals contain a lone pair of electrons that leads to a slight attraction to a magnetic field (a feature known as paramagnetism), which is the occurrence of unpaired electrons in a material (Trubetskaya et al., 2016). This trait is measured using electron paramagnetic resonance (EPR) spectroscopy, a useful environmental analytical method to elucidate the levels and chemical compositions of free radicals, in addition to the many transition metals present in chars (Liao et al., 2014; Liu et al., 2018; Xiao et al., 2018). These adsorbing radicals react with metal centers, resulting in electron transfer, which initiates an increase in the amount of EPFRs in biochar, making them less available (Fig. 1a and b).

Previous studies have reported the presence of EPFRs on the surface of metals only in the post-flame and cooling zones of hazardous waste combustion systems (Dellinger et al., 1986; Dellinger et al., 2000; Dellinger et al., 2001; Dellinger et al., 2007); however, they have also been documented to be generated during biochar pyrolysis, due to the combinations in the feedstocks between organic contaminants or their derivatives, and transition metals (Fang et al., 2014; Fang et al., 2015a, 2017a; Lian and Xing, 2017; Tian et al., 2016). As EPFRs are generated during carbonation of organic chemicals, it is nonexceptional that biostable free radicals are generated during biochar production (Lomnicki et al., 2008a; Lomnicki et al., 2008b). EPFRs are composite organic/metal oxide pollutant particles that induce the formation of reactive oxygen species (ROS). Also referred to as biologically damaging species or activated species, they are a particular type of oxygen-centered radicals e.g., hydroxyl, hydroperoxy and superoxide anion radicals, as well as nonradical derivatives of O_2 such as alkoxyl, peroxyl/peroxy, and semiquinone radicals, along with hydrogen peroxide (Blocquet et al., 2013; Dellinger et al., 2007, 2009, 2000, 2001; Fang et al., 2017; Kelley et al., 2011, 2013; Khachatryan et al., 2011; Patterson et al., 2017, 2013; Pryor et al., 2006; Tian et al., 2009; Truong et al., 2008). Their stable nature makes them persist in the atmosphere for hours or days (Fang et al., 2014). EPFRs in biochars have also been associated with inhibition of seed germination and growth during soil amendments because biochar is capable of inducing oxidative stress (Liao et al., 2014). Oxidative stress is a condition of severe imbalance linking ROS generation and antioxidant defense mechanisms of a living organism, whereby the levels of ROS produced surpass the capacity of antioxidant defense of that organism (Khachatryan et al., 2011; Tian et al., 2009). Hence, the likelihood of EPFR production during biochar pyrolysis (charring) may have potentially adverse implications in downstream applications in agro-environmental sustainability.

It is imperative to consider EPFRs when improving the evaluation of the overall effects of biochars in the biosphere, particularly their potentially adverse impacts and various ways of mitigating these emerging contaminants (Liu et al., 2018). Furthermore, the various analytical technologies employed in measuring and assessing the negative environmental impacts of free radicals can fast track the development and adoption of high-quality biochar amendments for food safety and environmental sustainability. This review is aimed at highlighting the detailed research on EPFR production in biochars, such as their occurrences, types, environmental fate, risks, and the underlying challenges (both scientific and regulatory) of utilizing these amendments. A future outlook will be expounded on, outlining the recommendations facing this contemporary problem of the existence of EPFR in biochars.

2. Occurrence of EPFRs in biochar

The biochar pyrolysis process entails the thermal decomposition of

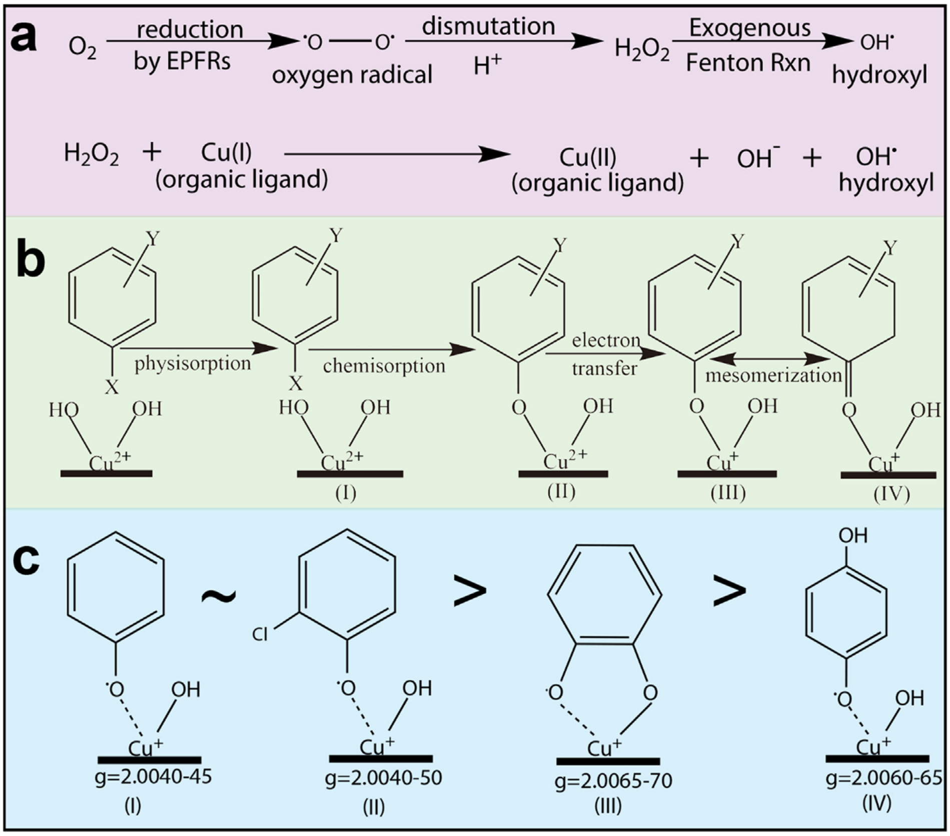


Fig. 2. (a) A schematic representation of the hydroxyl-radical-generating pathway through the exogenous Fenton reaction. It involves (1) electron transfer from EPFR to molecular oxygen, forming superoxide radical ion, and (2) hydrogen peroxide and a hydroxyl radical are produced via dismutation and Fenton reactions, respectively. Adapted from the following references: Vejerano et al. (2018) and Khachatryan and Dellinger (2011), Khachatryan et al. (2014), Khachatryan et al. (2011). (b) The lifetimes of the various free radicals in the air. (I) phenoxyl radical (II) chlorinated phenoxyl radical (III) *o*-semiquinone radical (IV) *p*-semiquinone radical. (i.e., I ~ II>III>IV). Adapted from Lomnicki et al. (2008b). (c) The conceptual mechanism of EPFR formation on a Cu(II)O surface. The combined figures are modified from the following references Lomnicki et al. (2008b)).

organic compounds in the biomass, with the carbonization conditions and feedstock type facilitating the formation of EPFRs. The parent compounds in the biomass, i.e., lignin, cellulose, and hemicellulose (Lian and Xing, 2017; Weber and Quicker, 2018), are the leading precursors controlling the generation of EPFRs in chars (Fig. 2). Cellulose and hemicellulose are decomposed into oligosaccharides through depolymerization; then, glycosidic bonds are cleaved together to form radical monomers (Zhang et al., 2013). However, the structurally dense lignin goes through an intense decomposition process involving progressive reactions of EPFRs (Kibet et al., 2012). During the pyrolysis of biochar, the radicals are formed as a result of homolytic cleavages of C–C and C–O bonds in α- and β-alkyl aryl ethers that necessitate a low amount of energy to dissociate and generate respective radicals (Kotake et al., 2013, 2014, 2015; Liu et al., 2016). Finally, the biomass undergoes dehydration, decarboxylation, aromatization, and intramolecular condensation to create black carbon (Anca-Couce, 2016; Bridgwater, 2012; Collard and Blin, 2014; Shen et al., 2015; Stefanidis et al., 2014; Wang et al., 2017; Zhao et al., 2017). The presence of EPFRs is attributable to physicochemical properties in chars, including electrical conductivity, pH, electrical charge density, calcium carbonate content, volatile and nonvolatile organic molecules, and elemental composition. These properties may differ, subject to the kind of raw materials used as feedstock, as well as the impact of the pyrolysis conditions (primarily the influence of pyrolysis temperature) on the extent of condensation during the pyrolytic process (Chintala et al., 2016). The above-mentioned features and the contaminant adsorption of EPFRs on biochar residues have led to the intensive investigation into their environmental fate and risks (Cao et al., 2009).

The charring temperature is a crucial determinant in the generation of EPFRs in biochars among all influencing pyrolytic conditions (see Table 1). Fang et al. quantified the concentration of EPFRs in biochars from several feedstocks at different temperatures, a wave of singlet signal hyperfine layout was observed (Fang et al., 2015b). Liao et al. (2014) revealed that EPFR signals were not detected in the subsequent feedstock that did not undergo the charring process, confirming that EPFRs are only produced during the biomass pyrolysis stage. In another study, Ulmschneider and Stegmann pointed out a sharp rise in the concentration of EPFRs with intensified carbonization temperature of the feedstock (Ulmschneider and Stegmann, 1980). An essential parameter is the isotropic g-factor signal of EPR useful in the identification of the types of EPFRs generated in black carbon, as reported in the cited studies (Dellinger et al., 2000; Hales and Case, 1981; Di Valentin et al., 2006; Wang et al., 2019). The g-factors decrease with rising pyrolyzing temperature (Fang et al., 2014; Liao et al., 2014); thus, oxygen-centered radicals are prevalent at low pyrolysis temperatures, while the carbon-centered types predominate at higher charring temperatures. More importantly, while the charring temperature plays an essential part in EPFR formation in biochars, the environmental persistence and stable nature of these bioactive radicals are attributed to their association with the surfaces of biochar residues, making them last for several days.

