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The Impact of Soil Contamination with Lead on the Biomass of Maize Intended for Energy Purposes, and the Biochemical and Physicochemical Properties of the Soil

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Abstract: The subject of our research was to assess the suitability of maize grown in lead-contaminated soil for energy purposes. Lead is toxic to the natural environment. Therefore, the recultivation of soil polluted with this element is very important in stabilizing the natural environment. In the present research, maize was used as a remediating plant, and its effects were enhanced by soil fertilization with biocompost and biochar. The aim of the research was to determine the influence of Pb^{2+} on maize biomass, its combustion heat and heating value, and the biochemical and physicochemical properties of the soil. It was accomplished in a pot experiment by testing the effects of 800 mg Pb^{2+} kg^{-1} d.m. soil and biocompost and biochar applied of 20 g kg^{-1} d.m. soil. Lead was found to drastically deteriorate soil quality, which reduced the biomass of maize. Lead negatively affected the activity of the soil enzymes tested and modified the physicochemical properties of the soil. Fertilization with biocompost and biochar mitigated lead-induced interference with soil enzymatic activity. The applied biocomponents also had positive effects on the chemical and physicochemical properties of the soil. Maize cultivated on lead-polluted soil did not lose its energetic properties. The heating value of maize was stable, which shows its potential in the recultivation of lead-contaminated soils.

Keywords: trace elements; biochar; compost; plant; soil enzymatic activity

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1. Introduction

The accumulation of heavy metals in the soil is a serious problem, because it adversely affects soil homeostasis and the growth and development of plants [1–5]. Lead (Pb) is one of the most toxic metals in the environment and is dangerous to humans and other living organisms [6,7]. Harmful trace elements of it threaten sustainable agricultural ecosystems when resulting from activities such as mining, landfilling and excessive use of fertilizers and pesticides [8,9]. Pb^{2+} accumulates in the soil and is easily taken up by plants, which can be dangerous to human and animal health [10,11]. The average content of lead in European soils in mg per kg is 16.40, in the USA—12.30, in Iran—6.12, and in China—25.56 [6,12]. According to Tótha et al. [13], the abundance of Pb^{2+} in the soils of the European Union member states varies from 1.63 to 151.12 mg kg^{-1}, but most often does not exceed 50 mg kg^{-1}. Nevertheless, certain plants, such as: *Triticum* L., *Hordeum* L., *Helianthus annunus* L., *Sinapis alba*, and *Glycine max*, are very sensitive to this metal and their growth may be inhibited even by a lead dose as low as 30 mg Pb^{2+} kg^{-1} d.m. soil [14]. There is also a group of plants, including *Noccaea rotondifolia* subsp. *Cepaeifolia*, which can tolerate Pb^{2+} doses of up to 1.000 mg kg^{-1} d.m. soil [15]. Lead has a strong influence on various developmental characteristics of exposed plants; for example, it inhibits seed germination, growth of aerial parts and roots, and photosynthesis [16–19]. Therefore, soil contaminated with Pb^{2+} should be remediated, as this is crucial for ensuring soil safety and sustainable agricultural development [20]. Physical extraction, chemical immobilization, and bioremediation are remediation methods deployed to mitigate the toxicity of heavy metals in the soil and improve plant performance [21–23]. Jiang et al. [24], Lahori et al. [25], and Zama et al. [26] have shown that the introduction of organic additives, such as compost and biochar, into the soil can immobilize heavy metals and that this type of soil amendment is considered environmentally friendly. Organic additives can modify the speciation of heavy metals by precipitation, adsorption, ion exchange reactions, and formation of organo-mineral complexes in the soil [27–29]. The efficiency of soil enzymes determines the cycling of nutrients needed by plants and is a good test of soil quality [30].

Compost increases the amount of humus in the soil and improves its structure, which indirectly contributes to plant development. Biochar is a solid renewable fuel produced from different types of biomass through pyrolysis [31]. The International Biochar Initiative [32] defines biochar is defined as a fine-grained carbonate with a high carbon content and low biodegradability. Its characteristic features include: an alkaline pH [33,34], a developed specific surface (from below 1 m^2 g^{-1} up to several hundred m^2 g^{-1}) [34], and a porous structure with pore sizes from nano- to micrometers [35]. The porous structure of biochar is formed upon the release of vapors during biomass pyrolysis [36].

Apart from the use of additives of organic origin, the negative influence of trace elements can be ameliorated by means of phytoremediation, an increasingly frequently deployed bio-remediation technique [37,38]. Nevertheless, the plant efficacy in phytoremediation depends on heavy metals type and content. Compared to other remediation methods, phytoremediation produces higher quality soil [39]. It increases soil fertility by releasing organic matter [38,40]. The present experiment focused on maize and aimed to analyze its phytoremediation potential in removing Pb^{2+} from the soil. Maize can be used not only for food purposes but also for the production of biofuels [41,42]. The advantage of this plant is its high productivity, which can reach more than 15–20 tonnes ha^{-1} [37].

The following hypotheses were proposed in the present work: (a) the heating value of maize grown on soil under Pb^{2+} pressure is stable, (b) biocompost and biochar mitigate the negative impact of lead on the growing maize, and on the enzymatic, chemical, and physicochemical properties of the soil. The aim of the research was to evaluate the impact of soil contamination with Pb^{2+} on the biomass, combustion heat, heating value of maize, enzymatic activity, and physicochemical properties of the soil, and to estimate the impact of biocompost and biochar on these parameters.

