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Impact of biochar, fertilizers and cultivation type on environmentally persistent free radicals in agricultural soil

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ABSTRACT

Environmentally persistent free radicals (EPFRs) have been considered as emerging contaminants due to their detrimental effects on human health. The adverse health impacts are attributed to oxidative stress induced by EPFRs through the formation of reactive oxygen species (ROS). In soils, it may also increase the degradation process of polymeric organic matter and/or undesired organic pollutants through hydroxyl radical activity. The biochar pyrolysis process entails the thermal decomposition of organic compounds in the biomass, with the carbonization conditions and feedstock type facilitating the formation of EPFRs. When biochar is used to amend soil, these radicals may promote the formation of ROS, and thus influence the transformation of organic and inorganic contaminants in soil and impact the rhizosphere. Agricultural soils are being amended with biochar to mainly increase carbon content and facilitate the plant growing conditions. Therefore, agricultural soils may become a source of EPFRs. However, the fate and transformations of EPFRs in soils after biochar amendment are not well understood or studied.

This paper presents the first (to our knowledge) studies of EPFRs behaviour in agricultural soil with different input of biochar, cultivation types and residence time period. Different cultivation types, addition of fertilisers and variation in biochar input, on the one hand, and presence of metals in soil, biochar and fertilizers, on the other hand, provide different conditions for EPFRs formation, accumulation and fate in agricultural soils.

Two significant factors have been found to determine the fate of EPFRs in soil: transition metal content (particularly those in reaction available form) and cultivation level of soil. Cultivation significantly decreased presence of EPFRs, both carbon-centered and oxygen-centered, in relatively short periods of time, while metal presence (and particularly through fertilizer supplementation) increases the half-life of radicals and transforms organic matter to more oxygen-centered EPFRs. The amount of biochar addition plays a secondary role as the EPFRs content in the soils is in a longer term primarily controlled by the other two factors.

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1. Introduction

Biochar is a predominantly stable, carbonaceous product formed by the pyrolysis of sustainably obtained biomass at the temperature ranging from 350 °C to 1000 °C in oxygen lean conditions (EBC, 2012-2022). Biochar, is widely considered as beneficial organic amendment for agricultural and environmental remediation purposes (Lehmann et al., 2006). Biochar, within its heterogenous composite lattice structure, may contain organic (labile and recalcitrant organic molecules such as polycyclic aromatic hydrocarbons (Ruan et al., 2019), furans, dioxins), as well as inorganic compounds, which contain oxides (Zhang et al., 2022), cations, anions and additionally environmentally persistent free radicals (EPFRs) (Huang et al., 2020).

EPFRs are surface-stabilized metal–organic radical complexes (Dellinger et al., 2001) that are formed during the thermal processes due to the interaction of metal centres with by-products of decomposition of organic compounds (Lomnicki et al., 2008; Vejerano et al., 2012a,b). Due to the association with the metal centre and solid surfaces thus formed radicals are persistent and stable in various environmental conditions (Liu et al., 2022), however, able to undergo a redox cycling process, producing reactive oxygen species (ROS) (Khachatryan et al., 2011; Vejerano et al., 2018) and as a result show toxicity in rhizosphere (Zhang et al., 2019a). EPFRs are generated during biochar production (pyrolysis) in a similar way as in the other thermal reactions, i.e. by interaction of organic molecules with transition metals (Tian et al., 2016). The implications of the EPFRs presence in the biochars and thus in the amended soils are so far unclear. It is known, that EPFRs have a detrimental impact on human health if inhaled with particulate matter (Kelley et al., 2013; Saravia et al., 2014), which is related to the onset of oxidative stress via EPFR mediated hydroxyl radical generation (Oyana et al., 2017; Sly et al., 2019). EPFRs present in biochars have been reported to impact the aquatic organisms Zhang et al. (2019b) and microbial organisms (Zhang et al., 2019a). On the other hand, the presence of EPFRs can potentially increase the degradation of soil bound pollutants (Ruan et al., 2019; Yang et al., 2016) and pesticides (Zhang et al., 2018; Qin et al., 2016), and thus improve the soil quality and availability of the nutrients to soil organisms and flora.

With that in mind, the long-term fate of EPFRs in soils is not known or understood. The environmental persistence and stability of EPFRs depend on the type of radical formed and types of metals involved (Vejerano et al., 2012a,b). Apart from biochar, fertilizers are expected to play an important role on EPFR formation, as the introduction of metals (and particularly redox active metals) with fertilizers can further promote EPFR generation. Arsenic, cadmium, chromium, lead, mercury, nickel and vanadium are significant metals that accumulate in soil with repeated fertilizer application (Mortvedt, 1996). For example, agricultural soils in the Sundgau region of Switzerland have about 18% of total cadmium input coming from commercial fertilizers (67% of input is from atmosphere and the rest comes from manure and biosolids) (Keller et al., 2002).

Moreover, upon application of biochar to soil, other factors, such as soil characteristics (e.g. soil organic material, humidity) (Jia et al., 2018), agrotechnical (e.g. different cultivation techniques) and agrochemical conditions (e.g. addition of fertilizers) affect the fate of EPFRs. Those are important changes that require detailed studies, as they contribute to the overall impact and performance of biochar treatment. This study presents the first attempt to look holistically on the long-term changes of EPFR chemistry upon the application of EPFRs-biochar systems into the soils including the impact of cultivation process and fertilizing. Such first insight onto long-term EPFRs presence/activity in soil will allow better assessment of risks and benefits of biochar use in agricultural setup.