The influence of the type of biomass used and the charring temperatures on EPFR generation in biochar has been recently studied (Table 1). Fang et al. detected EPFRs produced in biochar residues by thermal decomposition of pine needle, wheat straws, and maize straw at various pyrolytic temperatures ranging from 300 to 550 °C (Fang et al., 2014). In another study, Fang and his colleagues investigated EPFR concentrations at various pyrolysis temperatures and time, which rose steadily for P300 and P400, whereas the EPFR levels in P500 and P600 decreased progressively with increase in pyrolysis time (Fang et al., 2015a). Qin et al. pyrolyzed chars at 300–700 °C using cow manure and rice husks (R), whereby the relative order of EPFR levels in the chars was R-300>C-300>C-700>R-700 (Qin et al., 2016). Furthermore, their study indicated that EPFR concentrations in R300 to R500 rose from 2.77×10^{18} spins g^{-1} to 17.10×10^{18} spins g^{-1}, respectively. However, the EPFR levels decreased further from 17.10×10^{18} spins to 0.16×10^{18} spins for R-500-R-700. The increase in charring temperatures facilitated the decomposition of phenolic compounds in the biomass, and, in the process, EPFRs are broken down, thus reducing

Table 1

Chemical phases during the thermal decomposition of biomass.

Stages of biochar pyrolysis	Types of chars	Char processes	Likely EPFRs produced in chars*
First stage	Transition char (HTT $< \sim 300\,^{\circ}C$)	A carbonization step comprised of a crystalline matrix of the unaltered plant biomass (mostly preserved.) However, mass loss occurs due to water elimination, bond breakage, appearance of free radicals, and formation of carbonyl and carboxyl groups (Collard and Blin 2014; Demirbas and Arin 2002)	Little or no free radical production in biochar pyrolysis at temperatures of $\leq 200\,^{\circ}C$
Second stage	Amorphous char stage ($\sim 300\,^{\circ}C < HTT < \sim 500\,^{\circ}C$)	This stage is generally constituted by heat-resistant aliphatic and (poly) aromatic carbon structures in a disorderly composition. It entails the depolymerization, fragmentation and secondary reactions (Van de Velden et al. 2010), which lead to maximum weight loss of the biomass feedstock (Collard and Blin 2014)	Oxygen- and oxygenated carbon-centered radicals are generated during this stage
Third stage	Composite char ($\sim 500\,^{\circ}C < HTT < \sim 700\,^{\circ}C$)	A pyrolysis step containing a combination of amorphous phase and progressive production of graphene crystalline structures	Drastic EPFR reduction during char formation. Carbon- and oxygenated carbon-centered radicals produced in this stage
	Turbostratic char (HTT $> 700\,^{\circ}C$)	A stage dominated by the stacking of graphene sheets (at very high HTT.) This involves the charring process, where the slow decomposition of biochar solid residues is attributable to the condensation of the polycyclic structure (i.e., benzene rings) (Collard and Blin 2014). These structures become larger and more condensed with increasing HTT	Little to no EPFR formation. (mainly oxygenated carbon-centered radical formation.)

Information on the biochar stages adapted from the following references Keiluweit et al. (2010), Lian and Xing (2017), while the likely generated EPFRs during biochar pyrolysis are inferred from the reported studies (Fang et al. 2014; Fang et al., 2015; Qin et al., 2018). However, the suggested EPFRs are not finite, as the biomass feedstock types and pyrolysis settings may influence the category and rate of EPFR formation. Abbreviations: EPFRs (Environmentally persistent free radicals); HTT (highest treatment temperature).

their concentration (Qin et al., 2017b). The EPFR signals decreased significantly at elevated pyrolysis temperature in biochar production. These cited findings show that the biomass type and pyrolytic temperatures have a great influence on EPFR formation and large-scale utilization of biochar, as those EPFR-contaminated biochars residues from various biomasses progress into agricultural ecosystems.

3. Formation and types of EPFRs in biochars

The formation conditions and types of EPFRs produced during biochar pyrolysis have been expounded in previous research articles and reviews, which have highlighted the impact of the highly variable synthesis methods, diverse precursors, and complex reaction processes (Ruan et al., 2018, 2019). Transition metals and substituted aromatics influence the formation of EPFRs in various environmental niches. Numerous studies have used different types of silica (hematite, goethite, magnetite, smectite, and montmorillonite) coated with multiple halogen- or hydroxyl-substituted aromatics and transition metals oxides (such as Al_2O_3, Fe_2O_3, Fe_3O_4 CuO, ZnO, MnO, and NiO) to serve as model particles for revealing the formation mechanisms and types of EPFRs (Kiruri et al., 2014; Li et al., 2014; Lomnicki et al., 2008b; Patterson et al., 2017; Vejerano et al., 2011; Vejerano et al., 2012b; Yang et al., 2017). In brief, depending on the type of precursor organic fractions in the biomass, the possible formation mechanisms include initial photodegradation/ physisorption, then chemisorption via elimination of water or hydrogen chloride, before the eventual single electron transfer from substituted aromatics to the transition metal centers (Dellinger et al., 2007; Jia et al., 2012; Xu et al., 2019). This leads to the simultaneous reduction of metal and EPFR generation and stability in biochar residues, owing to the synergy of metals and aromatic compounds (Lomnicki et al., 2008b).

3.1. Biochar pyrolysis conditions leading to EPFR formation

Lignocellulose (lignin, cellulose, and hemicellulose) degradation commences at pyrolysis temperatures of just above 120 °C, which is subjected to the char- and gas formation pathway at heat treatment temperatures below 300 °C (Ruan et al., 2018, 2019). The homolytic bond cleavage process instigates a free-radical formation process in biochars. EPFRs are primarily created through the thermal activity on the oxygen atom and inorganic substances in the feedstock. A further supply of free radicals may emanate from low atmospheric O_2 levels that may occur during the infancy period of biomass pyrolysis (Pan et al., 2019; Trubetskaya et al., 2018). Also, carboxyl and carbonyl groups are produced and subsequently broken down to produce CO_2 and CO during the charring process (Brennan et al., 2001; Shafizadeh, 1982). From the partial decomposition of biochar constituents such as lignin and cellulose, the formation of likely precursor compounds like hydroquinone, catechol, and phenol are the progenitors of phenoxyl, cyclopentadienyl and semiquinone-type radicals (Adounkpe et al., 2009; Khachatryan et al., 2010a; Khachatryan et al., 2008a; Khachatryan et al., 2006; Khachatryan et al., 2004). In the pyrolysis of cellulose, three formation mechanisms (i.e., glucose intermediate, free-radical mechanism, and ionic mechanism) are postulated in the production of levoglucosan (which is generated at > 300 °C), either as an intermediate or final product (Fang et al., 2017). Moreover, the highly dangerous polyaromatic hydrocarbons (PAHs), which are associated with human health deficits i.e., carcinogenic and toxic disorders (Roslund et al., 2019), are formed during biochar production process through lignocellulose degradation (Freddo et al., 2012; Matheson and Tratnyek, 1994; Oleszczuk et al., 2013; Parajuli et al., 2017; Vejerano et al., 2013). PAH formation occurs in the unimolecular reaction pathways, e.g., dealkylation, dehydrogenation, cyclization, aromatization, and/or radical reactions (Kuśmierz and Oleszczuk, 2014). Finally, the dehydration reactions result in water loss in the residues, as some PAHs may materialize into free-radical fractions that may recombine in various forms with each other and with the biomass materials to produce an EPFR-polluted biochar residue (Kuśmierz and Oleszczuk, 2014).

3.2. Phases of biochar pyrolysis that induce the generation of EPFRs

The physicochemical features of the raw materials used will have a direct impact on the final composition of the produced biochars, as well as the formation of EPFRs. Fig. 2 and Table 1 details the impact of the rising HTT on the aspects of the biochar production process, i.e., charring activity, the reactions involved, and the evolution of the different phases (Keiluweit et al., 2010). At high temperatures (> 120 °C), organic materials in biomass initiate the thermal decomposition process, resulting in the loss of chemically bound moisture. The rising HTT leads to the breakdown of hemicellulose, cellulose, and lignin at temperatures (HTT) ranging between 200–260 °C, 240–350 °C, and 280–500 °C, respectively (Sjostrom, 1993). However, these HTT ranges differ with Yang et al., who utilized pure forms of hemicellulose, cellulose, and lignin, with their respective heating temperatures during the thermal decomposition ranging from 220–315 °C, 315–400 °C, and 160–900 °C (Yang et al., 2007). According to Lian and Xing (2017), charring is a complex physicochemical activity influenced by the pyrolysis mechanisms of the primary feedstock components (cellulose, hemicellulose, and lignin), the interactions between these constituents, and the impacts of the intrinsic inorganic species like the alkali and alkaline earth metals. These parameters show that the biomass feedstock type and pyrolysis conditions greatly induce the final structure of biochars, and the formation of EPFRs.

The phase transitions in biochar pyrolysis are quantitatively characterized by two critical parameters, as pointed out by Lian and Xing (2017). Aromaticity of chars is a property relating to the total proportion of aromatic carbon phase (i.e., the amorphous and condensed C) in biochars (Wiedemeier et al., 2015). The degree of aromatic condensation is a parameter of evaluating only on the basis of the proportion of condensed aromatic C in the thermosequence of biomass (McBeath et al., 2011). An important factor in EPFR formation is the presence of transition metals, which may significantly impact on biochar formation, especially in the conversion of aliphatic C into aromatic C, the size of the aromatic groups, the degree of graphitization, and the species and distribution of these metals in chars (Lian and Xing, 2017). Furthermore, the produced and stabilized EPFRs formed during the latter stages of biomass pyrolysis may have significant outcomes on the environmental functionality of biochar residues in ecosystems such as crop production (Liao et al., 2014) and organopollutant detoxification (Fang et al., 2014). Hence, considerable awareness is warranted on the impacts of charring settings and composition feedstock structure on the formation, characteristics, and reactivity of EPFRs in biochars.