2. Materials and Methods

2.1. Study Design

The pot experiment was carried out in north-eastern Poland under controlled conditions (average air temperature was 16.90 °C and air humidity was 76.50%). The soil used in the study was loamy sand (sand—78%, silt—21%, clay—1%), which had the following properties: pH_{KCl}—4.20; HAC—21.13 mmol(+) kg^{-1}; EBC—34.00 mmol(+) kg^{-1}; CEC—55.13 mmol(+) kg^{-1}; BS—61.68%; content of C_{org}—5.79 g kg^{-1}, and N_{Total}—0.89 g kg^{-1}. The above abbreviations are explained in Table 1. This was a two-factor experiment: (1) dose of Pb^{2+} [$Pb(NO_3)_2$]: 0 and 800 mg Pb^{2+} kg^{-1} d.m. soil, (2) use of biocompost and biochar in doses of: 0 and 20 g kg^{-1} d.m. soil. These additives have been applied to the soil in order to mitigate the potentially adverse influence of Pb^{2+} on maize growth and development, soil enzymatic activity and its chemical and physicochemical properties. Chemical composition of the biocompost and biochar are provided in Table 2 and their appearance in Figure 1. The dose of lead was determined based on the results of our preliminary research and the Regulation of the Minister of the Environment [43], according to which the allowed abundance of lead in 1 kg d.m. soil at a depth of 0–0.25 m varies from 100 mg for agricultural areas and allotment gardens to 1000 mg on the premises of production facilities, mining areas, and areas of public and internal roads. The soil was also amended with macronutrients according to the nutritional demands of the test plant (in mg kg^{-1} soil): N—140 [$CO(NH_2)_2$], P—50 g [KH_2PO_4], K—100 [KCl], and Mg—15 [$MgSO_4 \times 7H_2O$]. When planning fertilizing doses of nitrogen, account was taken of its content that has been introduced into the soil in the form of $Pb(NO_3)_2$. During experiment preparation, the aqueous solution of lead nitrate, biocompost and biochar, as well as macroelements was mixed with a 3.5 kg portion of soil that was then transferred to plastic pots. Maize was selected as a phytoremediating plant because it is relatively resistant to heavy metal stress. An additional advantage in favor of using maize in the study was the fact that it is a frequently cultivated plant around the world [44,45]. Maize of the Garantio cultivar was used in the study. Throughout the experiment (60 days), soil moisture level was kept at 50% of the capillary water capacity, and the leaf greenness index (SPAD) was determined twice. The experiment was conducted in four replications. The maize was harvested in phase BBCH 39, and the biomass and their lead content were determined. The aerial parts of maize were also determined for the Q. Soil samples taken on the day of harvest were used to determine the activity of soil enzymes Deh, Cat, Ure, Pac, Pal, Glu, and Aryl, and the content of lead, C_{org}, N_{Total}, pH, HAC, EBC, CEC, and BS [Table 1].

Table 1. Soil and plant analysis methods.

Parameter	Parameter Determination Methods/Source of Methodology	Parameter	Parameter Determination Methods/Source of Methodology
		Soil	
Deh—dehydrogenases	Öhlinger [46]	Lead	SpectrAA 240 FS spectrophotometer (Varian Inc., Mulgrave, Australia) with atomic absorption spectrophotometry
		Total organic carbon (C_{org})	Elementary macroanalyzer Vario MaxCube CN (Hanau, Germany)
Cat—catalase	Johnson, Temple [47]	Total nitrogen (N_{Total})	
Ure—urease	Alef, Nannpieri [48]	pH_{KCl} soil	soil to solution ratio KCl 1:2.5
Glu—ß-glucosidase		Hydrolytic acidity (HAC)	Kappena [49]
Pac—acid phosphatase		Total exchangeable cations (EBC)	
Pal—alkaline phosphatase		Total exchange capacity of soil (CEC)	Klute [50]
Aryl—arylsulfatase		Basic cations saturation ratio in soil (BS)	
		Plant	
Heat of Combustion (Q)	Calorimeter C-2000 by IKA WERKE, Northchase Pkwy Se, Wilmington, USA [51]	Greenness index (SPAD)	Chlorophyll Meter Spectrum Technologies, Inc. (KONICA MINOLTA, Inc., Chiyoda, Japan
		Lead	SpectrAA 240 FS spectrophotometer (Varian Inc., Mulgrave, Australia)

Table 2. Characteristics of biocompost and biochar.

Biocompost Companies KRONEN (Poland)	Biochar Companies NTP Sp. Zoo. (Poland)
pH—8.25	pH—9.79
N_{Total}—0.50%	N_{Total}—0.91%
C_{org}—8.70%	C_{org}—83.92%
C:N ratio—10.09	C:N ratio—92.22


(a) (b)

Figure 1. Appearance of biocompost (**a**) and biochar (**b**).

Detailed procedures for determining the enzymatic activity of the soil were provided in our earlier work [52,53], as were those for the analysis of its physicochemical properties [54]. To determine the lead content of the soil and plant samples, the experimental material was crushed in a mortar. Then, samples of plant material weighing 0.3 g were mineralized in 10 cm^3 65% HNO_3, and soil samples weighing 0.5 g were mineralized in 9 cm^3 HCl and 3 cm^3 65% HNO_3 in the MARS 6-CEM Corporation mineralizer (Matthews, NC, USA). The mineralized samples were diluted with demineralized water to 100 cm^3 and the lead content was determined [Table 1].

2.2. Calculations and Statistical Methods

On the basis of the activity of the soil enzymes under investigation, a soil quality index (BA) was calculated [53]. In addition, the indices of the effect of the biocompost (IF_K) and biochar (IF_B) on the enzymatic activity of the soil were calculated using the following formula:

$$IF_{K/B} = \frac{A_{K/B}}{A} \quad (1)$$

where
$IF_{K/B}$—index of biocompost/biochar,
$A_{K/B}$—enzymes in soil with biocompost/biochar,
A—enzymes in soil without biocompost/biochar.

Using the heat of combustion (Q) of maize biomass and the biomass of its aerial parts, the heating value of plants (Hv) and the amount of energy generated from plant biomass (Y_{EP}) from 1 kg of soil were determined [52,55]. The results of the study were developed statistically based on the analysis of variance (ANOVA) using the Statistica 13.5 program [56]. The coefficient of variation of all analyzed variables (η^2) was determined using the analysis of variance method (ANOVA), and Pearson correlation coefficients were computed between dependent and independent variables. Principal Component Analysis (PCA) was performed as well.