2. Material and methods

2.1. Biochar properties

Biochar produced from mixed hard wood species (at 450 °C, 2 h) was obtained from Ignalina region (Lithuania). The basic biochar properties are provided in Table 1 (as determined methods published by Usevičiūtė et al. (2022)) and Fig. 1.

Biochar had eight peaks indicating the development and alterations of functional groups in its structure: alcoholic –OH (3442 cm^{-1}), acidic C=O (1684 cm^{-1}), aromatic C=C (1684 cm^{-1},1584 cm^{-1}, 1429 cm^{-1}), anhydride C–O (1174 cm^{-1}) and aromatic C–H (805 cm^{-1}, 879 cm^{-1}, 752 cm^{-1}) (Fig. 1) (Usevičiūtė et al., 2022). FTIR spectrum of initial biochar showed strongly condensed biochar structure which can be seen from intensive C=C ring region. It indicates the growth of biochar aromaticity and thus developing the stability during the pyrolysis process (Baltrėnaitė et al., 2017). Carboxyl structures observed at ∼1430–1460 cm^{-1} are known to increase biochar ability to retain nutrients (Glaser et al., 2001).

2.2. Soil amendment with biochar

This study is a part of the project implemented by Vilnius Gediminas Technical University (VilniusTech) and the Institute of Agriculture at the Lithuanian Research Centre for Agriculture and Forestry (Lithuania). Agricultural soil was amended with biochar in April 2019 in a field subject to the ongoing long-term (20 years) soil tillage-fertilization system in Dotnuva region, Lithuania (55°23′N and 23°51′E). The soil was sandy loam (*Endocalcari-Epihypogleyic Cambisol*) with the largest portion (53.7%) of sand particles (2–0.05 mm), average portion (32.6%) of silt particles (0.05–0.002 mm) and the smallest portion (13.7%) of clay particles (<0.002 mm).

Table 1
Physical and chemical properties of biochar (mean and standard deviation (SD))

Property	Mean ± SD
pH	8.53 ± 0.13
Electrical conductivity, μS/cm	8.28 ± 2.11
Wettability, s	1810 ± 10
Water holding capacity, times	4.5
C, %	88.7 ± 0.20
O, %	3.40 ± 0.46
H, %	11.07 ± 0.20
N, %	0.25 ± 0.01
Cation exchange capacity, $cmol_c$/kg	0.69 ± 0.11
Specific surface area, m^2/g	2.77
Ash, %	16.60 ± 0.32

Table 2
Elemental concentration of fertilizers (superphosphate, potassium chloride, ammonium nitrate) and biochar (n.d. denotes to "not determined").

Element	Soil	Superphosphate	Potassium chloride	Ammonium nitrate	Biochar
	(%)				
Si	30.3	0.327	0.334	0.0442	0.0196
P	0.104	6.73	0.56	0.106	0.0191
C	3.47	1.82	7.98	3.61	92.6
N	n.d.	n.d.	n.d.	84.1	7.17
S	0.348	15.5	0.465	0.328	0.0061
Cl	0.0102	0.0842	23.2	0.0658	0.0029
Br	n.d.	n.d.	0.0938	n.d.	n.d.
F	n.d.	2.51	n.d.	0.37	n.d.
Na	0.378	0.253	1.39	0.0245	n.d.
K	3.35	0.199	34.3	0.0131	0.0579
Ca	0.731	24.6	0.412	0.132	0.0867
Mg	0.697	0.106	0.0599	0.481	0.0337
Ba	0.0584	0.0494	n.d.	0.163	n.d.
Al	6.11	0.0516	0.0817	0.0202	0.0082
	in ug/g				
Fe	16 200	2000	1810	114	33
Zn	42	267	n.d.	n.d.	79 400
Cr	56	162	n.d.	n.d.	n.d.
Ni	31	52	n.d.	n.d.	82 900
Cu	n.d.	29	n.d.	n.d.	n.d.
Zr	308	n.d.	n.d.	n.d.	n.d.
Sr	96	1580	91	n.d.	n.d.
Y	11	51	n.d.	n.d.	n.d.

Biochar was applied to the soil at two different rates (5 t/ha; 15 t/ha) by direct drilling with a disc drill having a rotary tiller before the sowing of summer triticale (*Triticum x Secale*). Studies were performed without and with initial mineral fertilization (ammonium nitrate (34.5%) systems with granular superphosphate ($Ca(H_2PO_4)2H_2O+CaSO_4 \cdot 2H_2O$ with 19% of P_2O_5) (98–177 kg/ha) and potassium chloride (KCl with 60% of K_2O), 60–98 kg/ha). Each following year additionally ammonium nitrate (NH_4NO_3 with 34.5% of N) was added (155–190 kg/ha) into fertilized soil.

Two types of soil tillage were applied: ploughless shallow tillage (stubble cultivation at 10–12 cm + pre-sowing cultivation at 5–6 cm) and direct drilling (soil not tilled, direct drilling with a disc drill having a rotary tiller). Elemental analysis of soil, fertilizers and biochar is provided in Table 2.

Amended and not amended soil were collected at three different times—at the beginning of the experiment, after 3 month and after 24 months. Samples were pulled using a soil auger for every treatment at the depth of 0–15 cm soil layer. Plant residues were removed from the samples before the analysis. The soil samples were dried in ambient conditions at 20 °C temperature and sieved through a 2 mm diameter sieve.

