International Journal of Research Publication and Reviews

Journal homepage: www.ijrpr.com ISSN 2582-7421

Fenoxaprop-Ethyl Herbicide and The Effects of Biochar to Its Toxicity: A Review

Aaron Giovanni Q. Espina[1], Yalova Vianka R. Almeria[1], Nicole Ann E. Balayon[1], Trixie Kaye E. Gamale[1], Ianna Kaylah A. Resma[1], David Nathaniel T. Uy[1], Erwin M. Faller[1,2]*

1,2 San Pedro College, 12 C. Guzman St., Davao City, 8000

A B S T R A C T

Fenoxaprop-ethyl Herbicide is a postemergence herbicide that is used in soil for the control of pests and wheat. Unfortunately, it is also notable to cause alarming risks to humans, animals, and plant life. Nevertheless, the application of biochar additions to soil could promote the decline of chemical contaminants in the soil ecosystem. In this review, fenoxaprop-ethyl toxicity, with the use of soils and biochar, were evaluated. It was concluded that the utilization of the amendment of biochar on heavy metals in soil can be beneficial as a remedy in farming procedures since it can be a useful method for the improvement of the quality of agricultural productivity. It could be a valuable technique for improving soil quality and environmental sustainability.

Keywords:Fenoxaprop-ethyl, Herbicide, Biochar, Toxicity, Soil, Earthworms

1. Introduction

Epa indicated that the herbicide, Fenoxaprop-ethyl, is a postemergence herbicide used to reduce pests, even weeds, in farms [1]. Fenoxaprop-ethyl (Figure 1) is a member of a herbicide family called APP or aryloxyphenoxypropionate, which inhibits a key enzyme, ACCase or acetyl co-enzyme A carboxylase, that is involved in the biosynthesis of fatty acids [2]. It works by inhibiting the ACCase in the plant chloroplast, through interfering with fatty acid production, it exerts an effect, specifically herbicidal, on the weeds. Herbicides, similar to pesticides used in farms, can be transfigured via a physical, chemical or biological process. In various types of soil, fenoxaprop-ethyl can be influenced by their fate and toxicity. Fenoxaprop-ethyl has been reported to be converted by soil, even plants, into fenoxaprop acid (Figure 2), an active herbicide that shows a much stronger activity on ACCase [3]. Both fenoxaprop-ethyl and fenoxaprop acid are reported and regarded as developmental and reproductive toxins which by most are highly toxic to humans, animals, and plant life [2]. In relation to this, once their residues are exposed to consumables and crops, concerns of pesticide or herbicide exposure to food and water may bring a catastrophic outcome to the ecosystem [2,3].

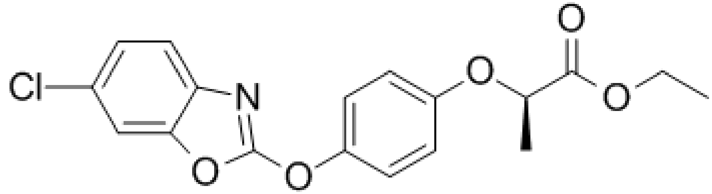

Figure 1. Chemical Structure of Fenoxaprop-ethyl

* *Aaron Giovanni Q. Espina*. Tel.: +639284516970
E-mail address: aarong_espina@spcdavao.edu.ph

