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Calorific Value of *Zea mays* Biomass Derived from Soil Contaminated with Chromium (VI) Disrupting the Soil's Biochemical Properties

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Abstract: One of the major challenges faced by contemporary agriculture is how to achieve better yields of crops and, consequently, higher biomass, even in unfavorable environmental conditions. This challenge corresponds to the assumptions of sustainable development, wherein it is envisaged that plant biomass should be used on a large scale for heat generation or conversion of biofuels. Keeping pace with observed trends, the following study was conducted in order to determine the effect of Cr(VI) on the net calorific value of *Zea mays*, to assess the impact of this element on soil enzymatic activity, and to identify the effectiveness of compost and humic acids in alleviating possible negative effects of Cr(VI) toxicity. These aims were pursued by setting up a pot experiment, in which soil either uncontaminated or contaminated with increasing doses of Cr(VI) of 0, 15, 30, 45, and 60 mg Cr kg^{-1} d.m. was submitted to biostimulation with compost and the preparation HumiAgra, a source of humic acids, and cropped with *Zea mays*. The plant height, yield, and net calorific value of the aerial parts of maize, as well as its root yield, were determined. Additionally, the activity of seven soil enzymes and the values of the impact indices of compost and HumiAgra relative to the analyzed parameters were determined. It was found that Cr(VI) decreased the amount of energy obtained from the plants by decreasing maize biomass, and additionally by distorting the biochemical balance of the soil. Dehydrogenases, urease, and arylsulfatase proved to be particularly sensitive to this element. It was demonstrated that HumiAgra was more effective than compost in mollifying the adverse effects of Cr(VI) on the activity of soil enzymes and, consequently, on the biomass of *Zea mays*.

Keywords: energy from biomass *Zea mays*; soil contamination with chromium; activity of soil enzymes; compost; humic acids

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1. Introduction

Degradation of the natural environment and climate change are existential threats to Europe and the whole world [1,2]. More and more restrictive laws on nature protection have been instituted in the past decades. In 2021, the European Commission set the goals for the European Union's policy on climate and energy adaptation [3]. In compliance with this package of legislative proposals, the EU member states are obligated to reduce their net greenhouse gas emissions by at least 55% by the year 2030 relative to 1990. This is conducive to the search for alternative biofuels, which should be characterized by low emission of pollutants to the atmosphere and the highest possible energy efficiency [4,5].

Much attention is devoted to the use of plant biomass, which is a resource for production of biofuels [6–8], and its incineration causes lesser emissions of undesirable nitrogen and sulfur oxides to the environment [9,10]. However, rational management of arable land resources is needed so as to produce biomass for energy purposes without compromising the agricultural production of food and fodder [11]. Thus, the land allocated to plant biomass production for energy purposes should be low use-value land or land excluded

from agricultural production due to contamination caused by industrialization. In this context, the use of biomass originating from fields polluted with heavy metals [12,13], petroleum products [14], phenols [15], plant protection chemicals [16], etc. for energy generation is an effective solution. Energy acquired this way is inexpensive and renewable. In addition, it contributes to energy safety, which supports environmental production and sustainable development [17]. These observed trends aroused the imperative to determine the effect of Cr(VI) on the net calorific value of *Zea mays* and to verify soil conditions under the pressure of this metal, determined on the basis of soil biochemical activity.

This approach aligns well with the concept of the circular economy, whose strategy is defined in the ISO 14044 standard [18,19]. It should be emphasized that policies aimed towards polluted biomass are becoming increasingly restrictive. Both in developing and in developed countries, many legal acts implicate controlling the mobility of this group of biowastes. They include "Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016" in Pakistan, "The Wastes Control Act" (no. 13038) in South Korea, and the "Resource Conservation and Recovery Act" (Public Law 94-580) in the USA. In Europe, these guidelines are constituted in Directive 2004/35/EC of the European Parliament and the Council of 21 April 2004 on environmental liability with regard to the prevention and remedying of environmental damage [20].