2.3. Properties of soil–biochar system samples

The soil pH was determined using a pH-meter (model SevenMulti ion/pH/ORP module Mettler Toledo, Switzerland) by suspending soil in water at the ratio of 1:1 (Motuzas et al., 1996). The electrical conductivity meter (model inoLab Cond 740 WTW) and soil/biochar water suspension at the v/v ratio of 1:1 was used to evaluate electrical conductivity (EC, μS/cm). The organic matter (OM) was determined using the combustion method at 550 °C using dried (at 105 °C) soil/biochar until constant weight. Amount of OM was calculated according to mass difference before and after the combustion (Buivydaitė and Motuzas, 2000).

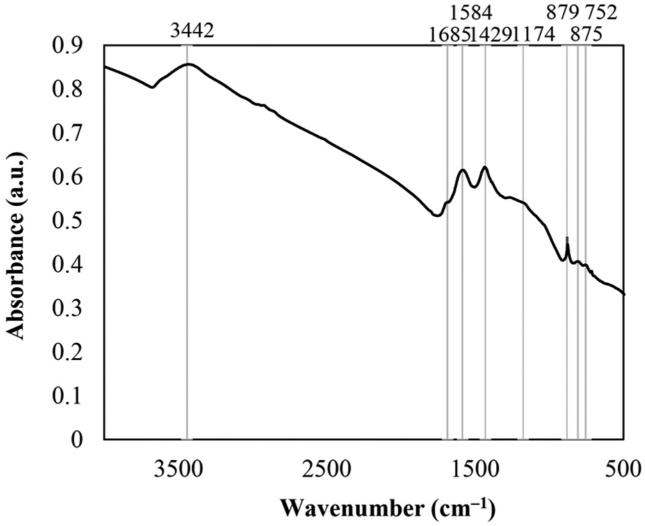


Fig. 1. Fourier transform infrared (FTIR) spectra for biochar (Usevičiūtė et al., 2022).

2.4. EPFR analysis

The soil samples were placed in EPFR tubes and EPFR spectra were determined at room temperature using a Bruker EMX–10/2.7 EPR Spectrometer with X-band microwave frequency of 9.72 GHz, microwave power of 2.02 mW, spectral window of 1000 gauss, and modulation amplitude of 4.00 gauss (dela Cruz et al., 2014).

Half-life of radicals were calculated based on the first order kinetics of the EPFR decay over time in soil, where standard regression analysis was used to find decay rate constant k ($\ln(\mathrm{EPFR}/\mathrm{EPFR}^0) = -\mathrm{kt}$), the half-life being defined as $t_{1/2} = \ln(0.5)/k$.

2.5. Statistical analysis

Two-dimensional scatterplots were plotted for the exploratory purpose, using levels of soil and EPFR characteristics. The compositional data was disintegrated to define the regression between EPFR and soil properties. Only cases with a regression coefficient higher than 0.45 were selected and discussed.

3. Results and discussion

3.1. EPFR concentration

Fig. 2 presents the comparison between EPFR concentration in four main treatments of the studied agricultural soil.

In no case, EPFR concentration exceeded 1E+17 spins/g, the concentration that corresponds to lower EPFR concentration limits commonly found in contaminated soils, for example, such as those found in contaminated (coking) soils (3E+17 spins/g) (Jia et al., 2017). Soil amendment with biochar initially increased the EPFR content, due to the EPFRs input to the soil with the biochar material (8.82E+18 spins/g), and as a general observation the EPFR concentration decreased over time - EPFR content decreased 4 times after 3 months since amendment with biochar and another 4 times after 24 months. Such EPFR decay was a result of natural degradation process of radicals due to the exposure to elements and particularly oxidizing effect of oxygen and water. It is worth to note, however, that after addition of biochar EPFR concentration remained elevated after corresponding time period compared to not amended soil.

The presence or absence of fertilizer in the soils had a distinct impact on the EPFR concentration. The initial concentration of EPFRs was lower in the presence of fertilizers compared to no fertilizer presence (but higher compared to soil not amended with biochar). Over time, the fertilizers appeared to stabilize the EPFR content and resulted in higher EPFR content after 3 and 24 months after biochar amendment. The initial drop and stabilization of EPFRs upon fertilizer addition was most likely associated with the metal content in fertilizers (see Table 1, in particular phosphate fertilizer). The increased presence of soluble metals may result in the cationic exchange of the soils, initial redox activity of metal and oxidation of EPFRs. However, over time, the same metals may result in the slow formation of new EPFRs through the reaction with humic substances present in soil (Nwosu et al., 2016; Shi et al., 2020) or PAHs present in biochar (Li et al., 2020; Jia et al., 2018). In view of the elemental composition of phosphate fertilizer a particular role of Zn, Cr, Cu and

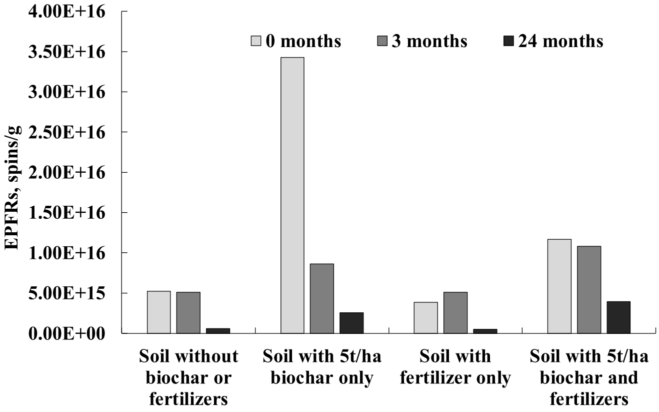


Fig. 2. Concentration of environmentally persistent free radicals (EPFRs) in agricultural soil of different treatment.