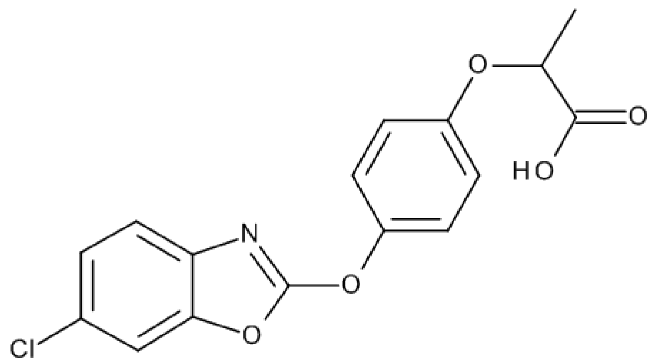

Figure 2. Chemical Structure of Fenoxaprop

Biochar, commonly known as black carbon, has gained attention as a sustainable product, an amendment utilized to increase soil quality, reducing the need for fertilizer and carbon emissions [4]. Using an amendment of soil, such as biochar, may change soil properties, both physical and chemical, and may also modify the microbial abundance of soil, activity, and structure [5]. Farmers have changed to more sustainable conservation tillage practices and adopted herbicide-tolerant varieties of crops, which has boosted global herbicide usage. However, they may pose a potential threat and raise risks to the soil environment due to their various chemical classes with distinctive modes of herbicidal action [6]. To address this, utilizing biochar may significantly decrease the environmental risk behaviors of herbicides, such as fenoxaprop-p-ethyl, in soil. Studies have shown that biochar may potentially accelerate microbial activity, which will also accelerate the biodegradation of soil, and, upon adding biochar to soil, the retention process of the herbicide can be potentiated more efficiently, which can contribute to the reduction of contaminants, particularly chemical contaminants, to the soil ecosystem [7,8]. The utilization of earthworms in evaluating the toxicity of a herbicide can greatly contribute to the agricultural ecosystems as it is a crucial constituent of soil fauna. [9]. Earthworms are an essential bioindicator organism in soil ecotoxicological research investigations [10]. It serves as a primary food supply for numerous wildlife such as reptiles and mammals. Some researchers evaluated the impact of the longevity of earthworms with the addition of biochar [10]. However, the evaluation of the effects of biochar amendment combined with herbicides, such as fenoxaprop-ethyl, have little to no studies published. This study aims to review the toxicity of fenoxaprop-ethyl herbicide using biochar amendments. Assessing the potential effects utilizing biochar on herbicides is vital for the soil ecosystem as well as protecting the health and quality of life.

2. Methodology

This article review makes use of retrieved research and peer-reviewed papers from several journal databases like Google Scholar, ResearchGate, SpringerOpen, NCBI, and Pubmed. For the methodology, the search started on April 14, 2022, which has a direct focus on the following, (1) Materials (2) Experiments involved and (3) Extraction

2.1. Materials

Biochar

In an oxygen-limited condition, biochar is formed by the thermal breakdown of materials [11]. It is compatible for multiple uses because of biochar’s distinct properties. Biochar offers various advantages, including ease of preparation, environmental friendliness, reusability, and low cost [11,12]. Biochar is a soil treatment that can enhance agriculture production and sustainability. It is created by pyrolyzing organic molecules at extreme temps in an atmosphere where there is an absence of oxygen [13,14]. Soil's properties have a direct impact on crop production productivity [15]. Biochar application has been shown in studies to boost crop production by improving its qualities. Biochar was shown to enhance soil structure [16], stability and permeability [13, 16], liquid capacities and nutrient cycling, strength properties and penetration tolerance, soil infiltration, and erosion [13]. It is notably more durable among other amendments and even improves nutrition in ways other than fertilizer. Biochar has also been found in studies to improve soil nutrient content, exchangeable cations, nutrient utilization efficiency, nutrient retention capacity, and decrease soil acidity [17].

Fenoxaprop-ethyl Herbicide

Fenoxaprop-ethyl is a member of a herbicide family called APP or aryloxyphenoxypropionate, which inhibits a key enzyme, ACCase or acetyl co-enzyme A carboxylase, that is involved in the biosynthesis of fatty acids [18]. It works by inhibiting the ACCase in the plant chloroplast, through interfering with fatty acid production, it exerts an effect, specifically herbicidal, on the weeds. Herbicides, similar to pesticides used in farms, can be converted via a physical, chemical or biological process.

Earthworms

Several studies have found that Earthworms in the soil can act as a biological vector for enzyme adsorption on biochar. [19]. Earthworms find the energy, nutritional supplies, water, and buffered climatic conditions they require in soil. Earthworms are classified into functional categories based on the food they eat and the basic environmental circumstances in which they inhabit. Morphology, distribution in the soil profile, capacity to dig galleries and make surface casts, and connections with soil microorganisms are some of the primary differences between these functional groups. [20]. Biological methods aimed at recovering degraded soils, earthworm utilization, and goods resulting from its activities (vermicompost) have developed as a potential environmentally friendly method [21].

2.2. Experiments Involved

Addition of Biochar to Pyrene and its Bioavailability and Toxicity in Soils

The toxicity of polycyclic aromatic hydrocarbons (PAH) and the effects of pyrene (PAH) on soil treated with biochar, compost, or both were studied to give a dependent variable. The influence on nematode reproductive rates was used as an endpoint. Caenorhabditis elegans, a soil microfauna that is the nematode, was used as a model organism. [22]. In soil ecosystems, nematodes are the most numerous and diverse metazoans, and they play important roles in soil food webs. Nutrient cycling is greatly influenced by webs [23]. The primary goal of this experiment was to provide data on the efficiency of biochar/compost to be a remedy at minimum to maximum pyrene hazardous levels., as well as comparing nematode rates of reproduction and biochar/compost efficacy [24]. Furthermore, the secondary harmful impacts of biochar and compost due to its characteristics, as well as the probable presence of toxic compounds and heavy metals in compost, were investigated using controls, which were contaminant-free soils altered with these materials [25].

