

Article **Changes in the Mineral Content of Soil following the Application of Different Organic Matter Sources**

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Abstract: A study conducted over three consecutive years examined the effects of using biochar, organic fertilizer and microorganisms on soil pH and the concentrations of macro and microelements in the soil. A tendency to increase soil pH was seen where biochar was used. The highest concentration of phosphorus was found in the soil after the application of organic fertilizer with the addition of microorganisms. The most potassium was found in the soil treated with biochar together with organic fertilizer, while the most magnesium was in the soil fertilized with organic fertilizer alone and organic fertilizer together with microorganisms. All the fertilization combinations resulted in an increase in boron and copper levels in the soil. The accumulation of iron in the soil was promoted by organic fertilization alone and organic fertilization together with microorganisms. The highest amount of manganese in the soil was found after fertilization with biochar together with organic fertilizer. In the combination where organic fertilizer was applied, the soil contained the most sodium, while the highest zinc content was found in the soil fertilized with biochar and organic fertilizer. The greatest increase in the carbon content in the soil occurred after the use of biochar together with microorganisms and biochar with organic fertilizer. The same treatments also resulted in the highest amount of organic matter. The study shows that the use of biochar, organic fertilization and the combined use of biochar and organic fertilization improved the quality of the soil.

Keywords: biochar; peach; organic matter; organic fertilizer; microorganism

1. Introduction

In recent years, the amounts of post-processing organic waste of plant and animal origin have been increasing and are becoming a growing environmental problem. Therefore, there is an urgent need to develop innovative methods of managing them and processing into biofertilizers and composts. The use of biochar in the composting process significantly improves the properties and quality of the produced composts, the mineralization of which in the soil is significantly prolonged [\[1\]](#page-9-0). Carbonification of safe organic waste by pyrolysis is one of the proposed solutions for managing waste biomass, as a result of which we can obtain a product called biochar with a very wide range of applications.

Biochar is produced in the process of pyrolysis of plant or animal biomass at a temperature of 350 ◦C to 1200 ◦C, under conditions of limited oxygen access. An important physical feature of biochars is their porous structure and large surface area. It is this structure that helps soil microorganisms such as mycorrhizal fungi and bacteria find shelter there [\[2\]](#page-9-1). Than et al. [\[3\]](#page-9-2) have reported that biochars made from wood chips of coniferous and deciduous trees have similar properties—a very large volume of micropores and a large specific surface area.

The feedstock and pyrolysis conditions directly affect the physicochemical properties of biochar, its chemical composition, and the availability of nutrients contained in it [\[4\]](#page-9-3).

Citation: Frac, M.; Sas-Paszt, L.; Sitarek, M. Changes in the Mineral Content of Soil following the Application of Different Organic Matter Sources. *Agriculture* **2023**, *13*, 1120. [https://doi.org/10.3390/](https://doi.org/10.3390/agriculture13061120) [agriculture13061120](https://doi.org/10.3390/agriculture13061120)

Received: 4 April 2023 Revised: 11 May 2023 Accepted: 22 May 2023 Published: 25 May 2023

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Chintala et al. [\[5\]](#page-9-4) examined three types of biochars obtained from three different raw materials (maize straw, wood chips, switchgrass straw), whose mineral composition and pH were different, and investigated their sorption and desorption capabilities. By activating them with concentrated hydrochloric acid (HCl), the specific surface area of each of the tested biochars increased almost 10 times, which is very important when they are introduced into the soil. A larger specific surface area results in better air-soil conditions, better water absorption, and reduces leaching of minerals, especially nitrogen, which migrates with water.

Baronti et al. [\[6\]](#page-9-5) and Genesio et al. [\[7\]](#page-9-6) in their experiments examined biochar obtained from waste biomass, i.e., from plant organic matter and branches from production orchards. The high concentrations of P, K, Mg and Ca in the biochar used by them indicates that that type of product can be of great importance in plant nutrition. However, its composition and properties are subject to significant fluctuations. Albuquerque et al. [\[8\]](#page-9-7) determined the pH and chemical composition of five different types of biochar and found that their pH was in the range of 8.38–11.51, the phosphorus content ranged from 82 to 845 mg·kg $^{-1}$, and the potassium content from 1551 to 7987 mg·kg⁻¹. The bulk density of these biochars also varied (0.190–0.740 g·cm⁻³). Hence the conclusion that the type of biochar used may stimulate the growth and development of crops to varying degrees.