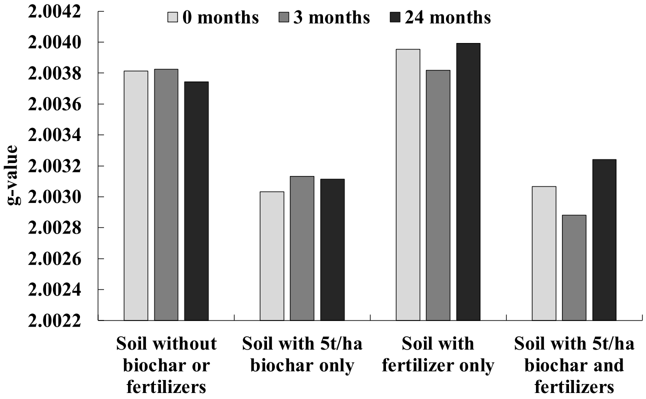


Fig. 3. g-value of environmentally persistent free radical spectra in agricultural soil with different treatment.

Ni should be highlighted (Zn and Ni are also present in biochar) as the reactive species responsible for slight increase of EPFR concentration in soils amended with fertilizer only – reactivity of those metals towards EPFR formation was reported earlier (Vejerano et al., 2012a,b).

3.2. g-value of EPFRs

g-value is an inherent property of EPFRs used to characterize the magnetic moment and gyromagnetic ratio of an atom to understand the structures of species with unpaired electron. In the case of organic radicals, g-value can be used to assess the localization of the free electron relative to specific atoms. Fully carbon-centered organic radicals such as that of pure graphite, where electron is delocalized on the polymeric aromatic ring and corresponds to a free electron moving along the carbon atoms has a value of 2.0023. Increasing g-value in a singlet spectrum is indicative of the presence of other than carbon atoms in the organic matrix and potentially partial localization of an electron. Since the localization of free electron at the vicinity of oxygen atom has significant radical reactivity consequences, and particularly to EPFR systems, the values above 2.003 indicate influence of oxygen atom on the radical structure, with $g = 2.005$ being a majority oxygen-centred radical species.

Two groups of samples were observed according to g-values. The first group included natural agricultural soil and agricultural soil with fertilizers only (Fig. 3). In this group, the g-value varied in the range of 2.0037–2.0040 and indicated carbon-centred radicals with heteroatoms such as O and Cl turning to more oxygen-centred radicals (Jebet et al., 2017). Such radicals are typical on the most soils and originated from the interaction of humins with the metals encapsulated in aluminosilicate structures of soil matrix.

The second group included agricultural soil with biochar addition and agricultural with combined biochar and fertilizers effect where the g-value varied in the range of 2.0029–2.0032 (Fig. 3). This is indicative of more carbon-centred type radicals. This was an anticipated results as the biochar addition dominates the total population of EPFRs and since they are formed at oxygen-starved conditions, mostly carbon-centered radicals can be expected. One should keep in mind, however, that dominance of the carbon-centred EPFRs in biochar does not exclude the presence of minor component of oxygen-centred EPFRs. In fact, that would be consistent with g-value not at 2.0023 but around 2.003. In fact, it is well-known that biochar contains terminal carbonyl and hydroxyl groups in their structure (Li et al., 2021) and these can be associated with oxygen-centred EPFRs. The importance of oxygen-centred EPFRs is that they are very active in redox cycling process and generation of hydroxyl radicals and other ROS species. The key factor is their surface availability – the natural EPFRs present in soils, as being trapped in between the aluminosilicate sheets are not available for the redox activity – this is in contrary with EPFRs in biochar—since oxygen-centred EPFRs in biochar are associated with surface terminations, they will be available and reactive, despite the fact that oxygen-centred EPFRs in biochar are at much lower concentration compared to carbon-centred ones.

3.3. Biochar load effect on EPFR quality and quantity in the soil

Fig. 4 presents changes in radical concentration and type as affected by four interrelating factors – *biochar content, cultivation process, fertilizer addition and time*. Addition of biochar to the soil has initially decreased the g-value of all detected EPFRs in the soil (Fig. 4a, c, e and g), a consequence of dominant biochar origin of EPFRs in amended soils (Fig. 4b, d and f). After the initial incubation time in the soil, the character of the EPFR was changing, with the degree of the change dependent on other treatment/additives to the soil. Firstly, soil cultivation accelerates the decay of all EPFRs in the soil with slow change in the g-value from carbon-centered radicals (as in biochar) to more oxygen-centered radicals (as in not amended soil), while no cultivation resulted in a more rapid change into higher g-values of EPFRs. This is a result of increased oxygen availability in the cultivated soils resulting in overall decomposition of all types of radicals, while in more “stagnant” anoxic conditions (where O_2 deficiency prevails) formation of new oxygen-centered radicals by the metal-organic interaction is more favoured (complete oxidation of EPFRs do not occurs). This seems to be supported by the data with non-cultivated soils with fertilizer addition (Fig. 4e) where due to further increase of available metals increase of g-values is more profound.