Dose for the Biochar

Biochar dose is determined upon using the chemical hapten, Hapten-1,4-2-[4-(6-Chloro-benzooxazol2-yloxy)-phenoxy]-propionylamino-3-fluoro-benzoic Acid. K-13209 in 1,4-dioxane combined with LiOHH2O in water will be placed in a cooled solution. The mixture will be stirred at room temperature for 6 hours. The mixture will be separated with dichloromethane when the pH is adjusted to 2. The organic phase will be dried over anhydrous sodium. The sulfate will then evaporate under low pressure, and the remnant will be refined in dichloromethane utilizing silica gel chromatography and an ethyl acetate/n-hexane solution as an eluent [26].

Degradation

Experiments involving degradation were utilized in analyzing soil and biochar. For the degradation experiments, the collected sample was first reduced to 30%. In a study, scientists have gathered multiple samples for the control and about half of a thousand grams of soil were only utilized, hence the dosage of biochar was fixed in accordance to the weight of biochar and of the soil [27]. The biochar application dosage corresponds to levels used in other biochar remediation experiments [28]. There are a total of 2 treatments that will be utilized for the experiment and both of them were exposed to fenoxaprop-ethyl with a dosage of 10 micrograms g^{-1} that is yield when mixing 1 ml of 5000 micrograms ml^{-1} solution of fenoxaprop-ethyl acetone [27].

Acute Toxicity

Acute Toxicity of materials were conducted on earthworms, which were the subject for the test, and were tested for possible results of fenoxaprop-ethyl from biochar-amended soil on toxicity [27]. Quantifying an active ingredient in the samples is important for a bioanalytical technique development program. Moreover, UHPLC's sensitivity and selectivity at the very minimum detecting range will lead to accurate, consistent data that may be used for several purposes, including pharmacokinetics, toxicology, and bioequivalence investigations [29]. Sample preparation strategies have grown in importance in bioanalytical methodologies. ULPC- tandem mass spectrometer has a very important part in bioanalytical experiments and cell biology [30].

Following the guidelines set by the OECD on testing chemicals, earthworms may be exposed to soil containing fenoxaprop-ethyl for fourteen days to have optimal results. It is recorded that the maximum concentration for exposure is 1000 micrograms g^{-1} [27]. Pretest studies indicated that exposure doses of fenoxaprop-ethyl-containing soil are set at 125, 250 and 500 micrograms g^{-1}. Treatment to exposure may conceive four duplications, with an addition of earthworms and contaminated soil in one liter glass beaker. There were also solvent control groups. At 20 ± 2°C. Breakable beakers were placed in a lighted incubator with non stop lighting. On the fourteenth day, mortality was reported upon exposure to the herbicide. The front end's reaction to mechanical stimulation was used to determine death. Presence or absence of biochar were tested out on soil for acute toxicity bioassays. To thoroughly examine and analyze the effects of fenoxaprop-ethyl on earthworms upon the addition of biochar, biochar amendment will be modified on appropriate concentrations [27].

2.3. Extraction

Analysis of HPLC-MS/MS (High Performance Liquid Chromatography Mass Spectrometry)

The researchers used HPLC-MS/MS analysis in the sample collection of Fenoxaprop and Fenoxaprop-ethyl analyses [27]. HPLC-MS/MS and HPLC-fluorescence were done using Agilent Technologies 6410 and 1200 Series high-performance liquid chromatography systems. equipment to perform precise and simple analysis of the targeted chemicals. [31]. Upon performing the analysis, a gram of earth dirt was deposited by a 4 ml ethyl acetate in a 15-ml polypropylene centrifuge tube. The earth dirt was mixed thoroughly for 10 minutes before being centrifuged at 3500 rpm for 3 minutes. After repeating the extraction with 4 mL of ethyl acetate, the supernatant was collected and dried with a nitrogen stream. [27].