One of the circular economy strategies being implemented is the use of maize contaminated with heavy metals for the production of bioethanol [21]. The interest in *Zea mays* as a plant with phytoremediation potential, eventually used not only for bioethanol production but also for the production of biogas or for direct combustion, is probably stimulated by the high potential of maize yields, which reach up to 12–15 Mg plant d.m. per 1 ha [22,23], or the fact that maize is equipped with genes which endow it with tolerance to biotic and abiotic stresses [24]. It is not without reason that the number of farms growing maize is predicted to reach 227 million worldwide by the year 2030 [25]. Significantly, the intensive cultivation of energy crops, including maize, in polluted soils can contribute to the biological improvement of soils and their remediation [26].

The implementation of the aforementioned waste management strategy is particularly important regarding soils contaminated with chromium, including Cr(VI), whose strong oxidizing properties make it a cancerous and mutagenic element for living organisms, and which is therefore considered as a priority contaminant by the US Environmental Protection Agency (USEPA) [27]. The major anthropogenic sources of this element in nature are electroplating; steel fireproofing; the broadly understood chemical industry, including the synthesis of chemicals for wood preservation, production of paints, textile dyes, glues, and catalysts [28,29]; and also tanning, which interferes severely with the natural environment [30].

In agricultural soils, the content of Cr can reach 350 mg kg^{-1} of soil, and its availability in soil depends on such properties as soil pH, redox potential, types of minerals composing the soil matrix, content of organic matter, and the structure of the soil microbiome [31]. Although this element, owing to its high redox potential, can easily transform in soil from one oxidation state to another (from −2 to +6), it is only Cr(III) and Cr(VI) that can co-exist in a dynamic equilibrium regulated by the processes of oxidation and reduction, precipitation and dissolution, and adsorption and desorption [31–33]. However, both of these forms of chromium differ in terms of bioavailability and translocation in soil [34]. Cr(III) is a more thermodynamically stable form of this element, occurring as $CrOH_2^+$, chromium hydroxide, $Cr(OH)_3$, iron chromium hydroxide ($(Fe,Cr)(OH)_3$), and as complexes with fluoride, sulphate, and thiocyanate [31]. In turn, oxyanions such as chromate CrO_4^{2-} and dichromate $Cr_2O_7^{2-}$ are mobile in soil and highly soluble [32].

Because Cr(VI) does not undergo biodegradation in soil, it is far more toxic than Cr(III) towards all living organisms, including plants [35]. Chromium induces changes in plants on the phenotypic, physiological, biochemical, and ultrastructural levels [36]. Admittedly, the response of plants to exposure to Cr is manifested by growth inhibition and decreased biomass, chlorosis, and deformation of the structure of chloroplasts through

the peroxidation of fatty acids and lipids in their membranes induced by an increase in lipoxygenase [37,38]. However, plants possess an antioxidant defense system which protects and regenerates them after oxidative stress. It involves such osmolytes as proline, cysteine, and betaine, which provide plant membranes with stability and ensure osmotic regulation [39,40]. Proline is also a marker of stress tolerance [41]. The defense system of plants is also composed of carotenoids and glutathione (GSH), as well as a wide array of antioxidant enzymes, which include ascorbate peroxidase (APX), superoxide dismutase (SOD), and catalase (Cat) [42]. The growth and development of plants are also controlled by plant hormones. Indole-3-acetic acid (IAA) is a plant hormone of the auxin class which plays a key role among auxins and whose activity is enhanced under the influence of the toxicity of heavy metals, including Cr [43].

Phytoremediation helps to sustain the stability of soil by removing pollutants. Apart from improving the soil's quality, it also prevents soil erosion [44]. Given the limitations of conventional soil remediation techniques and the contents of legislative motions, including the EU Fertilizer Regulation adopted by the EU Parliament, which recommends the use of organic products [45], biostimulation of soils with composts appears to be an effective solution that is non-invasive to the environment [46]. A compilation of compost and biochar, relying on the synergistic action of both substances, seems to be a promising method for improving the condition of soil contaminated with Cr [47]. Likewise, the abundance of carboxyl and hydroxyl functional groups contained in humic acids complexing heavy metals also allows for the effective immobilization of this group of pollutants [26,48].

The fact that soil enzymes are early, stable, and sensitive biological indicators implicating both the degree of degradation and the recovery of the functional equilibrium state of soils contaminated with heavy metals after the application of chosen remediation techniques makes it an imperative to quantify their activity [49]. It should also be highlighted that soil enzymes catalyze reactions essential for the stabilization of the soil's structure and decomposition of organic matter determined on the basis of their kinetic parameters, such as the Michaelis constant (Km), related to the strength of the enzyme–substrate complex and maximum reaction rate (Vmax), indicating the rate of division or dispersion of this complex [50,51].