3. Results

3.1. Energy Value of the Biomass of Maize Grown on Soil Contaminated with Lead

In the experimental variants without the addition of biocompost and biochar, soil contamination with a lead dose of 800 mg Pb^{2+} kg^{-1} d.m. resulted in a significant reduction in the amount of biomass of the aerial parts (by 17.42%) and roots (by 25.76%) of maize (Table 3 and Figure 2). Soil amendment with biocompost had a significant effect on plant growth and development. In the uncontaminated soil samples, only biocompost caused a significant increase in the yield of aerial parts (by 7.6%) and an increase in root biomass (by 45.5%). On the other hand, in soil contaminated with Pb^{2+}, there was a reduction in the yield of aerial parts by 9.58% in facilities with biocompost and by 13.82% with biochar, and of roots by 37.97% and 9.70%, respectively, compared to soil uncontaminated with this metal (Table 3). Both preparations significantly mitigated the negative effects of Pb^{2+} on the yield of the aerial parts of maize, while biocompost also mitigated the effects on the roots. In conclusion, biocompost elicited better results compared to biochar.

Table 3. Effect of biocompost and biochar on the amount of dry biomass of maize, g pot^{-1}.

mg Pb^{2+} kg^{-1} d.m. soil	Control	Biocompost	Biochar
		Aerial parts	
0	59.163 ^{b} ± 0.217	63.688 ^{a} ± 0.527	59.205 ^{b} ± 1.154
800	48.858 ^{d} ± 0.650	57.585 ^{b} ± 0.946	51.020 ^{c} ± 0.921
		Roots	
0	8.890 ^{b} ± 1.299	12.935 ^{a} ± 1.990	7.658 ^{ab} ± 0.314
800	6.495 ^{c} ± 1.016	8.023 ^{ab} ± 1.272	6.915 ^{c} ± 1.475

Homogeneous groups are indicated by the letters a–d.

(**a**) (**b**)

Figure 2. Maize at BBCH 39 stage. (**a**)—0 mg Pb^{2+} kg^{-1} soil; (**b**)—800 Pb^{2+} kg^{-1} soil; C—Control; K—Biocompost; B—Biochar.

The impact index of biocompost (IF_K) and biochar (IF_B) confirms the positive effect of these additives on the biomass of the aerial parts and roots of maize (Figure 3). In uncontaminated sites, both biocompost and biochar stimulated the biomass of maize. The exception was root biomass from soil supplemented with biochar. Also, in soil contaminated with Pb^{2+}, the stimulating effect of the applied improvers was found.

Soil contamination with Pb^{2+} induced a significant decrease in the value of the leaf greenness index (SPAD) of maize, both on day 14 and 48 of plant growth (Table 4). The introduction of biocompost and biochar to the soil did not cause significant changes in SPAD value on day 14, while decreased it on day 48 of plant growth. The adverse effect of Pb^{2+} on SPAD was only visible on day 14, in both biocompost- and biochar-treated soils. In all soil samples, both uncontaminated and contaminated, treated and not treated with the enhancers, the SPAD values were significantly lower on day 48 than on day 14 of crop vegetation.

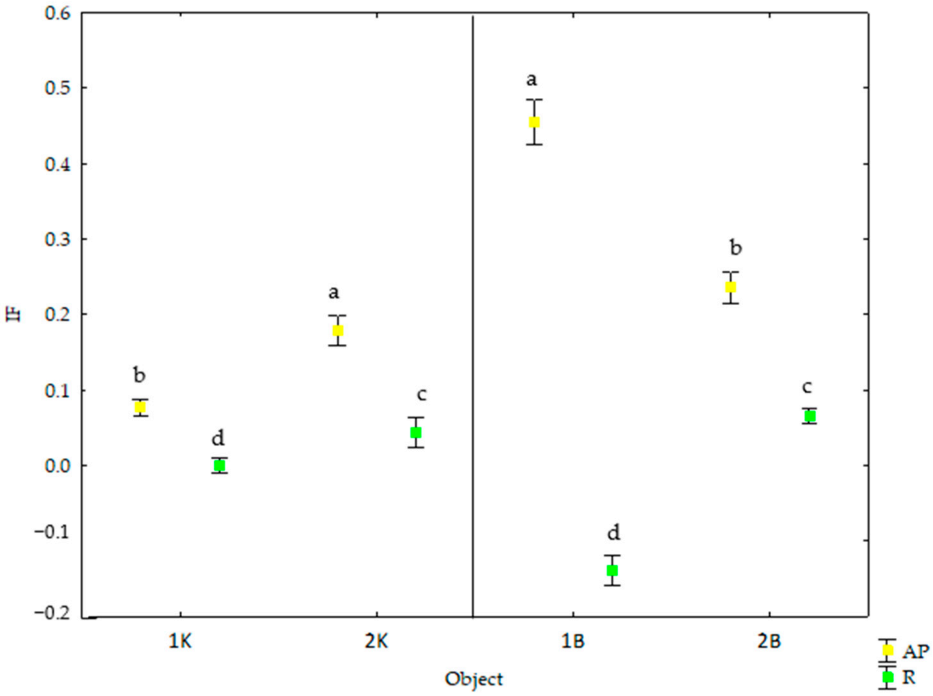

Figure 3. Indicator impact of biocompost (IF_K) and biochar (IF_B) on maize biomass. K—biocompost; B—biochar; 1—0 mg Pb^{2+}; 2—800 mg Pb^{2+}; AP—yield of aerial parts; R—yield of roots. Homogeneous groups are indicated by the letters a–c for biocompost and a–d for biochar.

Table 4. Leaf greenness index (SPAD) of maize.

mg Pb^{2+} kg^{-1} d.m. soil	Control	Biocompost	Biochar
14 days			
0	44.881 ^{a} ± 0.984	44.869 ^{a} ± 2.057	43.369 ^{a} ± 1.629
800	39.600 ^{b} ± 2.071	37.600 ^{c} ± 2.805	37.894 ^{c} ± 0.954
48 days			
0	26.631 ^{d} ± 9.757	22.325 ^{e} ± 0.788	23.056 ^{e} ± 2.089
800	22.375 ^{e} ± 0.706	21.881 ^{e} ± 2.186	23.463 ^{e} ± 1.432

Homogeneous groups are indicated by the letters a–e.