In addition, An Agilent Eclipse XDB-C18 column with a Thermo Scientific TSQ Quantum Access Max was used for Fenoxaprop-ethyl and Fenoxaprop HPLC-MS/MS analysis. Smaller particle column separations improve efficiency per unit time;however efficiency cannot be improved at greater mobile phase flow rates or linear velocities [32]. Moreover, the detector on the mass spectrometer was configured to ESI. Equipped with ion sweep gas pressure along with sheath gas pressure (0,15,35 arb) and auxiliary gas pressure with a spray voltage (2500 V). with a temperature of 200 and 300 celsius by the vaporizer and capillary, along with recoveries for fenoxaprop-ethyl and fenoxaprop 0.1,1, and 10 g was in between of 85%:102% with the control soil and 83%:106% in the biochar amended soil [27]. This equation (Ct = A1 + A2ekt) was utilized [27,32].

UHPLC (Ultra-high performance liquid chromatography)

UHPLC (ultra-high performance liquid chromatography) is a kind of liquid chromatography which separates columns with particles smaller than 2.5–5 m in size and it is often a technique being used in high-performance liquid chromatography (HPLC) [33]. This technology is now an established, common method that offers significant advantages on the basis of separation, efficiency and speed. UHPLC apparatus and stationary phases are now widely accessible from a variety of suppliers. Every major LC manufacturer offers one or more systems that provide the user a diverse range of instrumental equipment that may be sensibly chosen depending on the demands of the laboratory [33, 34]. The capacity to do ultra-fast and/or high-resolution separations while using columns filled with sub-2-m particles and chromatographic systems which can endure pressures of up to 1400 bar is referred to as UHPLC and it is one of its major benefits [35].

3. Results & Discussion

3.1. Herbicide in controlled soil

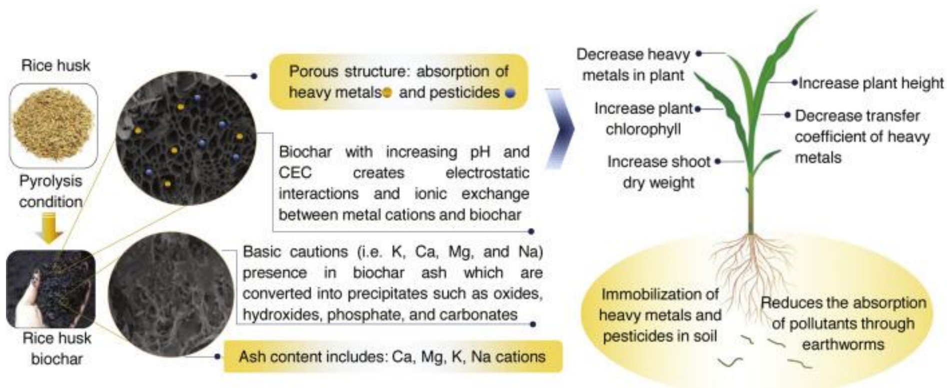

Figure 3. Mechanisms of biochar for immobilization of heavy metals and organic pollutants [36].

Biochar is produced by subjecting agricultural wastes like rice hull, corn cobs and coconut husk to high temperatures with minimal oxygen [37]. A remarkable climate change mitigation technology offers new possibilities for impoverished rural communities that can use it to create marketable products for green energy and other environmental products and services [38]. In an effort to improve soil fertility, some farmers and gardeners have used cellulose-rich materials created by slow pyrolysis as an amendment to provide nutrients to their crops. It is also thought to improve the retention of fenoxaprop-ethyl, an insecticide with high mammalian toxicity, thus, reducing its likelihood of harming earthworms [39].

Biochar might help minimize herbicide toxicity, according to the data. Two compounds, such as wheat grain and stem, were unidentifiable in the soil in the investigation, demonstrating that the correct amount of fenoxaprop-P-ethyl can be utilized securely into wheat crops and delivery [39]. The dispersion dynamics of fenoxaprop-p-ethyl as well as its metabolite, fenoxaprop acid, were studied at two treatment levels for two seasons in wheat fields to assess the technique's sensitivity, precision, repeatability, and linearity [40]. Fenoxaprop-p-ethyl is a harmless substance to use and will not affect the environment. Under field circumstances, humans and animals eat both parent as well as metabolite residues below the European Union limiting residue value. [41].