3.3. *Stages of EPFR formation during biomass carbonization*

The chemistry of formation of EPFRs in the pyrolysis stage of biochar has recently been well illuminated (see Fig. 3; I and II). As mentioned earlier, the most well-known contributing factor to EPFR formation in biochar residues in the environment is the presence of the transition metals. These transient metals undergo complexation with EPFRs via electron transfer before the subsequent stabilization of the free radicals (Assaf et al., 2016; Li et al., 2014). As expounded by Ruan et al. (2019b), the generation of EPFRs may occur in three stages. First, the adsorption of precursor molecules (containing substituted aromatic compounds like phenolics) occurs on the surface of the metal oxide via physisorption. Secondly, chemisorption (or chemical adsorption) between organic precursor molecules and the particles containing transition metals form strong bonds between phenolic and metal oxide by removing water in the HCL molecules (Heringa et al., 2011; Joseph et al., 2010; Kiruri et al., 2013). In lignin carbonation, the resultant chemisorption of oxygen by the high radical content is due to the depolymerization of the organic molecules (Bourke et al., 2007), bringing about a spontaneous pyrolysis of biochars at low temperatures (< 100 °C) (Kiruri et al., 2013). Finally, the unpaired electrons on the transition metal get transferred on the precursor molecules forming EPFRs (Khachatryan and Dellinger, 2011; Khachatryan et al., 2014).

Liao et al. investigated the two stages of pyrolysis at a charring temperature of 200 °C in order to elucidate the stages of EPFR formation in biochar (Liao et al., 2014). The cleavage of the biomass structure during carbonization resulted in the breakup of chemical bonds, which promoted EPFR generation. Therefore, the formation of EPFRs in biochars from biochar carbonization is mainly a product of the pyrolysis conditions (charring temperature and time) and the component of the biomass materials (e.g., the type of transition metals present). The generated EPFRs may also join to the finer biochar residues, i.e., inorganic impurities either through adopting biochar amendments in farmlands may also combine with particulate matter (PM) or from emissions of biochar production (Feld-Cook et al., 2017). These particulates are complex mixtures of gaseous organic and inorganic fractions, combined with the EPFR-polluted finer biochar residues (Feld-Cook et al., 2017). This has led to the identification of combustion-generated EPFRs in airborne settings, namely; coarse PM_{10} (≤ 10 µm); fine $PM_{2.5}$ (≤ 2.5 µm); and ultrafine $PM_{0.1}$ (≤ 0.1 µm) (Dellinger et al., 2000; Dellinger et al., 2001). The ultrafine particles make up $> 70\%$ of the overall particulates (Fahmy et al., 2010; Khachatryan et al., 2010b). The EPFRs in PM are capable of generating ROS, which initiates their capacity to stimulate the oxidation of biomolecules *in vitro* (Khachatryan et al., 2008a). The formation of ROS is due to the Fenton-type reactions on the particulate surface, whereby the interactions between EPFRs and transition metal contents in PM may cause ROS production via the redox cycle (Fahmy et al., 2010). EPFRs can also be potentially misidentified as molecular pollutants in particulate matter, due to their property as precursors in the formation of organopollutants (Truong et al., 2010). For instance, in haze-associated atmospheric PM in Beijing China, the levels and particle-size distributions of free radicals have been reported, including an unstructured single signal of persistent semiquinone radicals identified via EPR (Yang et al., 2017). Properties such as the similar structural features to organic pollutant precursors point towards the hazardous nature of EPFRs in PM as a result of their stability and persistence in fine airborne particles.

3.4. *Types and properties of EPFRs*

Free radicals are designated as either carbon-, oxygen-, nitrogen- or metal-centered radicals, depending upon the core atom that possesses the unpaired electron (International Union of Pure and Applied Chemistry, 2014). In biochar residues, the main types of generated EPFRs, as detailed in Tables 2 and 3, are classified into oxygen-, carbon-, and oxygenated carbon-centered radicals (dela Cruz et al., 2011; Gehling and Dellinger, 2013; Gehling et al., 2014; Tian et al., 2009). Examples of these stable bioreactive radicals are hydroxyl, superoxide, hydrogen peroxide, alkyl peroxy (or alkyl peroxyl or peroxy), ortho-semiquinone (or *o*-semiquinone), para-semiquinone (or *p*-semiquinone), benzosemiquinone, phenoxy (e.g., chlorophenoxy radicals such as 2-chlorophenoxy), phenoxyl (e.g., 2,4-dichlorophenoxyl radical or $DCP^{\bullet}$), catechol-type radicals (ipso-catechol and α-catechol) and phenyl radicals (Carlier et al., 1984; dela Cruz et al., 2012; Dellinger et al., 2000; Farquar et al., 2003; Hales, 1975; Khachatryan et al., 2004; Khachatryan et al., 1982; Lomnicki and Dellinger, 2003; Mosallanejad et al., 2016). In terms of their stable behavior, the oxygen-centered species (e.g., semiquinone-type radicals) are stable in the air (Khachatryan et al., 2008b), while carbon-centered radicals (e.g., cyclopentadienyls) are vulnerable to oxidation in the atmosphere (Ruan et al., 2019; Tian et al., 2009). From the significant precursor lignin, EPFRs like cyclopentadienyl, phenoxyl, and semiquinone types are formed from phenolic precursors (Dellinger et al., 2009). Therefore, EPFRs portray the following properties to reach environmentally significant concentrations, as reported by McFerrin et al. (2008). These are:

- a molecular precursor and beneficial formation pathway;
- a stable property, whereby the free radical can resist decomposition;
- and a low-reactive feature, i.e., the ability to resist reaction with other molecular or radical species.

In summary, three key aspects have been described in EPFR generation in biochars. One, the postulated mechanisms of EPFR generation in biochars are photodegradation/ physisorption, chemisorption, and single electron transfer (Dellinger et al., 2007; Ruan et al., 2019). Two, the g-values of the EPR spectra is a useful measure to classify a radical as either carbon-centered or oxygen-centered, i.e., the nearer

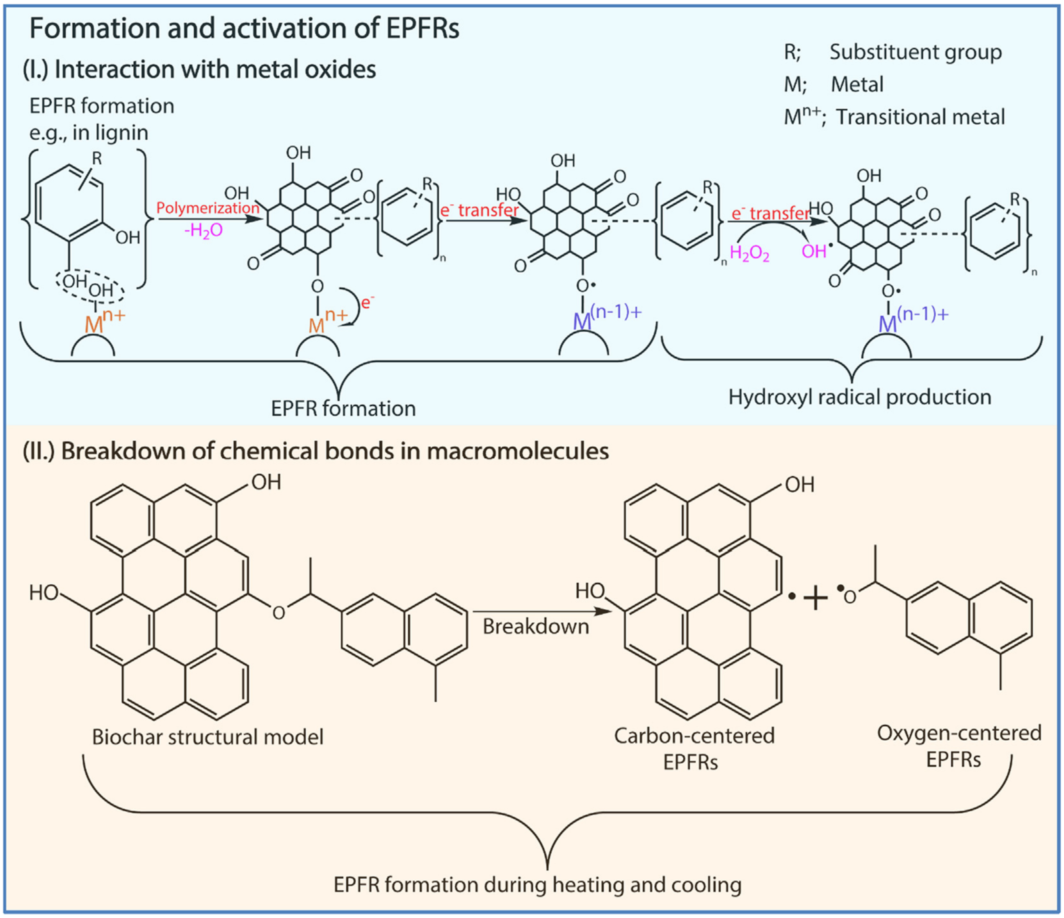


Fig. 3. Diagrammatic representation of the mechanisms of EPFR formation and free radical generation on biochar. The two-step process includes: (I) the interaction between organic compounds containing oxygen functional groups and metal oxidation, and (II) the breaking of chemical bonds in macromolecules during heating and cooling. The figure is modified from the following references Fang et al. (2014), Liao et al. (2014), Zhu et al. (2017).

the free electron is to the adjacent oxygen atom, the higher the g-value (Herring et al., 2013). Three, the continued increase in pyrolysis temperature (> 700 °C) and time may eventually lead to the decomposition of the phenolic compounds, which reduces the parent compounds taking part in EPFR formation (Khachatryan et al., 2016; Lomnicki et al., 2008a; Lomnicki et al., 2008b; Qin et al., 2017b; Vejerano et al., 2012b). A high temperature range gives rise to the cleavage and re-organization of the organic structures, thus, eliminating the free radicals. Thus, the stability and persistence properties of EPFRs are ascribed to these facets, which enhances the synergy between transition metals and aromatic compounds formed during biochar production.