The heat of combustion of maize biomass obtained in the control variant increased significantly under the influence of Pb^{2+}, was constant regardless of the soil type amended with biochar, and significantly decreased in the soil contaminated with lead and treated with biocompost (Table 5). The values of this parameter in the biomass of maize grown on lead-contaminated and uncontaminated soil with the addition of biocompost ranged from 18,325 to 18,510 MJ kg^{-1} p.dm. In turn, the heating value of maize was independent of soil contamination with Pb^{2+}, and of its treatment with biocompost and biochar. It ranged from 16.301 to 16.621 MJ kg^{-1}, and the differences between the soil samples were statistically insignificant. The energy obtained from maize biomass produced from 1 kg of soil was higher in the variants with biocompost and biochar than in those without these additives. A dose of 800 mg Pb^{2+} kg^{-1} reduced energy production from maize biomass. This adverse effect of Pb^{2+} was in part alleviated by both biocompost and biochar.

Table 5. Heat of combustion and heating value of maize.

mg Pb^{2+} kg^{-1} d.m. soil	Control	Biocompost	Biochar
Heat of Combustion in MJ kg^{-1}			
0	18.395 ^{bc} ± 0.008	18.510 ^{a} ± 0.040	18.483 ^{ab} ± 0.037
800	18.486 ^{a} ± 0.038	18.325 ^{c} ± 0.031	18.528 ^{a} ± 0.027
Heating Value in MJ kg^{-1}			
0	16.478 ^{a} ± 0.016	16.541 ^{a} ± 0.013	16.621 ^{a} ± 0.012
800	16.540 ^{a} ± 0.015	16.301 ^{a} ± 0.014	16.620 ^{a} ± 0.011
Energy Production in MJ kg^{-1}			
0	0.279 ^{b} ± 0.012	0.301 ^{a} ± 0.013	0.281 ^{b} ± 0.014
800	0.231 ^{e} ± 0.015	0.268 ^{c} ± 0.013	0.242 ^{d} ± 0.015

Homogeneous groups are indicated by the letters a–e.

The Pb^{2+} amount in the aerial parts and roots of maize and uncontaminated soil, regardless of the application of the substances used, remained at similar levels (Table 6). The content of Pb^{2+} in the aerial parts of maize grown on soil with lead at 800 mg kg^{-1} d.m. soil in the series without additives was 17.39 times, and in the series with biocompost 13.64 times and biochar 12.48 times higher compared to uncontaminated soil. In the soil samples with lead at 800 mg kg^{-1}, the highest Pb^{2+} content in the aerial parts of maize was determined in sites with biochar, followed by control, and the lowest one on the sites with biocompost. For roots and soil, the highest Pb^{2+} content was determined in the control object, followed by the biochar and biocompost objects. The Pb^{2+} content of maize roots and soil in lead-contaminated sites was 35.78–fold and 63.50–fold, respectively, in the series without biocompost, 26.38–fold and 33.45–fold, and with biochar 11.38–fold and 45.99–fold higher compared to uncontaminated soil.

Table 6. Lead content in maize and soil, mg kg^{-1}.

mg Pb^{2+} kg^{-1} d.m. soil	Control	Biocompost	Biochar
Aerial parts			
0	4.550 ^{d} ± 0.083	5.283 ^{d} ± 0.617	8.716 ^{d} ± 1.650
800	79.142 ^{b} ± 2.916	72.043 ^{c} ± 3.316	108.772 ^{a} ± 1.183
Roots			
0	24.080 ^{d} ± 1.650	19.965 ^{d} ± 0.067	61.011 ^{d} ± 4.916
800	861.531 ^{a} ± 4.809	526.581 ^{c} ± 6.727	694.414 ^{b} ± 2.014
Soil			
0	10.400 ^{d} ± 0.540	15.730 ^{d} ± 0.690	12.980 ^{d} ± 0.840
800	660.380 ^{a} ± 6.700	526.220 ^{c} ± 6.040	596.910 ^{b} ± 0.610

Homogeneous groups are indicated by the letters a–d.

3.2. Effect of Lead on the Enzymatic Activity and Chemical and Physicochemical Properties of Soil

The soil samples uncontaminated with Pb^{2+} were characterized by the highest enzyme activity regardless of biocompost and biochar addition (Figure 4). After soil treatment with a lead dose of 800 mg kg^{-1} d.m., the activities of Deh, Cat, Ure, Pac, Pal, Glu, and Aryl were suppressed, both in the control soil samples and those supplemented with biocompost and biochar. In the control variant without biocompost and biochar addition, Deh, Cat, and Pal were more sensitive to Pb^{2+} than Ure, Pac, Aryl, and Glu. The sensitivity of enzymes to Pb^{2+} could be ordered as follows: Deh > Pal > Cat > Ure > Pac > Aryl > Glu. In addition, it can be concluded that the added substances contributed to alleviating lead stress in the soil.