In experimenting, the first to be identified is the outcome of Fenoxaprop-ethyl throughout the control soil. The decomposition of the Fenoxaprop-ethyl has a 0.5-day half-life [27]. Moreover, Fenoxaprop-ethyl was reduced by more than 90% after two days [27]. 35 days after the Fenoxaprop-ethyl was applied, the toxic effects of the chemical had all but dissipated [27]. Furthermore, the Fenoxaprop concentration initially increased, peaking during the 12th hour [27]. After that, the Fenoxaprop's concentration gradually decreased. Lastly, Fenoxaprop had a half-life of approximately 56.9 days in control soil, which was much more prolonged than fenoxaprop-ethyl (half-life of 0.5 days) [11]. As configured, upon that 35th day, substantial fenoxaprop deposits visible in the control soil are significantly high [27].

3.2. Herbicides in biochar-amended soil.

The next to be identified is the outcome of fenoxaprop-ethyl inside of the biochar-amended soil. Moreover, fenoxaprop-ethyl also decomposes rapidly in biochar-amended soil. In comparison, in biochar-amended soil, the half-life of fenoxaprop-ethyl was substantially longer than in control soil. [27]. Soils treated with biochar and control soils, 90 percent degradation took 2 and 17 days, respectively [27]. Compared to the control soil, biochar application considerably enhanced fenoxaprop-ethyl residues [27]. On the 35th day, it was ten times greater than the control dirt [27]. In other words, biochar increases the fenoxaprop-ethyl residue risk within the soil.

Based on the biochar-amended soil, the metabolite fenoxaprop first raised, then declined. Fenoxaprop levels peaked in the control soil at 12 hours. Biochar, on the other, significantly reduced fenoxaprop residues in the soil [27]. The maximum residue shows a decrease of over 33% [27]. Due to biochar's limited absorption of fenoxaprop and favorable effects on microorganisms, remarkable results were shown. The amount of biochar in the modified soil was much lower than in the control soil [27]. Furthermore, the soils with and without biochar can be examined to determine whether different forms of bacteria are present. Biochar aided the fenoxaprop degrading bacteria in the soil and altered the biodegradation pathway in the study [27]. Upon that 35th day, biochar considerably reduced the amount of fenoxaprop in the soil. More than 85% of the reduction was achieved. Thus, biochar may help mitigate the risk of fenoxaprop contamination in soil [27,43].

These findings suggest that biochar might be utilized to mitigate the detrimental effects of xenobiotic compounds on soil earthworms. Thus, in the soil that is treated with biochar made from local plants and leaves, earthworms showed a higher survival rate than the control group. This is because the biochar has no or low toxicity to earthworms [39]. In addition, earthworms benefit from the use of biodegradable organic remains such as manure and crop litter [44]. Biochar produced by pyrolysis, which is a carbon - containing byproduct, is becoming increasingly popular in temperate agricultural soils. A team of researchers went to a dairy farm on Quebec's St. Francis River watershed to conduct their study. Earthworm populations in soils amended with biochar were examined [45]. Comparing earthworm quantity and biomass in areas with and without wood-based biochar prompts us to assume that in this cold, humid temperate climate, earthworm populations in biochar-amended soils remain stable [46].

3.3. Experiment on Acute Toxicity with Earthworms

When exposed at specific concentrations, fenoxaprop-ethyl can be toxic to earthworms. In the study, earthworms were exposed to varying levels of fenoxaprop-ethyl, and their survival rates were monitored [27]. The earthworms in the solvent control group survived, while all of those in the test group died. In contrast, at specific concentrations, all of the experimental group earthworms died within 14 days [27]. In accordance with these findings, few deaths were observed in the solvent-treated control soil. This result suggests that biochar toxicity may be limited, similar to previous studies [47]. Biochar absorbed fenoxaprop-ethyl and reduced toxicity to earthworms, suggesting that biochar lowers the bioavailability of herbicide in soils; therefore, biochar does not generate perilous risk of toxicity towards organisms in soil environments. Building from these facts, the researchers concluded that biochar could certainly reduce the toxicity of pesticides to earthworms [47]. However, more research is needed to understand this phenomenon better and its implications for soil conservation [48].