4. Half-lives and persistence of EPFRs

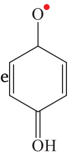
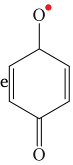
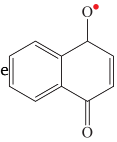
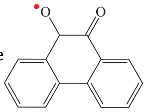
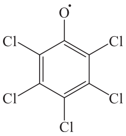
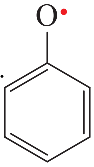
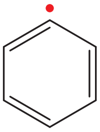
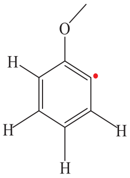
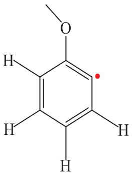
As EPFRs are thermally active, they may have half-lives ranging from a few hours to several days in the atmospheric conditions, and perpetually under vacuum (Kiruri et al., 2014; Lomnicki et al., 2008b; Vejerano et al., 2011). Typically, the EPFRs generated on the solid

Table 2
Concentrations, *g*-factors and line widths of EPFRs in biochar samples at different pyrolysis temperatures.

Sample	Type of feedstock	g-factor	Line width	EPFR conc. (10^{18} spins/g)	EPFR type(s)	References
P300	Pine needles biomass	2.0044 ± 0.0003	7.2 ± 0.1	5.38 ± 0.02	Oxygen-centered	Fang et al. (2015)
P350	Pine needles biomass	2.0034 ± 0.0001	6.6 ± 0.1	1.96 ± 0.01	Oxygenated carbon-centered	
P550	Pine needles biomass	2.0028 ± 0.0002	4.5 ± 0.2	13.7 ± 0.06	Carbon-centered	
P400	Pine needles biomass	2.0037 ± 0.0001	6.8 ± 0.2	15.2 ± 0.03	Oxygenated carbon-centered	
P500	Pine needles biomass	2.0032 ± 0.0001	6.5 ± 0.2	22.3 ± 0.04	Oxygenated carbon-centered	
W300	Wheat straw biomass	2.0036 ± 0.0001	6.5 ± 0.1	7.72 ± 0.05	Oxygenated carbon-centered	
W400	Wheat straw biomass	2.0030 ± 0.0002	5.0 ± 0.2	16.5 ± 0.09	Oxygenated carbon-centered	
W500	Wheat straw biomass	2.0029 ± 0.0001	4.8 ± 0.1	28.6 ± 0.12	Carbon-centered	
M300	Maize straw biomass	2.0037 ± 0.0001	6.8 ± 0.3	3.88 ± 0.08	Oxygenated carbon-centered	
M400	Maize straw biomass	2.0031 ± 0.0002	6.2 ± 0.2	6.25 ± 0.12	Oxygenated carbon-centered	
M500	Maize straw biomass	2.0029 ± 0.0002	5.2 ± 0.1	30.2 ± 0.09	Oxygenated carbon-centered	
C300	Cow manure biomass	2.0046 ± 0.0001	2.20 ± 0.01	7.1 ± 0.1	Oxygen-centered	Fang et al. (2014)
C700	Cow manure biomass	2.0036 ± 0.0002	0.95 ± 0.06	3.4 ± 0.1	Oxygenated carbon-centered	
R300	Rice husk biomass	2.0041 ± 0.0001	2.77 ± 0.05	6.9 ± 0.1	Oxygen-centered	Qin et al. (2018)
R700	Rice husk biomass	2.0036 ± 0.0001	0.16 ± 0.09	1.8 ± 0.1	Oxygenated carbon-centered	

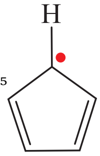
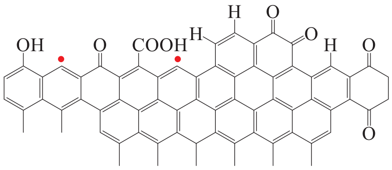
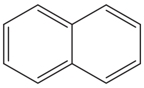
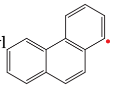
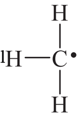
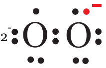
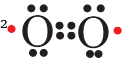
Values represent the pyrolyzed feedstock at indicated temperatures.

Table 3
The various types, properties and environmental impacts of free radicals in biochars (EPFRs and ROS).

Types of EPFRs	Examples of EPFRs	Chemical formula and/or structure/Lewis electronic configuration	g-factor	Properties	Reference
(A.) Environmentally persistent free radicals (EPFRs) or resonance-stabilized radicals					
Oxygen-centered radicals ● Semiquinone species	*o*-Semiquinone (*ortho*-semiquinone), *p*-semiquinone (*para*-semiquinone), *ipso*-catechol, hydroquinone, 1,4-benzoquinone, 1,4-naphthoquinone and 9,10-phenanthrene quinone radicals	Hydroquinone  1,4-benzoquinone  1,4-naphthoquinone  9,10-phenanthrene quinone 	>2.0045	● They are derived from the reaction of phenolic compounds with reactive radicals (e.g., from hydroxyquinone precursor).	Dellinger et al. (2000), Khachatryan et al. (2010), Ulmschneider and Stegmann (1980), Wang et al. (2019)
Oxygenated carbon-centered radicals	*Phenoxy-derived species:* Phenoxyl radical (e.g., pentachlorophenoxyl radicals) (PCP-O$^{\bullet}$) Phenoxy radical Phenyl radical 2-hydroxyphenyl radical	$C_6Cl_5O^{\bullet}$  $C_6H_5O^{\bullet}$  $C_6H_5^{\bullet}$  $^{\bullet}C_6H_4$-OH  	2.0030–2.0040	● Phenoxy radicals are defined as monovalent oxygen radical species (which can be formed formally from phenols by homolysis of the O-H bond) ● Phenyl radicals are derived from benzene and are part of the isolated phenyl groups. They are also the parent compounds of aryl radicals (the reactive intermediates obtained from an arene compound incorporating one free radical carbon atom as part of the ring structure) ● In general, many of these phenols form relatively stable free radicals. Plus, both these phenols and their phenoxy radicals are significant in the autoxidation inhibition of organic substances.	Altwicker (1967), Dai et al. (2005),; dela Cruz (2012b), Dellinger et al. (2000), Nagata et al. (2004), Ruan et al. (2019), Terzian et al. (1991), Williams (1969)

(*continued on next page*)

Table 3 (*continued*)

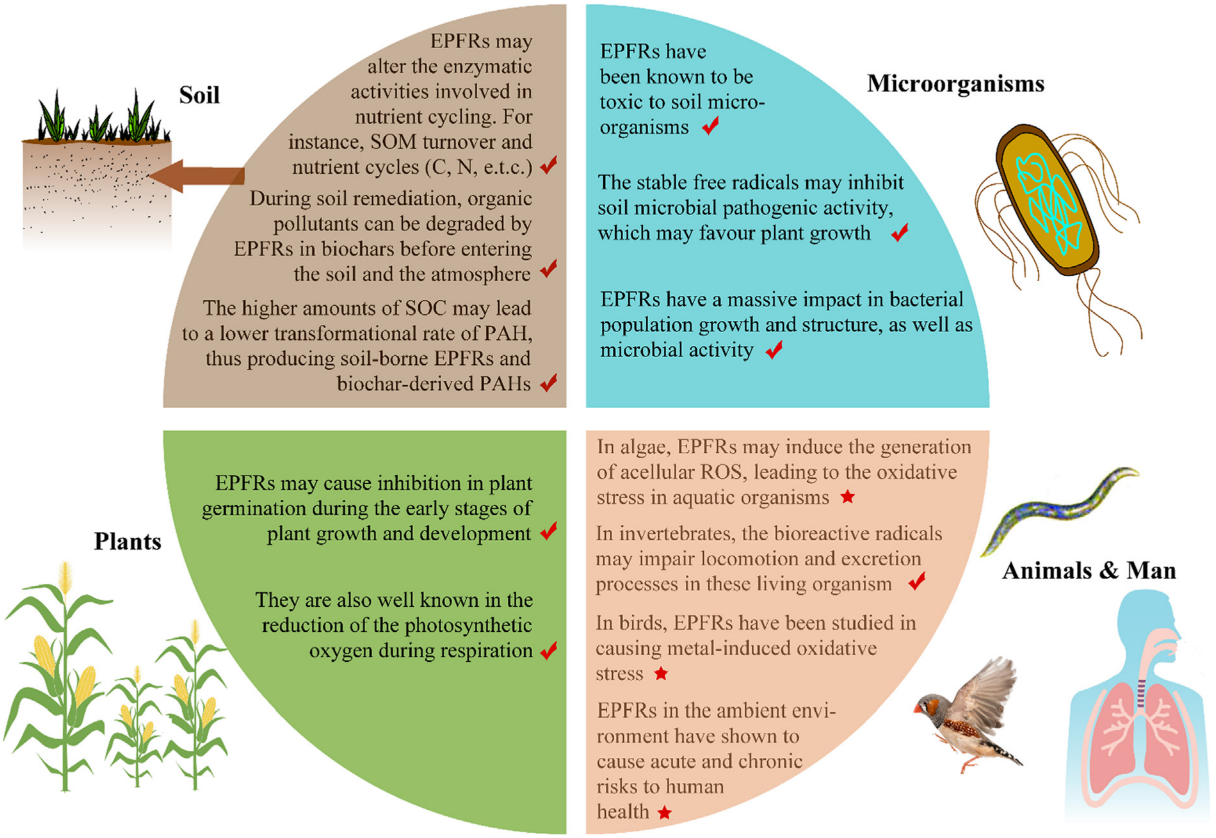
Types of EPFRs	Examples of EPFRs	Chemical formula and/or structure/Lewis electronic configuration	g-factor	Properties	Reference
Carbon-centered radicals	Aromatic radicals (cyclopentadienyl radical)	$^{\bullet}C_5H_5$ 	< 2.0030	● They are dominant (highly stable) at higher pyrolysis temperatures. ● They are potent reducing agents that can combine with Oxygen to induce the formation of ROS (Stohs and Bagchi 1995),	Barrière and Downdard (2008), dela Cruz et al. (2012, 2011), Dellinger et al. (2000), Pryor et al. (1983), Pryor et al. (1998), Richter et al. (2000), Richter and Howard (2000), Truong et al. (2008), Di Valentin et al. (2006)
	Graphitic carbon	Graphitic carbon (edge plane) 	2.0028		
	PAH radicals	1-naphthyl  1-phenanthryl 	~2.0026		
	Alkyl radicals	methyl radical  $H-\overset{H}{\underset{H}{C}}{}^{\bullet}$			
(B.) Reactive Oxygen Species (ROS) or transient free radicals					
Oxygen-centered radicals	Hydroxyl radical	$OH^{\bullet}$ 	> 2.0040	● These oxygen-centered species induce oxidative stress. ● They are stable for hours or days in the atmosphere. ● In plants, these radicals are capable of inhibiting seed germination and growth when incorporated into soil amendments. ● They are dominant at low pyrolysis temperature	Dellinger et al. (2000)
	Superoxide radical	$\cdot O_2$ 			
	hydrogen peroxide radical	$O_2^{\bullet -2}$ 			