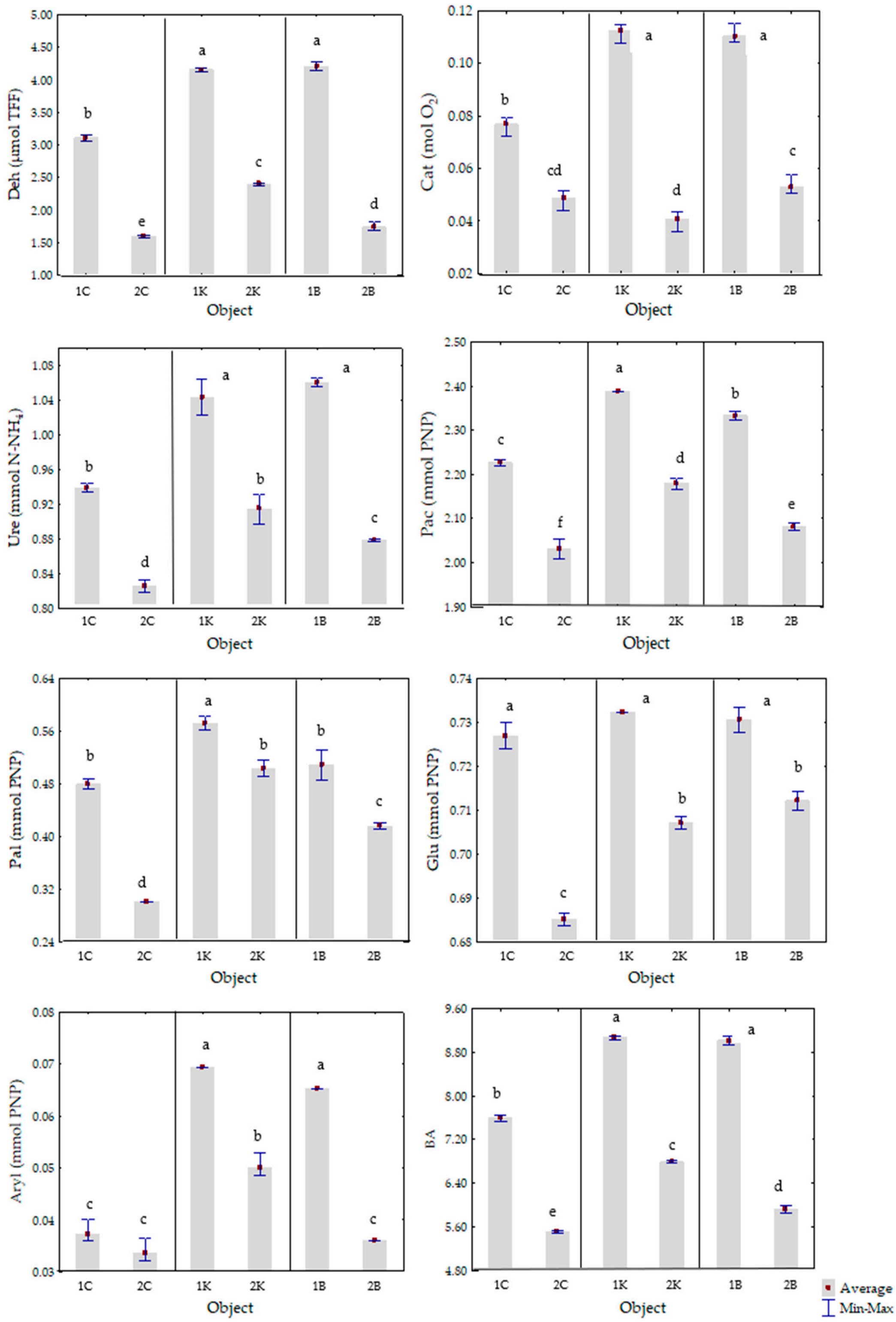

Figure 4. Enzyme activity in 1 kg of d.m. soil h^{-1}. The abbreviations of the enzyme names are given in Table 1. TFF—triphenyl formazan; PNP—p-nitrophenol; BA—soil quality index. The abbreviations of the object names are explained in Figure 2. Homogeneous groups are indicated by the letters a–f.

The measures of the indicator of the impact of biocompost (IF_K) and biochar (IF_B) on enzymatic activity confirms the positive effect of these additives on soil biochemical properties (Figure 5). In the uncontaminated soil, both biocompost and biochar stimulated the activity of all enzymes. Their stimulating effects were also observed in the soil samples contaminated with Pb^{2+}. The exception was catalase activity in the soil supplemented with biocompost. In the case of Pal, higher IF_K and IF_B values were computed in the case of the contaminated soil samples than in the uncontaminated samples. Similar was the case with Deh, except in the variants with biocompost addition.

The application of biocompost and biochar and the influence of Pb^{2+} on soil enzyme activity resulted in changes in the soil quality index (Figure 4). In the control variant, its value decreased by 27% under the influence of Pb^{2+}, as well as by 25% and 34% upon soil treatment with biocompost and biochar, respectively. Soil supplementation with both biocompost and biochar resulted in a 19% increase in BA in the uncontaminated soil. In soil exposed to Pb^{2+}, biocompost increased the BA value by 23% and biochar by 7%.