Based on that data, it is important to stress two significant factors impacting EPFR concentration and speciation in the biochar amended soils: transition metal content (particularly that in reaction available form) and cultivation level of soil. These two factors contribute mostly to the fate of EPFRs – while cultivation significantly decreases presence of both types of EPFRs in relatively short period of time, metal presence (and particularly through fertilizer supplementation) increases the half-life of radicals (Fig. 5) and transforms organic matter to more oxygen-centred EPFRs. The amount of biochar addition played a secondary role as the EPFRs content in the soils was in a longer term primarily controlled by the other two factors.

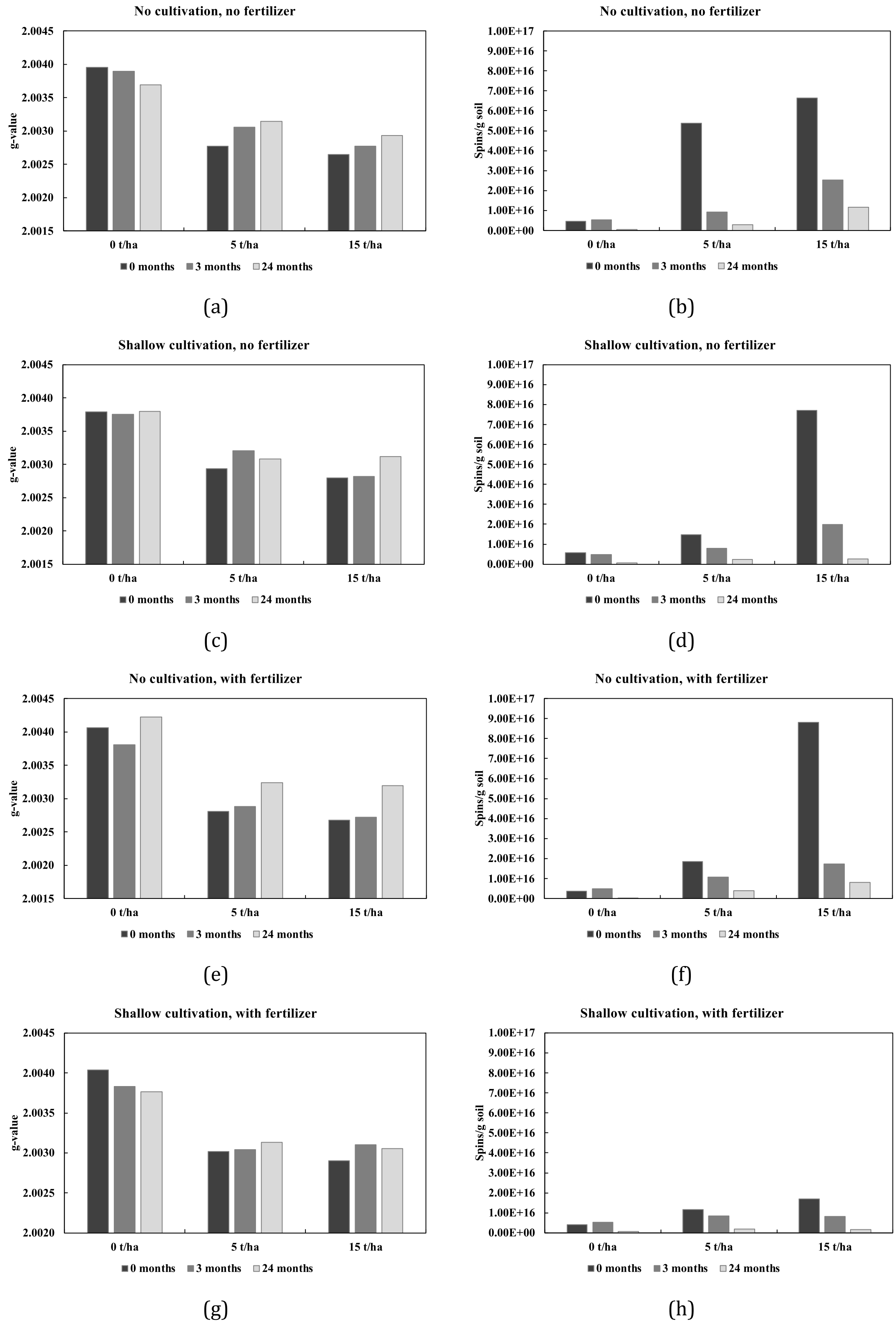
3.4. Relationship between EPFR concentration and type

The above conclusions are further supported by further analysis of the data. Figs. 6 and 7 show relationships between radical concentration and type (g-value) at different soil conditions. In Fig. 6, independently of a time period, radical concentration decreased while g-value increased, i.e. the amount of radicals decreased as radicals become oxidised. The correlation was strong (r=0.71) during the entire studied period of 0 to 24 months in the samples amended with biochar and fertilisers. In natural agricultural soil with fertilisers, the relationship between radical concentration and type was dependent on the time period of investigation. Initially (0 months, Fig. 7a) and after 24 months (Fig. 7c), the higher radical concentration corresponded to higher g value g-value. The opposite trend in correlation between radical concentration and type is observed after the 3-months period (Fig. 7b) from fertilizer addition. The positive correlation between radical concentration and g-value was detected. This indicates that fertilizer addition resulted in overall increase of g-value of EPFRs and should be attributed to new radical generation as well as oxidative progress (more radicals get more oxygen-centred). Since fertilizers contain transition metal (as per Table 2) that are available for cationic exchange and reaction with organic matter, those metals should be considered as the source of new EPFR formation.