particle surface tend to have intense interactions with particulates due to steric hindrance, which enhances the stability of the created free radicals (Petrakis and Grandy, 1978; Petrakis and Grandy, 1983). However, these commonly existing bioreactive radicals have short half-lives, ranging from 10^{-9}–10^{-4} s, i.e., OH·. Dellinger's group have done in-depth studies into the relatively long-lasting free radicals, which are similar to EPFRs (Lomnicki et al., 2008a; Lomnicki et al., 2008b; Vejerano et al., 2011; Vejerano et al., 2012b; Vejerano et al. 2012c). The stable property of bioreactive free radicals is due to their long-term occurrence on the airborne particulate surfaces (Stephenson et al., 2016), as a result of redox reactions taking place at atmospheric conditions (Nwosu et al., 2016). This shows that the half-lives of EPFRs are no longer compared to free radicals since EPFRs from biochar production are stabilized on the surfaces of transition metals and can also persist in the atmospheric environment (Vejerano et al., 2018).

It has been shown that in the comparisons of the EPR signals of various biopolymers such as lignin, cellulose, and biomass, a similar EPFR spectrum was observed in biomass while cellulose and lignin had varied EPFRs due to the differences in the aromatic structure. EPFR stability and persistence in biochar are also determined by the metals to which the EPFR is bound (Kiruri et al., 2014). Among the transition metals, ZnO has the most extended half-life ranging from 3 to 73 days (Vejerano et al., 2012a). The EPFR on ZnO can translate to almost a year-long persistence (Kiruri et al., 2014; Vejerano et al., 2012a; Vejerano et al., 2018). Therefore, the stability of EPFRs is associated with their ability to accept electrons and reduction potential of the metals. EPFRs display either fast decay, slow decay, or no decay (see Fig. 1c); for instance, phenoxy-type radicals decay faster, while semiquinone radicals decay slowly (Gehling and Dellinger, 2013). Therefore, the rate of decay depends on their reactions with molecular oxygen in the atmosphere.

5. Environmental fate and risks associated with EPFRs

The generating of EPFRs is well known in the production of ROS useful in the removal of organopollutants from contaminated soils and activated sludges. They are also used as a reductant of heavy metals ions because of their higher redox capacity, in addition to their utilization as electron scavengers (International Journal of Radiation Biology, 1992; Fang et al., 2013; Fang et al., 2014; Xu et al., 2019; Yuan et al., 2017; Zhao et al., 2018). Regardless of these advantages, the implication that the ability of EPFRs in producing activated species in PM may contribute to long-term impacts in biological systems. As seen in Fig. 4, EPFRs have been reported in inducing oxidative stress, DNA damage and carcinogenicity (Balakrishna et al., 2009; Burn and Varner, 2015; dela Cruz et al., 2012; dela Cruz et al., 2014; Lee et al., 2014; Reed et al., 2011; Reed et al., 2014; Reed et al., 2015a). Below are the possible and confirmed impacts of EPFRs in biochars that lead to the



EPFRs may alter the enzymatic activities involved in nutrient cycling. For instance, SOM turnover and nutrient cycles (C, N, e.t.c.) ✓

During soil remediation, organic pollutants can be degraded by EPFRs in biochars before entering the soil and the atmosphere ✓

The higher amounts of SOC may lead to a lower transformational rate of PAH, thus producing soil-borne EPFRs and biochar-derived PAHs ✓

EPFRs have been known to be toxic to soil micro-organisms ✓

The stable free radicals may inhibit soil microbial pathogenic activity, which may favour plant growth ✓

EPFRs have a massive impact in bacterial population growth and structure, as well as microbial activity ✓

EPFRs may cause inhibition in plant germination during the early stages of plant growth and development ✓

They are also well known in the reduction of the photosynthetic oxygen during respiration ✓

In algae, EPFRs may induce the generation of acellular ROS, leading to the oxidative stress in aquatic organisms ★

In invertebrates, the bioreactive radicals may impair locomotion and excretion processes in these living organism ✓

In birds, EPFRs have been studied in causing metal-induced oxidative stress ★

EPFRs in the ambient environment have shown to cause acute and chronic risks to human health ★

Fig. 4. Diagrammatic representation of EPFRs effects on soil, flora, and fauna (microbes and higher-level living organisms). The symbols √ and * represent the impacts from either confirmed studies of biochar-related EPFRs or inferred from investigations into non-biochar EPFRs (i.e., combustion-generated PM), respectively.

environmental fates in various parts of the biosphere (i.e., soil, plants, other living organisms, and man).

5.1. Impact of biochar-borne EPFRs in soils

In soil amendments and wastewater treatment system applications, biochars are transported in soil matrixes via decomposition, runoff, and infiltration. Biogeochemical cycle processes may occur in the interfaces between soils/sediments and biochars, or with the aqueous phase interactions with biochar. The prevalent processes are sorption/desorption, transformation by ecological elements, and their relationships with plant roots, microorganisms, and soil organic matter/minerals (International Journal of Radiation Biology, 1992). Thus, the organic chemicals in soluble biochars may take part in a broad arraay of biological and chemical redox and metal complexation reactions in both soils and the rhizosphere (Gomez-Eyles et al., 2013). In this way, these organic compounds influence the abovementioned essential biogeochemical processes along the soil-microbe-plant continuum, namely microbial ecology and function, nutrient cycling, root uptake of nutrients, and free radical scavenging (Elad et al., 2012; Graber et al., 2013; Husson, 2013). All of these can have significant impacts (whether positive or negative) on plant responses to the environment.

Furthermore, as phenolic compounds act as antioxidants due to their scavenging nature towards the stable bioreactive radicals, they terminate the oxidative chain reaction accountable for soil organic matter (SOM) degradation (Rimmer, 2006). Some biochar constituents (i.e., volatile organic compounds and free radicals) significantly impact activities of microbes, restructure the soil microbial community, and alter the enzymatic actions in the soil that induces numerous key biogeochemical processes such as SOM turnover, along with N, P, and S cycling (Spokas et al., 2011; Zhu et al., 2017). The catalysis by EPFRs in black carbon stimulates the occurrence of activated species which stimulates the microbial biotransformation and detoxification of environmental pollutants (Oh et al., 2013a). As seen in Fig. 3I, this catalysis occurs through the formed EPFRs on biochar residues, which substitute the reactional groups on the surfaces of metal oxides with aromatic compounds, with the metal oxides themselves being reduced (Balakrishna et al., 2009; Doong et al., 2014; Fang et al., 2014; Zhu et al., 2017). The chemical bonds in the macromolecules are then broken down, as observed in Fig. 3II (Dellinger et al., 2007; Liao et al., 2014). However, the induced reactions by EPFRs may alter the microbial community structure due to the transfer of electrons among the char surfaces and microbial cells during contaminant remediation, which may trigger potential toxicity to some soil microorganisms (Fang et al., 2015a; Truong et al., 2010; Yang et al., 2016; Yu et al., 2015; Zhu et al., 2017).

Low pyrolysis temperatures in biochar manufacture can induce EPFR production, which may impact the biogeochemical processes in both the lithosphere and biosphere during soil remediation. dela Cruz et al. (2012) reported that using low temperature thermal desorption for the rehabilitation of polluted soils (containing pentachlorophenol) influenced the generation and persistence of EPFRs. Therefore, the protracted half-lives of free radicals related to PM discharged from thermal rehabilitation processes may result in human exposure. They may also be transferred into the atmosphere, thus, ultimately contributing to atmospheric reactions. This means that the simple detection of these harmful bioactive free radicals existing in the thermal treatment systems should be considered during the designing stage of the systems for soil decontamination of hazardous materials that can generate free radicals. Though thermal treatment techniques have an average temperature of above 100 °C, some particulates will go along the flow paths that have reduced times and temperatures (Joseph et al., 2010).

The transformational impact of EPFR-contaminated biochars may be two-fold, i.e., redox impact on the rhizosphere and PAH transformational impact. In the case of their redox impact, the converted biomass into biochar residues is still thermodynamically volatile in oxidative conditions of various soil surfaces, which may bring about the presence of EPFRs in biochars, with the EPFR values hinging on the pyrolysis process situations (Feng et al., 2004; Joseph et al. 2010a). Therefore, the presence of the stable bioreactive radicals intensifies the oxidation reactions, especially to the point of being pyrophoric (Amonette and Joseph, 2009). Also, biochar may alter the complex redox potential existing in the rhizosphere, which changes the reactions involving free radicals on their exteriors. The rhizospheric zone consists of an essential redox interface, as the reductive and oxidative environs are closely connected to each another (Bartlett, 1999). These reactions include C, N, and S transformations, which entail reactions with Fe and Mn species (the metal surfaces binding to EPFRs). A study by Jia et al. drew attention to the influence of PAH-contaminated biochars in the transformation of PAHs in soils, resulting in the production and persistence of EPFRs, such that the increased aromaticity may result in the increased stability of EPFRs (Jia et al., 2019). They observed that a higher amount of organic carbon in the soil led to a lower transformational rate of anthracene, with the produced stable EPFRs present in the long-term. The resultant PAH transformations in such soils may be a causative feature of biochar-borne PAHs, which bring about the formation and stability of EPFRs (Jia et al., 2019). Biochar may alter the C availability for the microorganisms soils, which, along with the catalytic reduction with minerals or radicals and adsorption of NH_3, may change the dominant role(s), fungal or bacterial communities may play in greenhouse gas production (Lehmann et al., 2011). This dual impact of EPFRs via pyrolysis conditions and contaminant types emanating in the biochar residues may be a potential long-term risk to the participants residing in or utilizing the soil, a valuable but under-protected environmental resource.