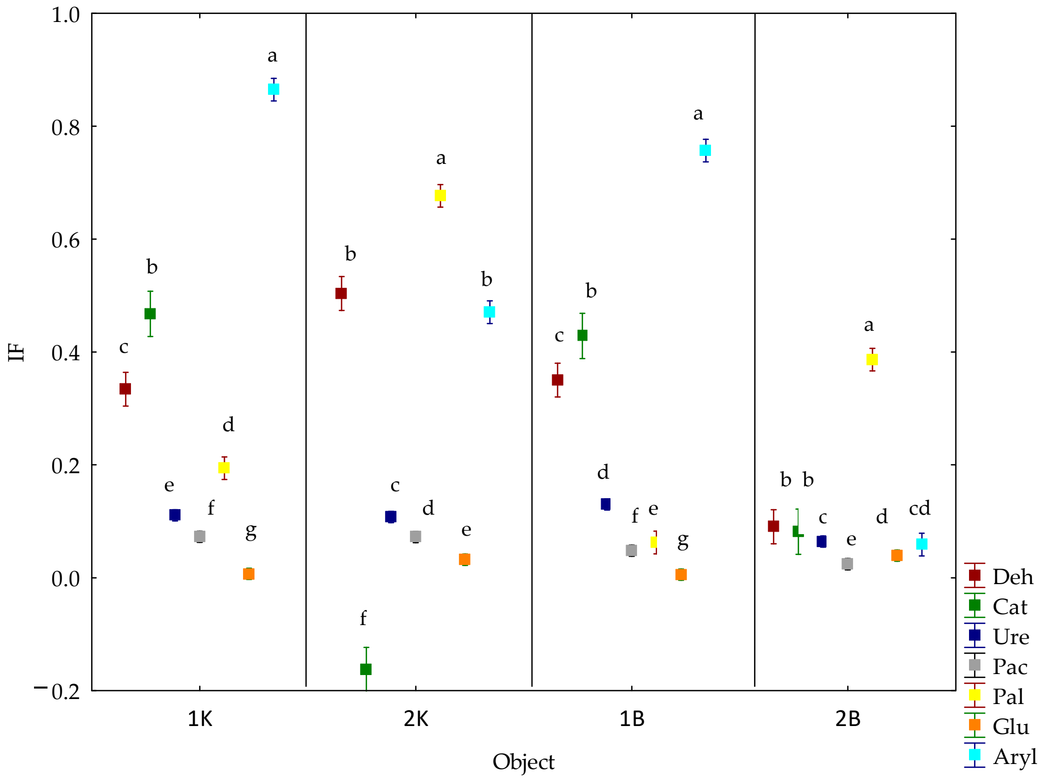

Figure 5. Indicator impact of biocompost (IF_K) and biochar (IF_B) on the soil enzymes. The abbreviations of the enzyme names are given in Table 1. The abbreviations of the object names are explained in Figure 2. Homogeneous groups are indicated by the letters a–g.

Soil contamination with Pb^{2+} did not significantly alter C_{org} and N_{Total} content (Table 7). In turn, the supplementation of uncontaminated soil with biocompost and biochar caused a significant increase in C_{org} and N_{Total} content by 16.5% and 91.1% as well as 17.9% and 19.1%, respectively. Also, in the case of soil contaminated with Pb^{2+}, both biocomponents increased the content of C_{org} and N_{Total}. Regardless of biocompost and biochar addition, the soil pH and EBC increased, whereas HAC decreased under the influence of Pb^{2+} (Table 6). Similar observations were made for CEC and BS, whose values were higher in the soil contaminated with Pb^{2+}. To sum up, biocompost and biochar positively influenced the chemical and physicochemical properties of the soil.

Table 7. Physicochemical properties of the soil at the end of plant vegetation.

mg Pb^{2+} kg^{-1} d.m. soil	Control	Biocompost	Biochar
Total Organic Carbon in g kg^{-1}			
0	6.060 ^{c} ± 0.010	7.060 ^{b} ± 0.010	11.580 ^{a} ± 0.018
800	5.960 ^{c} ± 0.011	6.100 ^{c} ± 0.003	10.840 ^{a} ± 0.016
Total Nitrogen in g kg^{-1}			
0	0.890 ^{b} ± 0.002	1.050 ^{a} ± 0.001	1.060 ^{a} ± 0.001
800	0.820 ^{b} ± 0.002	1.010 ^{a} ± 0.001	1.030 ^{a} ± 0.001
pH_{KCl}			
0	4.067 ^{d} ± 0.058	4.400 ^{b} ± 0.029	4.300 ^{c} ± 0.028
800	4.300 ^{c} ± 0.029	4.500 ^{a} ± 0.050	4.433 ^{ab} ± 0.027
Hydrolytic Acidity in $mmol^{(+)}$ kg^{-1} soil			
0	20.750 ^{a} ± 0.217	18.250 ^{e} ± 0.210	20.125 ^{b} ± 0.220
800	19.750 ^{bc} ± 0.220	19.250 ^{cd} ± 0.222	18.875 ^{d} ± 0.218
Total Exchangeable Base Cations in $mmol^{(+)}$ kg^{-1} soil			
0	20.000 ^{e} ± 0.110	28.000 ^{d} ± 0.120	28.000 ^{d} ± 0.116
800	30.000 ^{c} ± 0.119	32.000 ^{b} ± 0.117	40.000 ^{a} ± 0.114
Total Cation Exchange Capacity in $mmol^{(+)}$ kg^{-1} soil			
0	40.750 ^{f} ± 0.217	46.250 ^{e} ± 0.222	48.125 ^{d} ± 0.223
800	49.750 ^{c} ± 0.220	51.250 ^{b} ± 0.220	58.875 ^{a} ± 0.219
Base Cations Saturation Ratio in Soil in %			
0	49.081 ^{e} ± 0.260	64.866 ^{a} ± 0.304	58.183 ^{d} ± 0.262
800	60.302 ^{c} ± 0.263	58.537 ^{d} ± 0.247	61.147 ^{b} ± 0.224

Homogeneous groups are indicated by the letters a–f.

3.3. Interactions between Soil Contamination with Lead and Maize Biomass, Enzymatic Activity, Chemical and Physicochemical Properties of Soil

The percentage share of the observed variability factors indicates that the yield of the aerial parts of maize was most influenced by biocompost and biochar (54.83%), and that of the roots by soil contamination with Pb^{2+} (50.51%) (Figure 6). Soil Pb^{2+} pollution had the most pronounced impact on the activity of the analyzed soil enzymes, and this effect accounted for: Pac—95.64%, Deh—93.47%, Glu—92.92%, Ure—87.01%, Cat—80.84%, Pal—68.42%, and Aryl—57.13%. The effect of biocompost and biochar on soil biochemical properties was weaker, with the strongest impact observed on Aryl (36.22%), Pal (21.99%), and Cat (15.85%).

All enzyme activity and maize biomass were significantly negatively correlated with soil and plant lead content (Figure 7), whereas plant biomass was positively correlated with soil enzyme activity. The biomass yield of the maize aerial parts and roots was negatively correlated with lead content in the plant, soil, the EBC, and the CEC. The activity of all tested enzymes was positively correlated with each other. A positive correlation was observed between C_{org} content and soil pH, EBC, CEC, and BS, whereas a negative one was observed between C_{org} and HAC. In turn, N_{Total} was positively correlated with soil pH and CEC.