3.5. Soil characteristics and EPFRs

Soil properties have a significant impact on EPFRs. Positive correlation was found between soil electrical conductivity and radical g-value in fertilized soil without biochar (Fig. 8a). The electrical conductivity of the soil can be impacted by the addition of biochar (Fig. 8b). In general, the higher concentration of EPFRs, the higher soil conductivity (Fig. 9d,e). Since biochar itself is not a carrier of significant amounts of ions, it indicated that EPFRs are reactive in the soil producing mobile ions. It may be an indication of the redox cycling process of EPFRs and formation of radical anions (such as superoxide anion). In the presence of fertilizers the conductivity correlation between the EPFR concentration and conductivity was even more dramatic (slope 2E−14 vs. slope 3E−15) which indicated a promoting effect of fertilizers on EPFR activity (Fig. 9a,b), however it could also relate to the general presence of mobile, water soluble ions of fertilizers. The fact, that conductivity increased with the decreasing g-value of the amended soils further confirmed that conductivity was associated with the amount of biochar addition (biochar had much lower g-values compared to pure soil). This is in general agreement with data indicating an increasing organic matter with decreasing g-values (Fig. 8c,d).

The EPFR reactivity towards superoxide formation is associated with the redox cycling initiated by the deprotonation of EPFR species. Thus, soils containing reactive EPFRs will be characterized by the lower pH values (Fig. 9c). In fact, such correlations were observed in these studies, where increasing content of EPFRs result in overall decrease of the pH.



(a) (b) (c) (d) (e) (f) (g) (h)

Fig. 4. Concentrations and types of EPFRs in different soil conditions, combining non-cultivated and shallow-cultivated soil, fertilized and non-fertilized soil, with and without biochar, over three time periods: initial stage (0 months), 3 months and 24 months.

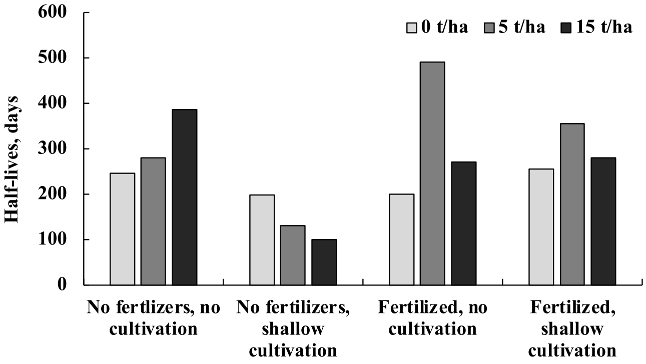


Fig. 5. Half-lives of environmentally persistent free radicals in soil with different treatments.