5.2. Impact of biochar-borne EPFRs in flora

In plant growth and establishment, EPFRs in biochar has been associated with inhibitive traits in plant germination and survival (Lian and Xing, 2017; Liao et al., 2014). This trait was investigated by Liao et al., who produced biochar from wheat, corn, and rice straws at 200 °C, 300 °C, 400 °C, and 500 °C (Liao et al., 2014). Rice straw chars at 500 °C were utilized in germination tests to evaluate the root and shoot lengths of wheat, rice, and corn seedlings, which depicted retarded growth. Moreover, the cell membranes exposed to biochar with high intensity of EPFRs were damaged, which portrayed the inhibitive effects of free radicals on seedlings, with the EPFR-generated ROS reacting with macromolecules such as glycoproteins, which destabilized the cellular membranes, thus, causing apoptosis. Steinberg and his colleagues (Steinberg et al., 2003) reported that EPFRs reduce photosynthetic oxygen of *Ceralophyllum demersum*. The mechanism of semiquinone-type bioreactive radicals inhibition in photosynthesis have been reportedly observed in substances such as lignin (a central component of biochars) and humic acid, as the EPFRs are formed through the spontaneous charge-transfer reactions via two single-electron phases amongst the quinone and hydroquinone units in the soil, with the additional reduction of quinoid compositions leading to the semiquinone radicals (Jezierski et al., 2000; Pflugmacher et al., 2006; Rex, 1960; Senesi, 1990a; Senesi, 1990b; Senesi, 1992; Senesi and Brunetti, 1996; Senesi et al., 1989; Senesi and Schnitzer, 1977). The formation of semiquinone radicals in biochars have been reported to hamper the effects on the electron transfer chain by acting as electron scavengers in humic substances and the plants grown in them, thereby hindering the photosynthetic oxygen production in plants (Chen et al., 2018; Choudhry, 1981; Paul et al., 2003; Pflugmacher et al., 2006; Rex, 1960; Saab and Martin-Neto, 2004; Scott et al., 1998; Steelink and Tollin, 1962; Steinberg et al., 2006; Steinberg et al., 2007). The cited investigations reveal the impact of amending soils with EPFR-containing biochars which would negatively influence the SOM (by affecting the humic acids) and, therefore, limit plant growth and establishment (through the reduction of photosynthetic oxygen.)

5.3. Impact of biochar-borne EPFRs in fauna (man and other animals)

EPFRs can induce oxidative stress in living organisms, from soil microorganisms and algae to animals and man, primarily in the soil or through the activated species in EPFR-containing PM. In the clay, mineral, or humic part of the soil, EPFRs have been detected and studied for their biotoxicity in luminescent bacteria (*Photobacterium phosphoreum*) (Zhang et al., 2019). Biochars have been reported to portray varied outcomes in the biomass growth, population structure, and activity in microorganisms as a result of the impact of the different properties and high reactivity of black carbon (Chen et al., 2016a; Luo et al., 2013; Tian et al., 2016). The diverse findings are mainly attributed by the wide-ranging physicochemical properties of biochars, namely the presence of labile carbon and nutrients, pore volume and surface area, degree of oxidation, particle size and the presence of free radicals in the biomass residues (Lian and Xing, 2017). The surface-stabilized EPFRs in biochar residues reduce significant cellular enzymatic levels (e.g., superoxide dismutase, glutathione, and glutathione peroxidase) and decrease the healthy cell membrane integrity during the production of the ROS types (Balakrishna et al., 2009; Dellinger et al., 2007, 2008; Liao et al., 2014). In aquatic algae (*Scenedesmus obliquus*), biochar toxicity showed a significant correlation with the biostable free radical concentration in biochar residues, which stimulated the generation of acellular ROS in water such as ·OH, thus, similarly causing intercellular ROS production in the aquatic organisms (Zhang et al., 2019). In non biochar-related research, EPFRs can restrict the activity of cytochrome P450 enzymes, which aggressively hinder the breakdown of extracellular organic substances (Reed et al., 2015b). Semiquinone-type species can react with oxygen to form superoxide, which then leads to hydrogen peroxide (H_2O_2) production and induced Fenton reactions via ubiquitous transition metal ions in biological systems such as Fe^{2+} and Cu^{2+}. The Fenton processes produce •OH that initiates the breakup of DNA strands, thus causing DNA damage (Dellinger et al., 2001).

In higher organisms, various reported studies have delved into the EPFR risks, whether as an impact to a specific organism or as an extrapolation of their impacts in humans (Chuang et al., 2017; Harmon et al., 2018; Jaligama et al., 2018; Lieke et al., 2018; Stephenson et al., 2016). In soil organisms, Lieke et al. explored the neurotoxic effect of rice straw biochar at 500 °C (0–2000 mg/L^{-1}) on a model organism *Caenorhabditis elegans* which depicted a hormetic effect by impairing locomotion and defecation. Their movement and defecation were both hampered by the EPFRs, which impaired the survival and fitness of these microbes in the soil (Lieke et al., 2018). Many of the research investigations have focused on research investigations unrelated to biochars, particularly in combustion-generated EPFRs in PM. In tests by Chuang and his colleagues, they observed that stable bioreactive radicals, made up of 1,2-dichlorobenzene chemisorbed onto CuO-coated silica beads, induced mortality in cultured mouse cardiomyocytes by causing oxidative stress, which initiated cell death, with the inherent mitochondrial pathway proceeding initially during apoptotic signaling (Chuang et al., 2017). This shows that the exposure to the generated biostable free radicals leads to cardiac toxicity and oxidative stress in experimental animals (Chang et al., 2013; Chuang et al., 2017; Gobe and Crane, 2010; Jomova and Valko, 2011). In the findings by Stephenson et al., gestational exposure to laboratory-generated, combustion-derived PM (MCP230) led to a decrease in energy expenditure, which, in part, was due to the adaptations to in the mitochondrial breakdown in the skeletal muscle (Stephenson et al., 2016). In birds, the increased formation of ROS led to metal-induced oxidative stress, which may decrease the incapability of antioxidants in the defense against growing amounts of free radicals (Koivula and Eeva, 2010). The cited investigations point towards a huge global concern in the potentially adverse impacts brought about by EPFRs and their induced ROS in animals.

In humans, numerous investigations have connected human exposure to combustion-derived-EPFRs in PM to declining metabolic health (Andersen et al., 2012; Cakmak et al., 2011; Chen et al., 2016b; Weidemann et al., 2016), in addition to animals (Li et al., 1996; Liu et al., 2014; Sun et al., 2009; Xu et al., 2011a; Xu et al., 2011b). However, no research studies have focused on the impact of biochar-related EPFRs to higher-level organisms like animals and man. In particular, representative experiments of human subjects that were terminally exposed to PM had showed connections with type 2 diabetes and cardiovascular diseases (Andersen et al., 2012; Brook et al., 2008; Cakmak et al., 2011; Thiering et al., 2013), while rodent models in continued PM exposure displayed the heightened inflammation of adipose tissue and insulin resistance by the pollutants (Liu et al., 2014; Sun et al., 2009; Xu et al., 2011a). Additionally, cytochrome P450 proteins (P450/CYP), the native proteins in the endoplasmic reticulum, are well-known for their metabolism of foreign compounds in man and animals (Park et al., 2014). In earlier investigations entailing model EPFRs produced by exposing rat liver microsomes silica containing 5% copper oxide to either dichlorobenzene or 2-monochlorophenol ($\geq 230\,^{\circ}\mathrm{C}$), the radicals hindered six kinds of P450 in the liver microsomes (Reed et al., 2011; Reed and Backes, 2016; Reed et al., 2014; Reed et al., 2015a; Reed et al., 2015b). As the experimental animals depict human body organs, the studies point toward induced metal-oxidative stress in man, which is a potentially adverse effect of ROS caused by EPFRs.

Attention has been raised on the toxic and carcinogenic impacts of EPFRs and their PM derivatives in human health (Balakrishna et al., 2009; Balakrishna et al., 2011; Brown et al., 2000; dela Cruz et al., 2012; dela Cruz et al., 2014; Dellinger et al., 2001; Fahmy et al., 2010; Laden et al., 2000; Lord et al., 2011; Mahne et al., 2012; Pope III et al., 2002; Vejerano et al., 2012c), with their primary source being combustion-generated particles (McFerrin et al., 2008). EPFRs in the atmospheric environment are correlated to human diseases, with acute risks like influenza infections, and respiratory toxicity, in addition to chronic risks like pneumonia, lung cancer, liver dysfunction, DNA damage, among others (Balakrishna et al., 2011; Cormier et al., 2006; Dellinger et al., 2001; Dugas et al., 2009; Fahmy et al., 2010; Harmon et al., 2018; Lee et al., 2014; McFerrin et al., 2008; Pope III et al., 2002; Squadrito et al., 2001). EPFRs are causative agents of carcinogenic toxicities, as well as bringing about aging (Harman, 1956; Van Remmen and Jones, 2009), reduced cardiac activity and escalated pulmonary artery pressure (Lord et al., 2011; Mahne et al., 2012). In the works by Dellinger and his group, they reported that PM produced during combustion of biomass contained organic molecules, metal particulates, and free radicals may lead to toxic human health issues (Dellinger et al., 2007; Dellinger et al., 2009; Dellinger et al., 2000; Dellinger et al., 2001; Dellinger et al., 1986; Dellinger and Taylor, 1998; Lomnicki and Dellinger, 2002; Lomnicki and Dellinger, 2003; Vejerano et al., 2013). The presence of semiquinone and phenoxyl radicals may cause activated species in combustion-generated particles and ambient fine PM (Dellinger et al., 2001; Lyu et al., 2018; McFerrin et al., 2008; Stone et al., 1995). By inducing the generation of activated species, EPFRs pose human health risks by causing oxidative stress (Dellinger, 2007). Moreover, the EPFRs persist in the air for a spell of time, which, when inhaled, can cause human health complications (Dellinger et al., 2000). In the bloodstream, the impact of stable bioactive radicals (e.g., peroxy radicals) has been observed by EPR spectroscopy, whereby EPFRs are generated when hydrogen peroxide is added to either ferric hemoglobin or myoglobin (Gibson and Ingram, 1956; Svistunenko et al., 1996). These reported studies show that EPFR-polluted finer particles, whether from pyrolyzer emissions or exposure to the ambient air may lead to potent risks in man and other creatures, with varied effects depending on the types of EPFRs and their concentrations in the combustion-generated fine particles.