The research hypothesis put forward assumed that Cr(VI) reduces the amount of energy obtained from the plants by decreasing maize biomass, additionally distorting the biochemical balance of soil. It was also assumed that both HumiAgra and compost would be effective in mitigating the adverse effects of Cr(VI) on the activity of enzymes and, consequently, *Zea mays* biomass. Considering the binding legal acts pertaining to the issues of production of biomass on soils contaminated with heavy metals, a study was conducted in order to determine the effect of Cr(VI) on the amounts of energy obtained from the biomass of *Zea mays*. Additionally, it aimed to determine the potential of humic acids, compost, and *Zea mays* to restore the balance of soil exposed to the pressure of this element, which was defined according to changes in the activity of seven soil enzymes.

2. Materials and Methods

2.1. Experimental Design

The experiment, including four replications, was carried out in a greenhouse at the University of Warmia and Mazury in Olsztyn, Poland in 3 dm^3 pots. The experimental factors were: I—level of soil contamination with Cr(VI): 0 mg, 15 mg, 30 mg, 45 mg, and 60 mg kg^{-1} d.m. and II—organic fertilization in doses: 0 mg and 3 mg C kg^{-1} d.m. Organic fertilizers consisted of composted grass in one series of the trials and humic acids in the form of the preparation HumiAgra in the other series. The trials were set up on soil with the grain size composition of sandy loam. The test plant was *Zea mays* L. of the LG 32.58 variety (a variety registered in the European Union). After emergence, four plants were left in each pot. The soil used in the research (sand—3.61%, silt—32.68%, and clay—3.71%) came from arable land that had not been fertilized with natural or organic fertilizers for several years. It was characterized by a C_{org} to N_{tot} ratio of 12.05, a sum of basic exchangeable cations

(CEC) of 8.97 cmol (+) kg^{-1} d.m., hydrolytic acidity (HAC) of 2.61 cmol (+) kg^{-1} d.m., sum of exchangeable base cations (EBC) of 6.36 cmol (+) kg^{-1} d.m., and alkaline cation saturation (ACS) of 70.90% and pH_{KCl}—4.40. Chemical properties of the soil per 1 kg^{-1} d.m. were as follows: N_{total}—0.83 g; C_{org}—10.00 g; $P_{available}$—81.10 mg; $K_{available}$—145.25 mg; $Mg_{available}$—71.00 mg; and Cr_{total}—12.37 mg. The compost was characterized by a C_{org} to N_{tot} ratio of 7.27, a sum of exchangeable base cations of 7.42 cmol (+) kg^{-1} d.m., and hydrolytic acidity of 8.20 cmol (+) kg^{-1} d.m. HumiAgra (AgraPlant, Kielce, Poland) is an ecological product containing 90% humous acids with a 1:1 ratio of humic acids to fulvic acids. It is a dark brown powder with a pH of 8–10 and contains 8% K_2O and 3% S.

2.2. Procedure of the Experiment

Each pot was filled with a batch of 3.5 kg of soil first passed through a 5 mm mesh net sieve. Then, the soil was mixed with the mineral fertilizers and, according to the experimental design, with the organic fertilizers and an aqueous solution of $K_2Cr_2O_7$ in amounts ensuring the target level of soil contamination with Cr(VI). The mineral fertilization was adjusted to the nutritional requirements of *Zea mays*, that is, N—140 mg, P—50 mg, K—140 mg and Mg—20 mg kg^{-1} soil d.m. Nitrogen was applied as $CO(NH_2)_2$, phosphorus as KH_2PO_4, potassium as KH_2PO_4 + KCl, and magnesium as $MgSO_4 \cdot 7H_2O$. Once the soil was placed in pots, its moisture content was increased to 60% of maximum moisture by adding deionized water, and then maize was sown. The *Zea mays* plants were grown for 50 days, maintaining the constant moisture content throughout that time. The average air temperature was 16.5 °C, and the air humidity was 77.5%. The daylight length varied from 15 h 5 min. to 17 h 5 min. At the 4th leaf development stage (BBCH 19), in 8 replicates, the SPAD (Soil and Plant Analysis Development) leaf greenness index was determined. The measurement was performed with a SPAD 502 Chlorophyll Meter 2900P (Konica Minolta, Inc., Chiyoda, Tokyo, Japan). In the BBCH 51 phase, *Zea mays* was harvested and the height of the aerial parts of the plants and the yield of the aerial parts of the plants and roots were determined. The plant material was dried for 4 days at 60 °C and the calorific value of the aerial parts of the plants was determined. On the day of the *Zea mays* harvest, soil samples were taken to determine the activity of seven soil enzymes. The soil intended for laboratory analysis was passed through a sieve with a mesh size of 2 mm.