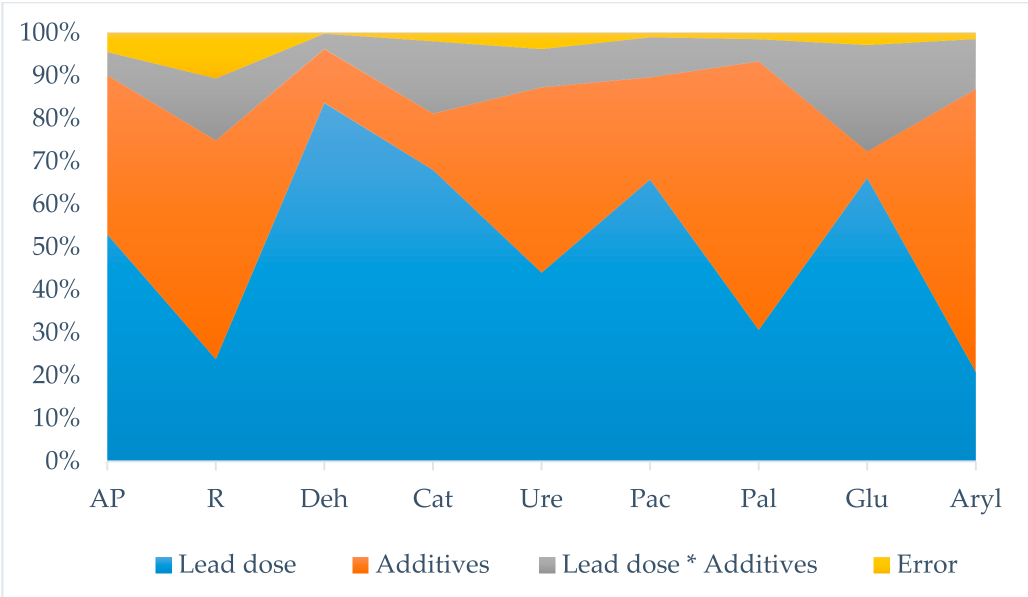

Figure 6. Percentage of factors contributing to the observed variability of η^2. AP—yield of aerial parts; R—yield of roots; The abbreviations of the enzyme names are given in Table 1. The abbreviations of the object names are explained in Figure 2.

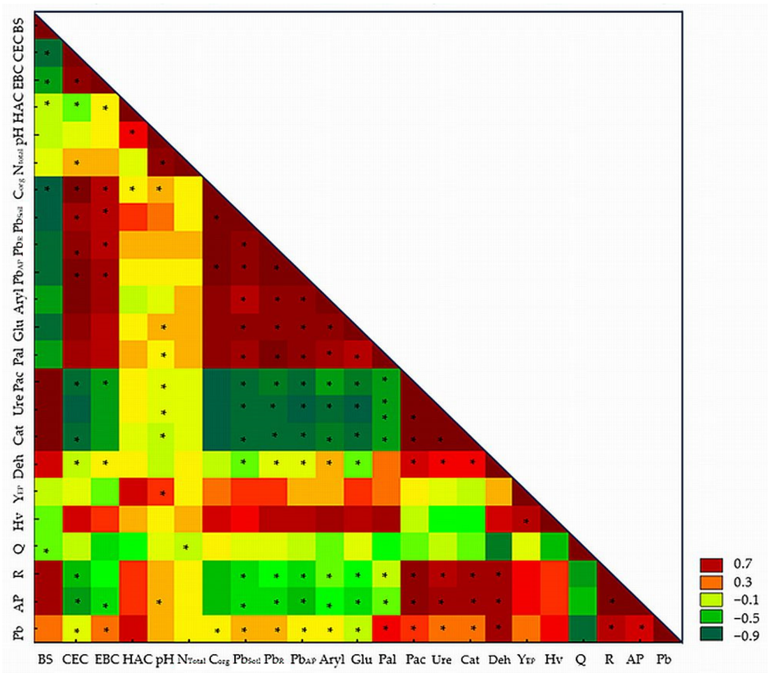

Figure 7. Correlation coefficients between variables in lead-contaminated objects. The abbreviations of the names of the tested parameters are given in Table 1. * r—coefficient of correlation significant at: $p = 0.05$, $n = 45$.

The distribution of vectors describing the correlations between the biomass of maize, enzymatic activity, Pb^{2+} content in the plant and soil, and the chemical and physicochemical properties of the soil was presented by means of the PCA (Figure 8). The activity of all soil enzymes, crop yield and the amount of energy obtained from maize biomass were negatively correlated with the increased content of lead in the soil and maize. Thus, the suppression of enzyme activity indirectly contributed to the impairment of maize growth and development, with lead likely also having a direct adverse effect on the cultivated crop.

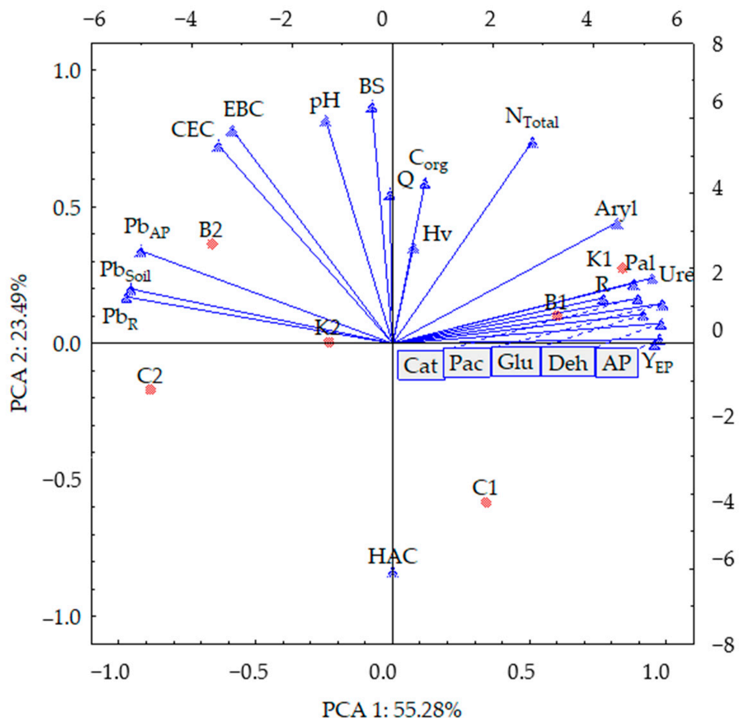

Figure 8. Relationships between variables illustrated by the PCA method. The abbreviations of the names of the tested parameters are given in Table 1, Figures 2 and 3.