Biochars, depending on the raw material used, pyrolysis time, and the type of installation, may have different pH. In the experiments by Amin and Eiss [\[9\]](#page-9-8), a biochar obtained from maize stalks had a pH of 6.65. Vaccari et al. [\[10\]](#page-9-9) had obtained a biochar from wheat bran carbonified at two temperatures of 800 and 1200 ◦C in the process of slow and fast pyrolysis with a pH of 11.2 and 8.3, respectively. The analysis performed by Houben et al. [\[11\]](#page-9-10) had shown that biochars produced from three different raw materials (coffee husks, wood chips, miscanthus) subjected to pyrolysis in the same installation at 600 ◦C for 30 min were characterized by similar pH values (10.1, 10.7, 10.1). However, the mineral composition and the organic carbon content of the tested types of biochar varied markedly. The biochar produced from wood chips had the highest concentrations of minerals.

Usman et al. [\[12\]](#page-9-11) subjected coconut plant residues to a slow pyrolysis process (4 h) in six temperature regimes (300, 400, 500, 600, 700, 800 °C), and then determined the pH level, C content, and concentrations of selected minerals. Their research shows that with increasing temperature the electrical conductivity (EC) increases and the pH rises by more than three units (8.32–11.49). The organic carbon content increased by 18% in the biochar produced at 800 ◦C compared to the biochar obtained at 300 ◦C. The biochar produced at 800 ◦C contained more calcium, potassium and sodium, and less nitrogen and sulphur. Biochars obtained from wheat straw by Bruun et al. [\[13\]](#page-9-12) at a similar temperature, but in a short and long pyrolysis process, differed in terms of pH and carbon content. Prolongation of the pyrolysis process caused an increase in pH by 3.3 and in carbon content by 20%. Similar research was conducted by Angin [\[14\]](#page-9-13), who found that biochar produced at 600 ◦C for 30 min had a higher pH than biochar obtained at the same temperature but in the pyrolysis process lasting 20 min longer (50 min). The above examples indicate a high dependence of biochar pH on the conditions of the pyrolysis process. The chemical composition, however, is most dependent on the raw material from which the biochar is produced. Depending on the capabilities of a given installation, using the same raw material, but changing the temperature and duration, we can obtain biochars with different pH values and different organic carbon content. In this way, biochars can be adapted to the pH of the soil. On acidic soils, in order to reduce the level of acidification, an alkaline biochar (i.e., with a higher pH) obtained at higher temperatures and with an extended pyrolysis time should be used.

Yargicoglu et al. [\[15\]](#page-9-14), testing biochars obtained from various types of wood waste, found them to vary widely in specific surface area (0.1–155.1 $\rm g\cdot m^{-2}$).

The effects of applying biochar to the soil can become evident not until several years later. Research conducted by Frac et al. $[16]$ with biochar in a peach orchard has shown that the positive effects of using biochar become more apparent some years after its application to the soil than in the first year. Adekiya et al. [\[17\]](#page-9-16) came to a similar conclusion, reporting that the use of biochar in crops with a short growing season without additional organic fertilization was not effective in the first year after its application. The same authors found that the combined application of biochar with organic fertilizer significantly increased the yielding of radish plants. On the other hand, Chan et al. [\[18\]](#page-9-17) had not observed a higher radish yield after applying biochar from green waste at a dose of 100 t \cdot ha $^{-1}$, but its combined use with a nitrogen fertilizer increased the yield compared to the combination where the plants were fertilized only with nitrogen.

Kulczycki et al. [\[19\]](#page-10-0), analyzing the results of their study, found the possibility of using low doses of biochar as an addition to synthetic fertilizers, which can improve soil fertility and benefit crops. In turn, Filho et al. [\[20\]](#page-10-1) demonstrated a slowdown in the release of phosphorus into the soil from a fertilizer containing biochar, which might have a positive impact on better plant growth throughout the season. Chan et al. [\[21\]](#page-10-2), studying the effects of biochars from chicken litter, obtained at 450 ◦C and 550 ◦C, had observed that the biochar obtained at the lower temperature showed better availability to plants of the phosphorus (P) contained in it. Increasing the temperature of pyrolysis by $100\degree$ C increased the pH of the biochar from 9.9 (450 °C) to 13.0 (550 °C).