2.3. Calorific Value Determination

To determine the calorific value of a material, its heat of combustion (Q) must be determined beforehand. The Q value of the aerial parts of *Zea mays* was determined in a C-2000 calorimeter produced by IKA WERKE, USA. A procedure was used in accordance with the PN-EN ISO 18125:2017 IKA C2000 standard [52].

The calorific value (Hv) of *Zea mays* was calculated with a formula proposed by Kopetz et al. [53]:

$$Hv = \frac{Q\ (100 - Mc)}{100} - Mc\ \times\ 0.0244 \quad (1)$$

where:

Hv—calorific value of air-dried plant biomass (MJ kg^{-1});
Q—heat of combustion of air-dried plant biomass;
M_C—biomass moisture content (%);
0.0244—correction coefficient for water vaporization enthalpy (MJ kg−1 per 1% moisture content).

The energy yield of *Zea mays* biomass per 1 kg of soil was calculated with Equation (2):

$$Y_{EP} = Hv \times Y \quad (2)$$

where:

Y_{EP}—energy yield of plant biomass (MJ);
Hv—calorific value of air-dried plant biomass (MJ kg^{-1});
Y—aerial biomass yield of (kg) *Zea mays* per 1 kg of soil.

2.4. Determination of Enzyme Activity

In the soil samples taken from all experimental objects, the activity of seven enzymes was determined using standard methods in three replicates. The activity of the dehydrogenases was determined using the Lenhard method modified by Öhlinger [54], and the catalase, urease, β-glucosidase, arylsulfatase, acid phosphatase, and alkaline phosphatase activities were determined using the method of Alef and Nannipieri [55]. Enzyme activity was expressed in moles or their subunits of the produced product per 1 kg of soil in the course of 1 h. The exact assay procedures have been described in our previous publications [56,57].

2.5. Physicochemical and Chemical Analyzes of Soil

In the soil used for the study, the granulometric composition was determined using the aerometric method [58,59], hydrolytic acidity, and cation exchange capacity using the Klute method [60] and the total content of nitrogen [61] and organic carbon [62]. All analyses were conducted in three replicates.

2.6. Statistical Analyzes and Calculations

The indices of the effect of chromium, compost, and HumiAgra on the tested parameters were calculated using Equation (3):

$$\mathrm{IFy} = \frac{\mathrm{Bx}}{\mathrm{Cx}} - 1 \quad (3)$$

where:

IF—index of the effect;
y—chromium, compost, or HumiAgra, respectively;
B—value of the dependent variable of the tested object;
C—value of the dependent variable of the control object;
x—tested parameter, e.g., biomass, enzyme activity, etc.

These indices were plotted on thermal maps using the R v1.2.5033 software [63] with the addition of R v3.6.2 [64] and a gplots library [65]. Additionally, "a color key and histogram" was used to show how many times particular data appeared in the matrix used in the thermal map. In order to determine the influence of each independent variable on the shaping of dependent variables, a Statistica 13.3 package was employed [66] and the η^2 coefficient was calculated using analysis of variance, ANOVA. Homogenous groups were determined for all independent variables with Tukey's test at $p = 0.05$. Furthermore, in order to highlight the relationships between the results obtained, Principal Component Analysis (PCA) and Pearson's simple correlation analysis were performed.