4. Discussion

4.1. Effect of Lead on Parameters Associated with Plant Growth

Soil pollution by trace elements, such as lead, is a major environmental problem [1,2,57–59], as it contributes to a reduction in crop productivity and directly or indirectly reduces biodiversity [7,60,61]. Our research showed that soil pollution with lead at 800 mg kg^{-1} soil significantly reduced the biomass of maize. This is because trace elements, including lead, exert toxic effects on various plant growth attributes. This is associated with improper nutrient uptake from plant roots [62–64]. The present study also showed a negative impact of lead on the SPAD of maize. In turn, Ali et al. [65] demonstrated that lead toxicity reduced plant growth and caused chlorosis and root blackening. Furthermore, this metal was found to inhibit photosynthesis, nutrient uptake, and enzyme activity, as well as inhibit seed production and seedling growth [66]. In addition, it can alter cell membrane permeability, initiate cation-sulfhydryl (-SH) reactions, and react with phosphate and active ADP and ATP groups [65]. Another study [67], showed that seed germination, root length, length of the aerial parts, and their dry matter content were reduced by increasing doses of lead (1, 25, 50, 100, 200, and 500 mM). Sofy et al. [68] found that lead could adversely affect plant metabolism. The use of biocompost and biochar in the soil in the present study alleviated its negative effects on maize. Both additives are of natural origin and have positive effects on soil characteristics. Plants grown on such soil are better able to tolerate its contamination with heavy metals [69].

The combustion heat and heating value of maize were also measured in the present study, and the results obtained prove that their values recorded in uncontaminated and lead-contaminated soil were similar. This indicates the feasibility of using biomass from the areas contaminated with Pb^{2+} for energy purposes. The calorific values of maize and other plants are shown below in Table 8.

Table 8. Calorific values of *Zea mays* compared to other plants.

Plant	Calorific Values in MJ kg^{-1}	References
Zea mays	16.48	Present study
Zea mays	16.87	[37]
Pinus spp.	17.60	[70]
Quercus spp.	19.50	[71]
Festuca rubra	18.21	[52]
Triticum	16.55	[72]
Helianthus	14.39	[72]
Sorghum	16.57	[72]

The biomass of the aerial parts of maize derived from such cultivation can serve as an alternative energy source and be used to produce biofuels [37]. Maize can also be used for phytoremediation purposes [73]. Plants can be hyperaccumulators or phytostabilizers of soils contaminated with trace elements. Plants such as *Alyssum bertolonia*, *Thlaspi caerulescens*, *Calendula officinalis*, and *Tagetes erecta* have a high capacity for hyperaccumulation of trace elements [74]. *Panicum aquaticum*, *Lolium perenne*, *Paspalum fasciculatum*, and *Vetiveria zizanioides* are also effective in remediating soils contaminated with Pb and other trace elements [74–78]. The present study has shown an increase in Pb^{2+} content in maize and in soil polluted with this metal. Dinake et al. [79] report that there are areas in the world where the content of lead in the 0 to 30 cm soil layer is very high, for example, Switzerland may have 471 mg, Norway 3200 mg, Belgium 2167 mg, Spain 720 mg, Australia 4697 mg, China 2763 mg, and Poland 4600 mg kg^{-1}.

4.2. Effect of Lead on the Enzymatic Activity and Chemical and Physicochemical Properties of Soil

Soil enzyme activity is an important property reflecting its fertility and quality [80,81]. Soil microorganisms are the main source of enzymes that determine the course of the most important biochemical processes [82]. Our study showed that the activity of the enzymes tested was negatively affected by excessive amounts of Pb^{2+} in the soil. Soil amendment with biocompost and biochar alleviated the detrimental impact of lead on its biochemical properties. As in the studies of other authors [83–85], biochar mitigated the adverse effects of lead on enzyme activity, such as urease and catalase. The increased enzyme activity observed in the biocompost- and biochar-amended soils in our study may be due to the protective effects of these amendments on the soil microbiota. Perhaps this effect was due to the metal being sequestered in the soil, making it inaccessible [86,87]. Biocompost and biochar can increase soil nutrients levels and improve water and air conditions, creating an environment conducive to the development of soil microbes. Numerous studies [88–90] show that the microbial community and the related soil enzymatic activity are positively influenced by the chemical elements and organic matter of compost and biochar.

Ondrasek et al. [91] showed that plant growth is influenced by soil organic carbon content, among other factors. In our current study, the application of biocompost and biochar, to both unpolluted and Pb^{2+}-polluted soils resulted in an increase in organic carbon and total nitrogen levels. Biochar [92] and biocompost [93,94] were also reported to increase soil abundance in macroelements and microelements and improve its physicochemical properties. Our research has shown that biocompost is more effective than biochar in improving the biochemical properties of Pb^{2+}-polluted soil and on maize growth and development. According to the literature [95–97], the addition of compost reduces the levels of trace elements in the soil solution as a result of precipitation or increased metal sorption (immobilization), due to the formation of strong complexes between organic matter and heavy metals. In addition, Angelov et al. [95] demonstrated that compost and vermicompost application generally decreased the heavy metal content of soil by immobilizing heavy metals with humic substances. In a study by Irfan et al. [57], both compost and biochar were found to reduce the presence of Pb, Cd, Cr in the soil, thereby reducing their toxicity to plants. The authors achieved better results by applying biochar. These elements increase the production potential of soil. This, in turn, positively correlated with its biological properties. Thus, the impact of compost and biochar on soil quality can be both direct and indirect.

5. Conclusions

A lead dose of 800 mg kg^{-1} d.m. soil drastically disrupts the enzymatic activity of the soil and reduces its productivity, measured by maize biomass yield. However, it does not cause any changes in the heating value of maize, which makes this plant suitable for the remediation of soils contaminated with this element, since it can be used for energy purposes without posing a risk to the natural environment in the broadest sense. The quality of soil contaminated with lead can be improved by its fertilization with biocompost and biocarbon. Based on the maize biomass obtained and the enzymatic activity of the soil, it is recommended to grow maize on lead-contaminated soil with simultaneous fertilization with biocompost, which is more effective at improving soil quality than biochar.

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