4. Conclusion

Biochar amendment of soil can decelerate the dissipation of fenoxaprop-ethyl, and it apparently takes 1.2 days for half of the fenoxaprop-ethyl applied to the biochar treated soil to be completely discharged. The amount of metabolite fenoxaprop formed in the biochar-amended soil is less likely to be lower in comparison with the control soil (maximum value of 3.865 µg g−1 against 5.787 µg g−1). Moreover, the dispersion of the metabolite fenoxaprop was quicker in the biochar-amended soil with a record of 1 and a half days standing duration than in the control soil with a record of approximately 57 days. The microorganism, together with the biochar present in soil can cause reduced toxicity for earthworms compared with control biochar-amended soils, the biochar amendment reduced toxicity to approximately 323 micrograms g−1 and above a thousand micrograms g−1. These angleworms, another term for earthworms, can surely live longer in amended soils with biochar than in regular soils, producing more biomass and enzymes as recorded. Biochar, therefore, can help reduce the impact of pesticides on the environment by removing heavy metals from contaminated soil. It may even be used as a natural fertilizer for farmlands. It could be a valuable technique for improving soil quality and a great addition to farmers' strategies.

Acknowledgement

The researchers would like to express their sincerest gratitude to San Pedro College Pharmacy Department for the support in making this research opportunity possible.

Disclosure Of Conflict of Interest

No conflict of interest from the authors

References

1. Jing X, Yao G, Liu D, Liu M, Wang P, Zhou Z. Environmental Fate of Chiral Herbicide Fenoxaprop-ethyl in Water-Sediment Microcosms. Scientific Reports. 2016;6(1).
2. Bielská, Lucie; Kah, Melanie; Sigmund, Gabriel; Hofmann, Thilo; Höss, Sebastian (2017). Bioavailability and toxicity of pyrene in soils upon biochar and compost addition. Science of The Total Environment, 595(), 132–140. doi:10.1016/j.scitotenv.2017.03.230
3. Li L, Bi Y, Liu W, Yuan G, Wang J. Molecular basis for resistance to fenoxaprop-p-ethyl in American sloughgrass (BeckmanniasyzigachneSteud.). Pesticide Biochemistry and Physiology. 2013;105(2):118-121.
4. TANDON S. Degradation of Fenoxaprop-p-Ethyl and Its Metabolite in Soil and Wheat Crops. Journal of Food Protection. 2019;82(11):1959-1964.
5. Glaser B, Haumaier L, Guggenberger G, Zech W. The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics. Naturwissenschaften. 2001;88(1):37-41.
6. Hardy B, Sleutel S, Dufey J, Cornelis J. The Long-Term Effect of Biochar on Soil Microbial Abundance, Activity and Community Structure Is Overwritten by Land Management. Frontiers in Environmental Science. 2019;7.