Archontoulis et al. [\[22\]](#page-10-3) reported a positive effect of biochar on the growth and yielding of wheat plants grown in a sandy soil. In contrast, the application of biochar to a clay soil had little effect on the growth of maize plants. According to these researchers, the impact of biochar is greater on the environment than on agricultural production. Crane-Droesch et al. [\[23\]](#page-10-4) were of the opinion that the effectiveness of biochar was more pronounced in moist tropical soils than in better-quality and more fertile soils. The use of biochar is most justified on less fertile soils. Similar conclusions were also reached by Jeffery et al. [\[24\]](#page-10-5). When biochar is added to soil, the availability of NH_4 and NO_3 varies greatly and depends on soil quality [\[25\]](#page-10-6).

This paper presents changes in the mineral composition of soil in a peach orchard as a result of treatments with a biochar, soil microorganisms, and an organic fertilizer over three consecutive years.

2. Materials and Methods

The experiment was set up in 2014 in the Experimental Orchard of the National Institute of Horticultural Research in Dabrowice, Central Poland $(51°54'51.5''$ N $20^{\circ}06'29.8''$ E), on peach trees of the cultivar 'Meredith', planted at a spacing of 4×2 m in the spring of 2013. The orchard soil on which the experiment was planted was classified as fawn soil, according to international soil classification system [\[26\]](#page-10-7). At the time of planting, the soil pH was slightly acidic with a pH of 6.2, and the average humus content of the soil was 1.4%. The experiment was designed in a random block layout, in 4 replicates, with 3 trees per plot representing one replicate. The biochar used for the study had the composition given in Table [1](#page-3-0) and was produced by the Polish company Fluid. In the spring of 2014, the following combinations of plant fertilization treatments were applied:

- 1. Control without fertilization (K)
- 2. Microorganisms (M)—strains of bacteria belonging to the species *Pseudomonas fluorescens* (Ps1/2) and to the genus *Pantoea* (N52AD). A single application was performed in the form of an aqueous suspension in the amount of 200 mL with each of the strains. The concentration of bacteria in the suspension was 2 \times 10⁹ CFU·mL⁻¹ for strain Ps1/2 and 1.5×10^9 CFU·mL⁻¹ for strain N52AD. Arbuscular mycorrhizal fungi were applied in a compost with the composition given in Table [2](#page-3-1) (at a dose of 0.3 kg of compost per tree). The mycorrhizal substrate contained *Glomus caledonium*, *G. intraradices*, and *G. coronatum*.
- 3. Organic fertilizer from Grupa Inco (O)—Florovit NPK (N—5%, P_2O_5 —3%, K₂O—2%, organic matter—30%), applied in a dose of 0.2 kg per tree (250 kg·ha⁻¹).
- 4. Microorganisms and organic fertilizer (M + O)—a strain belonging to the species *Pseudomonas fluorescens* (Ps1/2) and a strain belonging to the genus *Pantoea* sp. N52AD), as well as compost-based arbuscular mycorrhizal fungi applied at a dose of 0.3 kg of compost per tree (375 kg·ha−¹) together with the organic fertilizer Florovit NPK in a dose of 0.2 kg per tree (250 kg·ha⁻¹).
- 5. Biochar (B)—produced by fast pyrolysis (at 280 °C for 5 min) from wood chips of coniferous trees, containing 80% organic matter and 20% organic carbon, applied in a dose of 1.6 kg per tree (2000 kg⋅ha⁻¹).
- 6. Biochar, with the composition as described above, in a dose of 1.6 kg per tree applied together with microorganisms $(B + M)$ with the following composition: a strain belonging to the species *Pseudomonas fluorescens* (Ps1/2) and a strain belonging to the genus *Pantoea* sp. (N52AD), and compost-based arbuscular mycorrhizal fungi in a dose of 0.3 kg of compost per tree (375 kg·ha⁻¹).
- 7. Biochar, with the composition as described above, in a dose of 1.6 kg per tree (2000 kg⋅ha⁻¹) applied together with the organic fertilizer Florovit NPK (B + O) in a dose of 0.2 kg per tree (250 kg⋅ha⁻¹).