6. Scientific and regulatory drawbacks of EPFR-induced production of biochars

6.1. Scientific issues

EPFRs, as toxic organic/metal oxide composite particles, emanate from organic fractions, chemisorbed onto metal oxides (Kiruri et al., 2014; Lomnicki et al., 2008b; Thibodeaux et al., 2015; Vejerano et al., 2011; Vejerano et al., 2012b; Vejerano et al., 2012c). Some transitional metals, such as iron, nickel, cadmium, have been recently reported as capable of forming stable complexes with organic free radicals to generate EPFRs in soils (Jia et al., 2017). Even though metals such as iron have been viewed as an efficient catalyst in facilitating the degradation of various organic chemicals, recent studies have challenged this notion (Yang et al., 2015). PAH interactions in the soil with clay minerals may result in the generation of toxic EPFRs and reactive oxygen species, which pose human health effects. Additionally, the roles of influential features such as organic molecular structure (such as molecular properties of PAHs), clay surface properties (relative humidity [RH], transition metal species/ ions, organic ligands, and reaction atmosphere), soil characteristics (soil organic carbon) and ambient conditions (ultraviolet radiation) should not be underestimated in the formation of EPFRs in the environment (Jia et al., 2014; Jia et al., 2018; Jia et al., 2019). The photolytic degradation (photodegradation) of benzo[*a*]pyrene (B[*a*]P) and the generated transformative products on Cu(II) montmorillonite in both dark and light irradiation initiated the

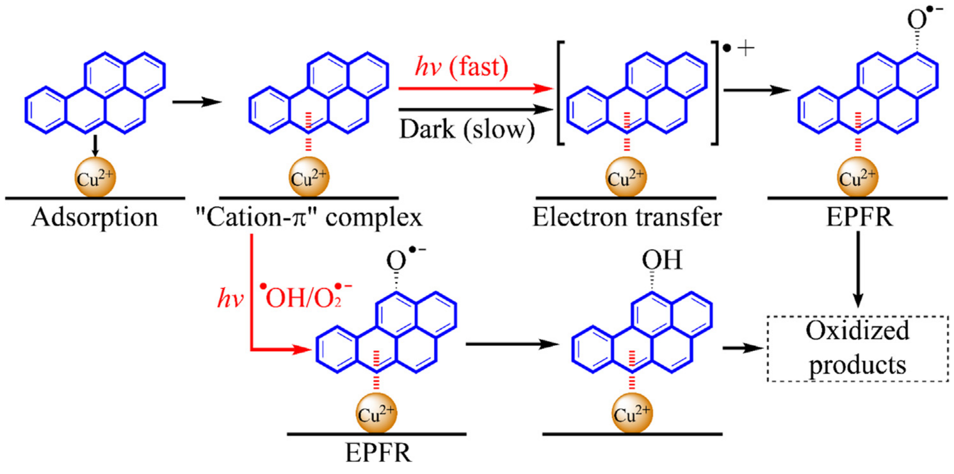


Fig. 5. Schematic representation of the proposed mechanism of EPFR formation on B[*a*]P contaminated Cu(II)montmorillonite system. The likely EPFR formation process is the dark stage route of the PAH-Cu(II)-montmorillonite composite (EPFR) arrangement (Adsorption "Cation-π" bonds electron transfer). The figure is adopted from the following reference (Zhao et al., 2019).

formation of ROS (superoxide and hydroxide radicals), which correlate to "cation-π" interaction on clay surfaces (see Fig. 5). The generated EPFRs in dark condition took some days, while in visible light, the biostable radicals were produced within hours (Zhao et al., 2019). Strong EPR signals were detected during dark reactions, while light irradiation enhanced EPFR production and decay. The electron-accepting sites on Cu(II) surfaces and electron-rich organics such as B[*a*]P forms "cation-π" interactions, facilitating the transfer of electron and oxidation of B[*a*]P to form B[a]P quinines (Jia et al., 2016). EPFR generation, as a result of B[*a*]P transformations, led to Cu(II) reduction to Cu(I), which may bring about potentially adverse effects to living organisms. Geochemical behavioral studies involving EPFRs should be incorporated into organic contaminants research, which will be a new contribution to their environmental fate models (Li et al., 2014).

Preliminary investigations have concentrated on the capability of biochar–borne EPFRs to induce oxidative stress that inhibits plant growth by damaging the cell membrane (Liao et al., 2014) and their potential to react with organic /inorganic contaminants in the soil environment, resulting in their degradation (Fang et al., 2015a). However, the mechanism of electron transfer /shuttle from biochars in the elimination of contaminants is uncertain due to unknown contributions by functional groups on the residue surfaces, transition metals and biochar-borne free radicals (Ruan et al., 2019). The EPFRs in biochars influence biogeochemical processes as they act as terminal electron acceptors during respiration, thereby alleviating nitrous oxide discharges from the ground by stimulating ROS formation and transforming contaminants (Alburquerque et al., 2015; Klüpfel et al., 2014; Oh et al., 2013b). The fate of biochars–EPFRs interactions with various soil minerals and different contaminants in the soil environment needs more investigation before it is fully adopted in various soil remediation practices.

6.2. Regulatory issues

Biochar laws and policies have been recently formulated since the turn of the millennium to curb haphazard production, as well as misuse during adoption (Meyer et al., 2014, 2017). Current protocols governing the pyrolysis process, standards on atmospheric pollution, and biochar quality requirements have weakly dealt with the prediction of EPFR regulation. The non-profit association called International Biochar Initiative (IBI), which is based in the US, is aimed at fostering good industry practices, stakeholder collaborations, and environmental and ethical measures to promote economically viable biochar products and systems (Meyer et al., 2017). In November 2015, the IBI published the version 2.1 guidelines "standardized product definition and product testing guidelines for biochar that is used in soil", i.e., IBI Biochar Standards (International Biochar Initiative, 2015a; Schmidt and Shackley, 2016; Camps-Arbestain et al., 2015; Meyer et al., 2017). However, this definition of biochar standard did not include the production and implementation threshold of EPFR contents, which is necessary for improving the quality requirements of biochars. Below is an outlook of policy issues surrounding biochars and EPFR formation in the USA, the European Union, and China.

In the US, laws such as the Clean Air Act (CAA) regulate the emissions from various combustion systems, including biochar pyrolyzers and hazardous waste incinerators (Dugas et al., 2016). Even though the CAA requires that the projected aerial discharges must account for metals, dioxins, and the presence of products of incomplete combustion in the incinerators, no requirement for EPFR monitoring has been indicated. Although the current version of the CAA stipulates the guidelines and procedures on the limits of both coarse and fine PM to mitigate respiratory diseases and symptoms brought about by the free radicals, EPFR-containing ultrafine particles have lately been indicated to trigger off critical health issues (Dugas et al., 2016). Furthermore, since the transition metals are essential as an entity necessary to form the pollutant-particle systems responsible for EPFR formation, different metals impart differences in radical formation and stability in the environment and in the host (Dugas et al., 2016). The approach undertaken by the US government, in collaboration with IBI is key to the mitigation of EPFR-containing ultrafine particles generated at the EPFR exposure level in the ambient environment. However, regulations on EPFR production, emission, and environmental transfer during and after biochar carbonization have not been proposed. Therefore, risk assessment studies and the development of additional policies for regulating PM exposure and EPFR generation during thermal decomposition of the raw materials to form biochars are necessary to reduce the contribution of EPFRs in the biosphere.

In the European Union, the European Biochar Foundation formulated the European Biochar Certificate (EBC) in 2011 to legally establish biochar as a class of agricultural amendments in the Union and its member states' legal frameworks (Meyer et al., 2017). This was done in conjunction with the REFERTIL project, which is an acronym for Reducing mineral fertilizers & chemicals use in agriculture by recycling treated organic waste as compost and biochar products (Someus and Pugliese, 2017). The main agenda of the project, which commenced on October 1, 2011, was to provide a strong policy support for the EU Commission (DG Industry & Enterprise) in the amendment of the Fertiliser Regulation number Reg. EC No. 2003/2003 (Someus and Pugliese, 2017). The REFERTIL project is a biochar policy support specific project for the conversion of biochar applied science into economically industrial practice (Someus and Pugliese, 2017; Someus and Pugliese, 2018). The vital goal undertaken in the project was to produce high-quality, unpolluted and affordable biochar to be utilized in farmlands, which will significantly enhance the food safety, supply security, and expanding the bio-based globalized economy, particularly in the horticultural SME farming sector (Someus and Pugliese, 2017). The 3R zero emission industrial pyrolysis equipment (rotary pyrolysis reactor from 3R Agrocarbon, which produces both biochar and syngas) has been proposed and slowly implemented in the EU for the economical production of animal bone biochars (ABC) or plant-based biochars (PBC). A proposed technique in the REFERTIL project is the production of high-quality, low-contaminant content biochars, which uses high-quality feedstocks such as ABC or PBC in the stated HTTs (Someus, 2008: Someus and Pugliese, 2018). As highlighted by Meyer et al. (2017), the main intentions of the EBC include: the introduction of a limit system, based on advanced strategies and practices; the delivery of a consistent quality resource for customers; giving the opportunity for biochar producers to demonstrate their products which meet the stipulated quality standards; and the provision of a strong, up-to-date knowledge transfer as a firm foundation for future lawmaking process that will check and deter any misapplication or threats from the offset. The compliance of biochar producers in the EU, in accordance to the requirements of the EBC, is overseen by the q.inspecta (the independent, governmental accredited quality assurance agency), with independent national inspection agencies under this body conducting inspections of production plants in member states (European Biochar Foundation, 2019). The pyrolysis technology design, quality, and efficiency in performance are critically important elements that will be reflected as unique and recognizable identifications in biochar quality and safety performance characteristics (European Biochar Foundation, 2019). The EBC also provides laboratory accreditation to undertake biochar analyses, in which the labs have to apply their analytical methods stipulated in the certificate for all quantities, and have to prove their compliance in regular ring trials or interlaboratory comparisons (Bachmann et al., 2016). In line with the EBC guidelines, two distinct biochar grades are specified, each with its threshold values and ecological requirements: "basic" and "premium" (European Biochar Foundation, 2019). The EBC indicates the enormous task of maintaining a unified approach to quality standards, especially with member states trying to work with local and regional biochar quality standards.