7. Rose M, Cavagnaro T, Scanlan C, Rose T, Vancov T, Kimber S et al. Impact of Herbicides on Soil Biology and Function. Advances in Agronomy. 2016;:133-220.
8. Smith A. Persistence and transformation of the herbicides [14C]fenoxaprop-ethyl and [14C]fenthiaprop-ethyl in two prairie soils under laboratory and field conditions. Journal of Agricultural and Food Chemistry. 1985;33(3):483-488.
9. Ferreira Mendes K, Francisco Dias Júnior A, Takeshita V, Paula JustinianoRégo A, Luiz Tornisielo V. Effect of Biochar Amendments on the Sorption and Desorption Herbicides in Agricultural Soil. Advanced Sorption Process Applications. 2019;.
10. Martinkosky L, Barkley J, Sabadell G, Gough H, Davidson S. Earthworms (Eisenia fetida) demonstrate potential for use in soil bioremediation by increasing the degradation rates of heavy crude oil hydrocarbons. Science of The Total Environment. 2017;580:734-743.
11. Lehmann J. Biochar for environmental management: An introduction. In 'Biochar for environmental management: Science and technology'.(Eds J Lehmann, S Joseph) pp. 1–12. International Biochar Initiative: Westerville, OH, USA. 2009.
12. Hemavathy RV, Kumar PS, Kanmani K, Jahnavi N. Adsorptive separation of Cu (II) ions from aqueous medium using thermally/chemically treated Cassia fistula based biochar. Journal of cleaner production. 2020 Mar 10;249:119390.
13. Adekiya A, Agbede T, Olayanju A, Ejue W, Adekanye T, Adenusi T et al. Effect of Biochar on Soil Properties, Soil Loss, and Cocoyam Yield on a Tropical Sandy Loam Alfisol. The Scientific World Journal. 2020;2020:1-9.
14. Adekiya A, Agbede T, Aboyeji C, Dunsin O, Simeon V. Effects of biochar and poultry manure on soil characteristics and the yield of radish. Scientia Horticulturae. 2019;243:457-463.
15. Benjamin J, Nielsen D, Vigil M. Quantifying effects of soil conditions on plant growth and crop production. Geoderma. 2003;116(1-2):137-148.
16. Kimetu J, Lehmann J. Stability and stabilisation of biochar and green manure in soil with different organic carbon contents. Soil Research. 2010;48(7):577.
17. Basak B, Sarkar B, Saha A, Sarkar A, Mandal S, Biswas J et al. Revamping highly weathered soils in the tropics with biochar application: What we know and what is needed. Science of The Total Environment. 2022;822:153461.
18. Bielská, Lucie; Kah, Melanie; Sigmund, Gabriel; Hofmann, Thilo; Höss, Sebastian (2017). Bioavailability and toxicity of pyrene in soils upon biochar and compost addition. Science of The Total Environment, 595(), 132–140. doi:10.1016/j.scitotenv.2017.03.230
19. Sanchez-Hernandez J, Ro K, Díaz F. Biochar and earthworms working in tandem: Research opportunities for soil bioremediation. Science of The Total Environment [Internet]. 2019 [cited 24 May 2022];688:574-583. Available from: https://www.sciencedirect.com/science/article/abs/pii/S0048969719327834#:~:text=Earthworms%20have%20the%20role%20of,the%20bulk%20soil%20(dynamic).
20. Lavelle, P. Earthworm activities and the soil system. Biol Fert Soils 6, 237–251 (1988). https://doi.org/10.1007/BF00260820
21. Rodriguez-Campos J, Dendooven L, Alvarez-Bernal D, Contreras-Ramos S. Potential of earthworms to accelerate removal of organic contaminants from soil: A review. Applied Soil Ecology [Internet]. 2014 [cited 24 May 2022];79:10-25. Available from: https://www.sciencedirect.com/science/article/abs/pii/S0929139314000638
22. Bielská, Lucie; Kah, Melanie; Sigmund, Gabriel; Hofmann, Thilo; Höss, Sebastian (2017). Bioavailability and toxicity of pyrene in soils upon biochar and compost addition. Science of The Total Environment, 595(), 132–140. doi:10.1016/j.scitotenv.2017.03.230
23. H. Ferris; T. Bongers; R.G.M. de Goede (2001). A framework for soil food web diagnostics: extension of the nematode faunal analysis concept. , 18(1), 0–29. doi:10.1016/s0929-1393(01)00152-4
24. Kraaij, R., Mayer, P., Busser, F., van het Bolscher, M., Seinen, W., Tolls, J., Belfroid, A., 2003. Measured pore-water concentrations make equilibrium partitioning work — a data analysis. Environ. Sci. Technol. 37, 268–274
25. Stefaniuk, M., Oleszczuk, P., Bartmiński, P., 2016. Chemical and biological evaluation of biochar produced from residues of biogas production. J. Hazard. Mater. 318: 417–424. http://dx.doi.org/10.1016/j.jhazmat.2016.06.013
26. Moon, Joon-Kwan; Keum, Young-Soo; Hwang, Eul-Cheol; Park, Byeoung-Soo; Chang, Hee-Ra; Li, Qing X.; Kim, Jeong-Han (2007). Hapten Syntheses and Antibody Generation for a New Herbicide, Metamifop. Journal of Agricultural and Food Chemistry, 55(14), 5416–5422. doi:10.1021/jf070358f
27. Jing X, Wang T, Yang J, Wang Y, Xu H. Effects of biochar on the fate and toxicity of herbicide fenoxaprop-ethyl in soil. Royal Society Open Science [Internet]. 2018 [cited 22 May 2022];5(5):171875. Available from: https://royalsocietypublishing.org/doi/10.1098/rsos.171875
28. Beesley L. Moreno‐ Jiménez E, Gomez‐ Eyles JL, et al. 2011. A review of biochars′ potential role in the remediation, revegetation and restoration of contaminated soils. Environmental Pollution.;159(12):3269
29. Weber, Kathrin; Quicker, Peter (2018). Properties of biochar. Fuel, 217(), 240–261. doi:10.1016/j.fuel.2017.12.054
30. Desai TK, Mahajan AA, Thaker A. Ultra performance liquid chromatography: a step ahead to HPLC. International Journal of Pharmacy Review and Research. 2012;2(1):61-8.
31. Kim, Eunseon; Jung, Chanil; Han, Jonghun; Her, Namguk; Park, Chang Min; Jang, Min; Son, Ahjeong; Yoon, Yeomin (2016). Sorptive removal of selected emerging contaminants using biochar in aqueous solution. Journal of Industrial and Engineering Chemistry, (), S1226086X16300077–. doi:10.1016/j.jiec.2016.03.004
32. Bielská L, Kah M, Sigmund G, Hofmann T, Höss S. Bioavailability and toxicity of pyrene in soils upon biochar and compost addition. Science of The Total Environment [Internet]. 2017 [cited 22 May 2022];595:132-140. Available from: https://www.sciencedirect.com/science/article/abs/pii/S0960852412007869
33. Rathod, R.H., Chaudhari, S.R., Patil, A.S. et al. Ultra-high performance liquid chromatography-MS/MS (UHPLC-MS/MS) in practice: analysis of drugs and pharmaceutical formulations. Futur J Pharm Sci 5, 6 (2019). https://doi.org/10.1186/s43094-019-0007-8
34. Nováková, Lucie (2017). Liquid Chromatography || Ultra-high performance liquid chromatography. , (), 719–769. doi:10.1016/b978-0-12-805393-5.00029-4
35. Fekete, Szabolcs; Schappler, Julie; Veuthey, Jean-Luc; Guillarme, Davy (2014). Current and future trends in UHPLC. TrAC Trends in Analytical Chemistry, 63(), 2–13. doi:10.1016/j.trac.2014.08.007
36. Asadi, H., Ghorbani, M., Rezaei-Rashti, M., Abrishamkesh, S., Amirahmadi, E., Chengrong, C., & Gorji, M. (2021, June 23). Application of rice husk biochar for achieving sustainable agriculture and environment. Rice Science. Retrieved May 30, 2022, from https://www.sciencedirect.com/science/article/pii/S1672630821000433
37. Khawkomol S, Neamchan R, Thongsamer T, Vinitnantharat S, Panpradit B, Sohsalam P et al. Potential of Biochar Derived from Agricultural Residues for Sustainable Management. Sustainability. 2021;13(15):8147.
38. Schröder P, Beckers B, Daniels S, Gnädinger F, Maestri E, Marmiroli N et al. Intensify production, transform biomass to energy and novel goods and protect soils in Europe—A vision how to mobilize marginal lands. Science of The Total Environment. 2018;616-617:1101-1123.
39. Katagi T, Ose K. Toxicity, bioaccumulation and metabolism of pesticides in the earthworm. Journal of Pesticide Science. 2015;40(3):69-81.