Table 1. pH and mineral content of the biochar used.

Table 2. pH and mineral content of the compost used.

All of the products were applied in May 2014, sprinkled around tree trunks (in the form of a ring, 0.5 m in diameter), and then mixed with the top layer of soil (to a depth of 20 cm). The application of microorganisms and organic fertilizer were repeated in the spring of 2015, and then continued in the following years of the experiment. After planting, the peach trees were pruned for proper rooting. During the growing season, tree training was performed, consisting in shortening and bending shoots, aimed at the correct formation of the tree crown. The trees in the experimental orchard were drip-irrigated during periods of drought. Plant protection against diseases and pests was carried out in accordance with the then-current recommendations for commercial peach orchards.

Soil Analysis

Soil for analysis was collected from a depth of 0–20 cm with a soil auger. Two soil samples were taken from under each tree and mixed with other soil samples taken within a particular treatment combination. In each year of the study, soil samples were collected from under the same trees. Soil analysis was performed in Laboratory of Quality Investigation of Horticulture Products of the National Research Institute of Horticulture, Skierniewice, Poland.

The pH of the soil was determined in KCl by the potentiometric method (pH). The concentrations of phosphorus and potassium were determined according to the Egner-Rhiem method, and the magnesium content was determined according to the Schachtschabel method. The concentrations of boron, copper, iron, manganese, sodium, and zinc were determined by inductively coupled plasma atomic emission spectrometry (ICP-OES) (Spectrometer iCAP 6500 duo, Thermo Fisher Scientific, Waltham, Massachusetts, USA) after extraction in a 1N hydrochloric acid extract. The concentrations of total nitrogen and organic carbon were determined according to the Dumas method [\[27\]](#page-10-8).

The results were statistically processed using the Statictica 10 software. Univariate analysis of variance was performed using the Tukey test at the significance level α = 0.05. Results that did not differ significantly from each other were marked with the same letters.

3. Results

Based on the soil analyses carried out in 2015–2017, it can be concluded that the experimental combinations used had little effect on changing the soil pH, which was in the range of 5.9 to 6.4. There was, however, a tendency to increase soil pH where biochar was used. The amounts of phosphorus in the soil varied in individual years. The least amount of this nutrient was found in the combinations where biochar was not used. The highest amount of phosphorus was recorded in the soil after organic fertilization with the addition of microorganisms (Table [3\)](#page-4-0).

Table 3. Soil acidity and P content of the soil in which peach trees grew in three consecutive years after the applications of biochar, compost enriched with microorganisms, and organic fertilizer.

* Means followed by the same letter within columns do not differ at $p = 0.05$.

The soil from the control combination had the lowest level of potassium in each year of the study. The highest amount of potassium was found in the soil fertilized with biochar alone and with biochar + organic fertilizer. The level of magnesium in the soil after the application of microorganisms and biochar alone did not change significantly relative to that in the control combination (without fertilization). The highest magnesium content was found in the soil fertilized with the organic fertilizer and the organic fertilizer + microorganisms (Table [4\)](#page-5-0).

Table 4. Concentrations of K and Mg in the soil in which peach trees grew in three consecutive years after the applications of biochar, compost enriched with microorganisms, and organic fertilizer.

Table 4. *Cont.*

* Means followed by the same letter within columns do not differ at $p = 0.05$.

The concentrations of boron and copper in the soil depended on the type of fertilization. The soil fertilized with the organic fertilizer + microorganisms contained the lowest amount of boron. The application of organic fertilizer alone and in combination with biochar markedly increased the level of boron in the soil. All the fertilization combinations increased the copper content in the soil compared to the control combination. The combination that contributed to the greatest extent to the increase in the level of these two components in the soil was biochar used together with the organic fertilizer (Table [5\)](#page-5-1).

Table 5. Concentrations of B and Cu in the soil in which peach trees grew in three consecutive years after the applications of biochar, compost enriched with microorganisms, and organic fertilizer.

* Means followed by the same letter within columns do not differ at $p = 0.05$.

In all three combinations where biochar was used, the soil had a lower iron content than in the control combination. The treatments that promoted the accumulation of iron in the soil to the greatest extent were organic fertilization alone and organic fertilization + microorganisms. The level of manganese was the lowest in the soil from the control combination and also in the combinations where organic fertilization + microorganisms, biochar alone, and biochar + microorganisms were applied. The study showed the highest amount of manganese in the soil after fertilization with biochar + organic fertilizer (Table [6\)](#page-6-0).