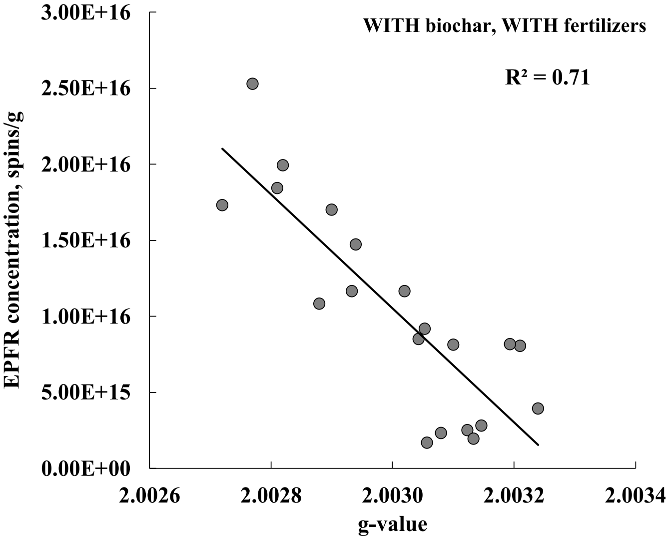


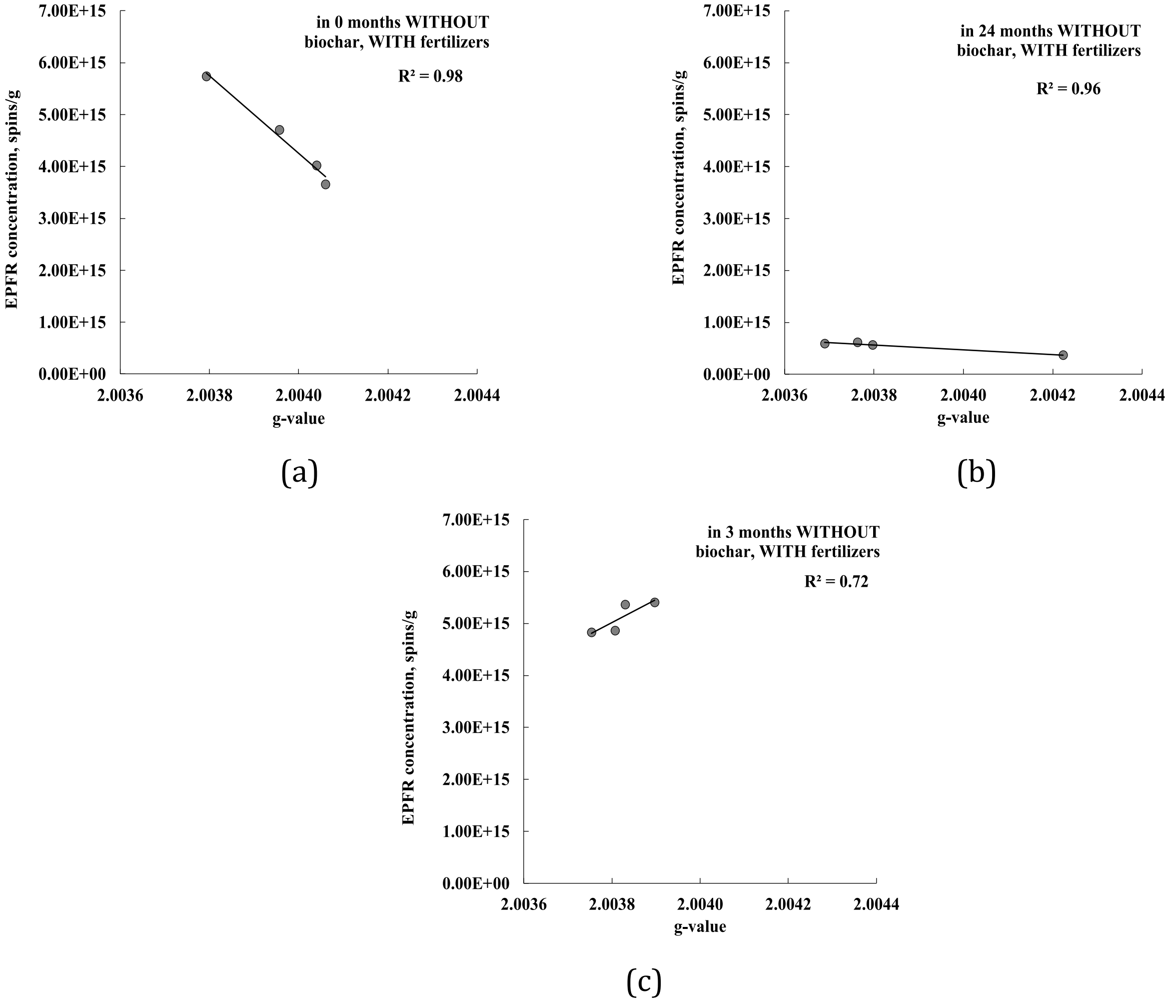
Fig. 6. Relationship between EPFR concentration and g-value in samples amended with biochar and fertilizers during the entire studied period.

4. Conclusions

Our studies have provided a unique view on the fate of EPFRs in soils upon the biochar amendment. Based on this data the fate of EPFRs in amended soils is determined by two factors: the cultivation methods and transition metal addition/content is soils.

- Cultivation and soil turning accelerates the decay of all type of EPFRs, both oxygen and carbon-centered, independently from their initial content or the level of biochar amendment. It take about 3 months from the amendment to dramatically decrease EPFR content in the biochar amended soils.
- Transition metal content in soils determines the speciation of the EPFRs. Though initial EPFRs from biochar are primarily of carbon-centered nature, transition metals in soil or introduced with fertilizer result in slow transformation/formation of oxygen-centered radicals. These radicals are formed primarily from the organic matter introduced with biochar.

These findings determine the potential method of application of biochars to the soils, depending on the desired outcome. For the biochar application as remediation agent to decontaminate soils, the application with addition of fertilizers is recommended, which will increase the half-life of EPFRs and increase the content of oxygen-centered EPFRs. Such system will be characterized by a higher propensity to in-situ generate hydroxyl radicals to decontaminate the soils. No cultivation should be applied in such case. For biochar use as a supplemental source of the organic matter to increase bioactivity of the soils, cultivation of the amended soil is recommended, to supress the content of EPFRs which may negatively impact the microbial communities.



(a) (b) (c)

Fig. 7. Relationship between EPFR concentration and g-value in fertilized soil samples without biochar during the entire studied period.

CRediT authorship contribution statement

Edita Baltrėnaitė-Gedienė: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing – original draft, Visualization, Supervision, Project management. **Slawomir Lomnicki:** Validation, Resources, Data curation, Writing – review & editing. **Chuqi Guo:** Software, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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This paper is dedicated to the memory of Prof Dr Habil Pranas BALTRĖNAS – the father of the main and corresponding author. Prof. Baltrėnas passed away while data for this paper were collected. He was the pioneer of air quality control technology development in Lithuania; the originator of the first environmental protection study program in Lithuania; the founder of Environmental Protection Department, the Institute of Environmental Protection, the Journal of Environmental Engineering and Landscape Management at Vilnius Gediminas Technical University, Lithuania (https://vilniustech.lt/aplinkos-inzinerijos-fakultetas/padaliniai/aplinkos-apsaugos-institutas/apie-instituta/51809#327662).