40. Chen, X., Yu, S., Han, L., Zhi, Y., & Li, W. (2011). PubMed.gov. Residues and Dissipation of the Herbicide Fenoxaprop-P-Ethyl and Its Metabolite in Wheat and Soil.
41. Tandon, S. (2019). PubMed.gov. Degradation of Fenoxaprop-p-Ethyl and Its Metabolite in Soil and Wheat Crops.
42. Singh S, Das T, Kulshrestha G. Persistence of herbicide fenoxaprop ethyl and its acid metabolite in soil and wheat crop under Indian tropical conditions. Journal of Environmental Science and Health, Part B. 2013;48(5):324-330.
43. Zablotowicz R, Hoagland R, Staddon W, Locke M. Effects of pH on Chemical Stability and De-esterification of Fenoxaprop-ethyl by Purified Enzymes, Bacterial Extracts, and Soils. Journal of Agricultural and Food Chemistry. 2000;48(10):4711-4716.
44. Rawat J, Saxena J, Sanwal P. Biochar: A Sustainable Approach for Improving Plant Growth and Soil Properties. Biochar - An Imperative Amendment for Soil and the Environment. 2019;.
45. Elmer W, Lattao C, Pignatello J. Active removal of biochar by earthworms (Lumbricusterrestris). Pedobiologia. 2015;58(1):1-6.
46. Bhunia S, Bhowmik A, Mallick R, Mukherjee J. Agronomic Efficiency of Animal-Derived Organic Fertilizers and Their Effects on Biology and Fertility of Soil: A Review. Agronomy. 2021;11(5):823.
47. Whalen J, Benslim H, Elmi A, Husk B. Earthworm populations are stable in temperate agricultural soils receiving wood-based biochar. Pedosphere. 2021;31(3):398-404.
48. Weyers S, Spokas K. Impact of Biochar on Earthworm Populations: A Review. Applied and Environmental Soil Science. 2011;2011:1-12.
49. Wang T, Cheng J, Liu X, Jiang W, Zhang C, Yu X. Effect of biochar amendment on the bioavailability of pesticide chlorantraniliprole in soil to earthworm. Ecotoxicology and Environmental Safety. 2012;83:96-101.