In 2015–2017, the soil in the combination where only the organic fertilizer was applied contained the highest amount of sodium, whereas the lowest amount of this element was in the soil fertilized with the organic fertilizer + microorganisms. The highest zinc content was found in the soil fertilized with biochar + organic fertilizer, whereas the lowest amount of this element was in the soil fertilized with biochar alone and in the control combination (Table [7\)](#page-6-1).

Table 6. Concentrations of Fe and Mn in the soil in which peach trees grew in three consecutive years after the applications of biochar, compost enriched with microorganisms, and organic fertilizer.

* Means followed by the same letter within columns do not differ at $p = 0.05$.

Table 7. Concentrations of Na and Zn in the soil in which peach trees grew in three consecutive years after the application of biochar, compost enriched with microorganisms, and organic fertilizer.

* Means followed by the same letter within columns do not differ at $p = 0.05$.

The use of biochar and organic fertilization increased the organic carbon content of the soil, compared to the concentration of this element in the control soil. The greatest increase in soil carbon content occurred in the combinations where biochar was used together with microorganisms or with the organic fertilizer. The same combinations were also found to contain the highest amount of organic matter. The soil from the control combination and the soil after application of only microorganisms were the poorest in organic matter (Table [8\)](#page-7-0).

Table 8. Amounts of C_{org} and organic matter in the soil in which peach trees grew in three consecutive years after the applications of biochar, compost enriched with microorganisms, and organic fertilizer.

* Means followed by the same letter within columns do not differ at $p = 0.05$.

4. Discussion

Many factors can affect the effectiveness of the biochar introduced into the soil. The application of biochar to agricultural crops has a very diverse effect on the growth and yielding of plants, depending on the geographical location, climatic conditions, and the biophysicochemical properties of individual soils. On soils with strong acidity and low fertility, the effectiveness of biochar application is significantly higher than on soils of better quality and richer in minerals. Also, the effectiveness of biochar application in crops with a short growing season is different from that in perennial crops ([\[22–](#page-10-3)[24\]](#page-10-5)).

The aim of this study was to assess the effect of biochar, organic fertilization and microorganisms on changes in the content of mineral components in the soil on which peach trees grew in the next 3 years. The effect of the applied products modified the content of mineral components in the soil in a varied and ambiguous way. The greatest positive changes in the concentration of mineral components were observed after the application of organic fertilization and biochar together with organic fertiliser. In the combination in which only biochar was used, the increase of individual elements in the soil was lower than after fertilization but higher than in the control soil.

Muhammad et al. [\[28\]](#page-10-9) found that adding different amounts and different types of biochar to the soil has been found to change the concentrations of available elements in the soil. The use of biochar is also known to affect soil microbial communities. Biochar increased soil pH and soil carbon content in *Abutilon theophrasti* and *Trifolium repens* [\[29\]](#page-10-10). In the studies Kulczycki et al. [\[19\]](#page-10-0) the pH of the soil was the lowest in combinations with biochar, while the carbon content in the soil was varied. The lack of the effect of increasing C in the soil is probably due to the very short time of the tests in which they were conducted (after 27 days). In own research, there was a slight increase in soil pH after applying biochar to the soil. This was due to the low pH of the biochar itself. On the other hand, the combined use of biochar and organic fertilization significantly increased the content of C in the soil between the first and third year. In contrast, Adekiya et al. [\[17\]](#page-9-16) observed an increase in soil pH from 5.45 to 5.94 when biochar was applied, and to 6.86 when biochar and chicken manure were applied together, and it remained the same the following year. The biochar used in their experiment had a pH of 7.56. In turn, Dempster et al. [\[30\]](#page-10-11) conducted two parallel studies in two locations. The biochar used in the experiment carried out in Australia increased the pH of the soil by 0.31, while in the experiment carried out in Wales, the carbon content under the influence of the biochar increased from 2.83% to 3.23%. In the research conducted by the authors of this paper, the greatest increase in the carbon