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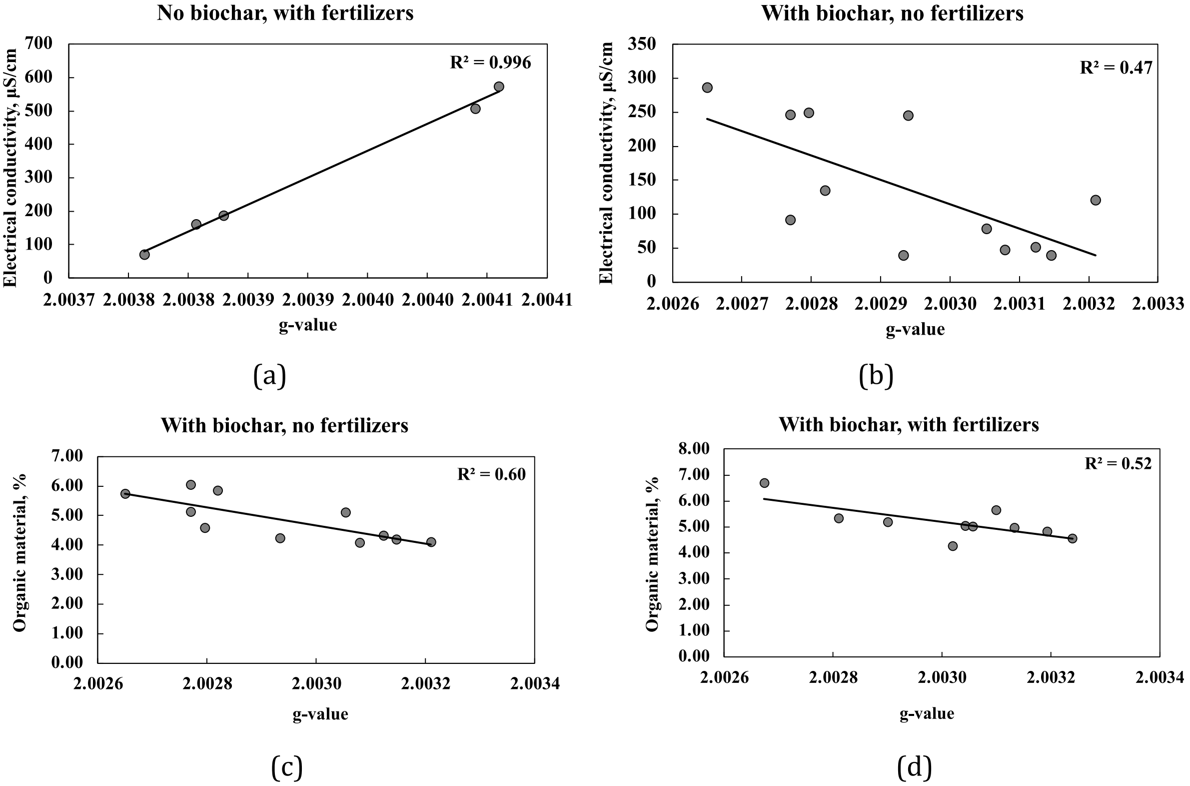

Fig. 8. Relationship between EPFRs g-values and some of soil properties in biochar/fertilizer soil systems.

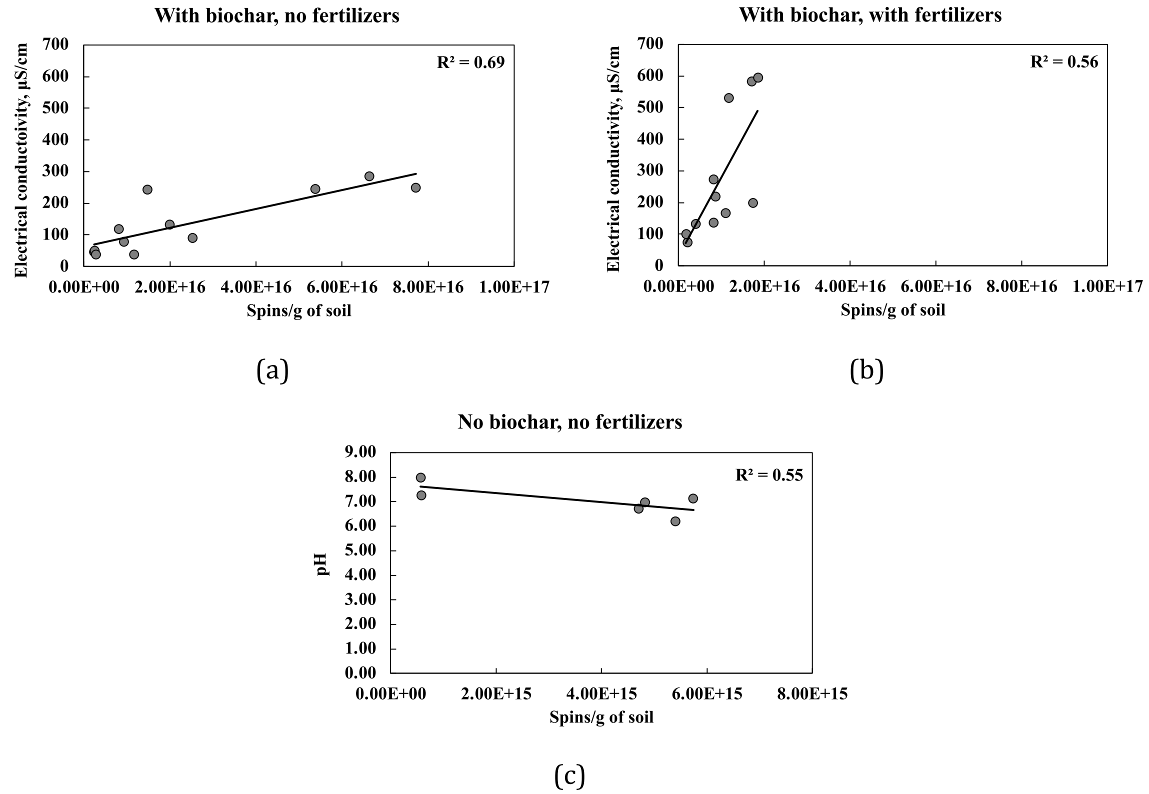

Fig. 9. Relationship between EPFRs concentration and some of soil properties.

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