China has equally taken various approaches in the agricultural amendments subsector. For instance, the carbonization of crop straw via pyrolysis/gasification techniques to form bioenergy and biochar is carried out under the National Green Energy Project introduced in 2012, with a low carbon economy framework launched in 2014. Additionally, coking ovens have been intensely closed down to execute the Coal Law (Jia et al., 2017). However, pollutants such as PAHs persist in soils around derelict coking sites, which at high concentrations, the abandoned sites still contain harmful impacts on the biochars that slows down or prevents PAH biodegradation (Jia et al., 2017; Jia et al., 2019). The long-term impacts of the abiotic processes (e.g., photolysis and chemical oxidation) influencing the persistence and fate of PAHs may result to EPFRs formation, which leads to the induction of ROS and their impacts in the biosphere (Jia et al., 2019). Furthermore, the lax regulatory oversight in enforcing the laws to mitigate the use of any amendments in farms and environmental niches (in either remediating or enriching the soil for food production applications) has led to the use of both high- and low-quality biochars and inorganic fertilizers with no quality check requirements for maintaining biochar quality standards. Also, China has done little towards creating biochar standards, along with a standard procedure to quantify biochar properties, which is crucial before large-scale biochar production and application (Zhang et al., 2019). If implemented, such biochar standards and a stipulated quantification technique would boost consumer and state confidence in biochar products in the Chinese market.

The approaches by these three countries paint a grim picture on the generation of toxic EPFRs throughout biochar production and their exposure in the biosphere. Given that a holistic strategy is not well elucidated in mitigating both EPFR-containing biochars and ultrafine particles in the environment, a huge global risk may occur. Therefore, advancements in pyrolysis/carbonization processing technologies that will produce high-quality, low EPFR content biochars is a key step to reduce the generation of surface-stabilized EPFRs in biochar amendments and in the atmosphere. Even with the various alleviation steps, such as winding down coal sites in China, or producing cleaner versions of organic amendments in EU, or implementing the Clean Air Act in the case of US, stricter regulations and policy enactment at all levels of biochar production and adoption is required. Moreover, risk assessment studies in biochar production and environmental studies are necessary to boost the production of high-quality biochars with little or no EPFR content.

7. Recommendations on biochar application in the reduction of EPFRs

The challenges of controlling the EPFR levels formed in biochars may have potentially adverse effects on the ecosystems and host organisms. The controlled production of biochars that has reduced EPFR content is vital to its adoption in farmlands and in environmental remediation. Thus, even though the REFERTIL project serves as a template to initiate the production of low EPFR-containing biochars, the project itself is a complex approach and, therefore, a comprehensive strategy is necessary. The enumerated recommendations cover all facets of this enormous undertaking to ensure high quality, low EPFR-content biochars;

(a) Incorporating technology advancements in carbonization equipment, which is essential in controlling the generation of inherent contaminants in biochar such as EPFRs. Pyrolysis conditions such as HTT (especially at material core pyrolysis temperatures of above 850 °C) should be maintained, as many EPFRs and their precursors cannot withstand such high-temperature conditions, leading to the combination with other compounds to form nonharmful products. Furthermore, the advanced 3R pyrolysis system is beneficial in utilizing the material core pyrolysis temperature and high-quality feedstocks such as ABC or PBC that would eliminate EPFR generation at the production and emission stages. Biochars with low EPFR contents can be deployed in farm and feed agricultural production.

(b) Analytical studies to quantify the toxic substances present in biochar feedstock (heavy metals) or generated during pyrolysis (EPFRs, PAHs, PCBs, VOCs among others), before the broader adoption of biochars in agroecological niches. Further investigations should also focus on the impacts of biochars on the stabilization and bioavailability of nutrient elements, agrochemicals, and contaminants.

(c) Environmental risk assessment studies should be promptly undertaken in past coking, petrochemical and superfund sites to ensure no contamination of biochar amendments applied to agricultural soils in the vicinity of these locations, as surface-stabilized EPFRs in polluted PM or soils may combine with biochar residues to become EPFR-contaminated biochars.

(d) Environmental risk assessment studies evaluating the effects of combustion-generated PM emissions from biochar factories into various ecosystem components, plus the specific associated biological and chemical risks damaging species then impacting flora and fauna, including human beings. Impacts on fauna and human beings can be either chronic or acute, whereas, in flora, the impacts include phytotoxic effects such as germination inhibition and retarded growth. Furthermore, the interaction mechanisms of biochar residues with soil components (such as minerals and SOM), plant roots, and microorganisms necessitate advanced studies.

(e) A global collaboration initiative by applied science researchers, industrial engineers, and policymakers is requisite in the development of extensive and unified regulations at the local, regional, and international levels. Such guidelines would regulate the generation of this class of emerging pollutants in the environment whilst maintaining the production of standard biochars. Above all, the policy measures would lead to the enactment of accredited laboratories to ensure quality control in terms of types and stages of biochar residue generation, and the ambient environmental emissions of EPFR-containing PM from biochars. Further policy actions include monitoring external influences, including hazardous waste emission sites such as coking companies, incinerators, gasifiers, and pyrolyzers. Such regulations would significantly enhance the confidence of farmers and environmental engineers in biochars adoption for either clean agricultural production or environmental rehabilitation practices, respectively.

Therefore, as biochars have a global impact due to its broad-based applications, the presence of EPFRs in these amendments, with minimum or no regulatory and standardization measures, may lead to potentially harmful effects in the biosphere. Therefore, key stakeholders such as the World Health Organization (WHO), United Nations Environmental Programme (UNEP), United Nations Framework Convention on Climate Change (UNFCCC), and United Nations Convention to Combat Desertification (UNCCD) need to factor biochars in their policies and safeguards as an emergent public health and environmental protection measure. Despite biochars being proposed in the application on agricultural croplands towards its carbon sequestration (in mitigating climate change) and soil amendment properties (Galinato et al., 2011; Steiner, 2007a, b), UNEP has advised that black carbon is ‘a poorly understood technology’ with its production and deployment being highly inadvisable due to the following issues. One, large-scale biomass feedstocks may emanate from ‘biofuels’ (agrofuels), which should be handled with extreme concern. Two, the successful adoption of biochar as a carbon-storing method will significantly depend on the economic and environmental factors. Lastly, its long-term agroenvironmental sustainability and impacts on biodiversity are still undetermined (Ernsting and Smolker, 2009; Paul et al., 2009; Trumper et al., 2009). Therefore, since biochar is still at its early stages, its full adoption as both an organic amendment and a climate change mitigation weapon is still uncertain until all the previously mentioned concerns are addressed (Trumper et al., 2009).

8. Conclusions and future perspective

EPFRs are ubiquitous environmental contaminants of emerging concern, composed of a unique pollutant-particle system with grave toxicological implications. The formation mechanisms of EPFRs in biochars, along with the carbonization conditions and the biomass feedstocks, have been reported to influence the generation of EPFRs in both biochar residues or combustion-generated PM from biochar pyrolysis. However, an extensive study is warranted to evaluate their environmental fate and risks in ecosystems before utilizing biochar amendments. The diverse structures of EPFRs in biochars have been classified as oxygen-, carbon-, or oxygenated carbon-centered radicals. The catalytic generation of these long-lasting radicals in biochar may occur in appropriate geochemical and operation conditions, with their previously unconsidered behaviors in multimedia environmental fates becoming a serious global concern.

Despite the wide-ranging environmental and agricultural applications of biochars, the occurrence and formation of EPFRs in these amendments may lead to environmental contamination and its associated health risks. The interactions between EPFRs and their precursor chemicals (e.g., PAHs) with transition metals in soils may lead to the generation of EPFRs, which alter their degradation pathways and bring about the issue of half-lives and persistence in the environment. These telluric organopollutants may interact with EPFRs or ROS, which leads to free radical-mediated DNA damage. Considerable attention has focused only on the toxicity of EPFR-embedded particles in biochars; however, few research investigations have been conducted on the toxicological contributions of their precursor chemicals and degradation by-products in biomass feedstocks. Therefore, elucidating the roles of the environmental factors influencing the stability and persistence of EPFRs in biochars, such as light irradiation, oxygen, humidity, and humic substances, may not only provide a detailed outlook into their mechanisms and environmental fates but also give solutions on how to mitigate EPFRs spread in biochar-amended soils and wastewater. Finally, the scientific and regulatory issues in EPFR formation in biochars have put a spotlight on the production and multifarious applications of black carbon. Even though biochar technology and application is still at its infancy, uncertainties still arise in its full adoption unless all pending issues such as EPFR generation are resolved. Toxicological studies should, therefore, be applied at the production and adoption stages of biochars to determine the specific risks to flora and fauna in relation to generated EPFRs in biochar. The recommendations raised herein, if embarked on, would have huge ramifications in the adoption of high-quality, low EPFR content biochars for utilization in sustaining agroenvironmental niches.

Declaration of Competing Interest

The authors declare no competing financial interests.

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