content in the soil was found with the combined application of fertilization and biochar $(B + O)$. The highest level of carbon was found in the soil after the application of biochar together with microorganisms $(B + M)$ and after the combined application of biochar with organic fertilizer $(B + O)$. Agegnehu et al. [\[31\]](#page-10-12) showed in their research the highest increase of C in the soil after the combined use of biochar and fertilization and biochar, fertilization and compost. However, the content of Ca, Mg, K in the soil was definitely higher after the combined application of biochar and fertilization than in the soil where only the fertilizer was applied. Depending on the type of biochar used, the content of K, Mg, Mn, Fe, Cu in the fertilized soil may have a very different effect on their content in the soil. This shows how biochar can affect the soil in a variety of ways [\[19\]](#page-10-0). In own research, the same type of biochar used in the same dose in 3 different variants had a different effect on the content of K, Mg, Mn in the soil. A clear increase in the potassium content in the soil was noted after the application of biochar with fertilizer, while the Fe content in the soil after the application of biochar decreased compared to the other combinations. In the studies of Agegnehu et al. [\[32\]](#page-10-13), a significant increase in P content in the soil was observed after the use of biochar, compost and fertilization compared to fertilized soil. In own research, the highest P content was found in soil treated with organic fertilizer in combination with microorganisms. The P content in the soil after applying biochar to the soil was at a similar level to that of the fertilized soil.

Gaskin et al. [\[33\]](#page-10-14), while analyzing the response of plants to the applied biochar, noticed a large variability between the results of tests conducted in consecutive years (2006 and 2007). In the first year of research, they observed an increase in soil pH after biochar application, whereas in the second year the soil pH varied considerably, regardless of biochar application or its absence. In the experiments by other researchers [\[34\]](#page-10-15), the biochar used did not modify soil pH, but both the soil and the biochar had a pH above 8.

Amin [\[35\]](#page-10-16), after applying biochar in three doses, obtained a slight increase in soil pH, while the amounts of organic matter, phosphorus and potassium in the soil increased significantly. The higher the dose of biochar was, the higher were the concentrations of phosphorus and potassium, and the organic matter content. The increases in the concentrations of potassium and boron in the soil after the use of biochar with organic fertilizer in the study decribed here were subsequently confirmed in the study conducted by Frac et al. [\[36\]](#page-10-17), where the concentrations of these elements in plant leaves also significantly increased with the combined application of organic fertilization and biochar.

Adekiya et al. [\[17\]](#page-9-16) clearly showed an increase in the concentrations of potassium, phosphorus, and calcium in the soil after the combined use of biochar and cow manure in the cultivation of radish. The use of biochar alone and manure alone had a much lesser effect on the increase in the concentrations of these elements in the soil, and also on the growth of plants.

Abujabhah et al. [\[37\]](#page-10-18) confirm that the application of biochar improves soil properties, positively influencing changes in the structure of fungal and bacterial communities three years after its application.

The response of perennial fruit plants to the application of biochar to the soil is not as dynamic as in plants with a short growing season. The abundance of minerals in the soil in which plants grow has a large impact on the effectiveness of biochar application. The pH of the soil must also be at the optimum level for a given plant species.

5. Conclusions

The effects of applying biochar to the soil will affect not only changes in the physical and chemical properties of the soil, but will also have an impact on the soil biological community. Biochar can also increase or decrease the availability of individual minerals in the soil, improving or limiting their availability to plants growing on it. The conducted experiment shows that the application of a small dose of biochar to the soil (2000 kg·ha⁻¹) may increase the concentration of elements in the soil. It also indicates the possibility of combining organic fertilizers and biochar already in the production phase, and this may open up new directions and trends in the production of fertilizers which, thanks to their properties, will increase the efficiency and availability of minerals taken up from the soil by plants. Biochar or fertilizers with biochar will slow down the movement of more mobile elements in the soil, which will affect their greater availability. Appropriate selection of microorganisms and their skilful combination with biochar and organic fertilizer can bring even better results for improving the quality of soil, which will improve the quality

and volume of plant production. Further research and implementation of innovative technologies in agriculture that are more environmentally friendly are needed. **Author Contributions:** Conceptualization, M.F., L.S.-P. and M.S.; methodology, M.F., L.S.-P. and

M.S.; investigation, M.F.; writing—original draft, M.S.; writing—review and editing, L.S.-P.; funding acquisition, L.S.-P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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