3. Results

3.1. Yields of Zea mays in Soil Contaminated with Cr(VI) and the Crop's Energy Efficiency

Soil contamination with Cr(VI) had a negative effect on the growth and development of *Zea mays* (Tables S1 and S2, Figures 1 and 2). In the experimental series without fertilization, with compost or with HumiAgra, a level of chromium contamination in a dose higher than 15 mg Cr(VI) kg^{-1} soil d.m. caused a significant decrease in the yield of the aerial parts (Table S1) and roots of maize (Table S2). The decrease in the plant's biomass yield was directly proportional to the degree of soil contamination. This was also confirmed by the coefficients of the correlation between a dose of Cr(VI) and yield of the aerial parts ($r = -0.984$) and roots ($r = -0.985$) of maize. The coefficient of the effect of the highest contamination level (60 mg Cr(VI) kg^{-1} soil d.m.) on the biomass of the aerial parts was -0.903, and on the biomass of the roots reached -0.917, which means that in the former case, the yield declined by 90.3%, and in the latter one, it declined by 91.7% (Figure 1). The application of compost alleviated the negative effect of chromium at the dose of 30 mg Cr(VI) kg^{-1} soil d.m. on the aerial parts and at the doses of 30–45 mg Cr(VI) kg^{-1} soil

d.m. on the roots. Fertilization with the preparation HumiAgra proved to be even more effective in mollifying the effects of chromium contamination on *Zea mays* as it eliminated the toxic effect of this heavy metal on the biomass of the aerial parts and roots at all levels of chromium contamination.

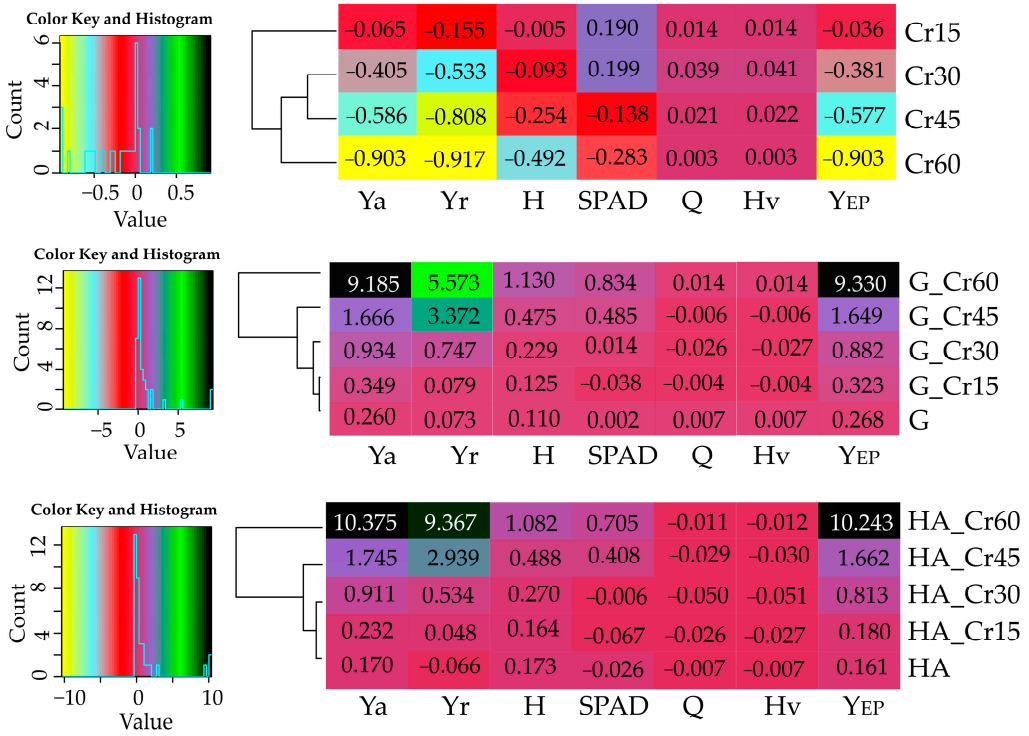


Figure 1. Index of the effect of Cr(VI), compost, and HumiAgra on *Zea mays* yield, plant height, SPAD, heat of combustion, calorific value, and biomass energy. Ya—yield of aerial parts, Yr—yield of roots, H—plant height, SPAD—greenness index, Q—heat of combustion, Hv—calorific value, and Y_{EP}—energy yield.

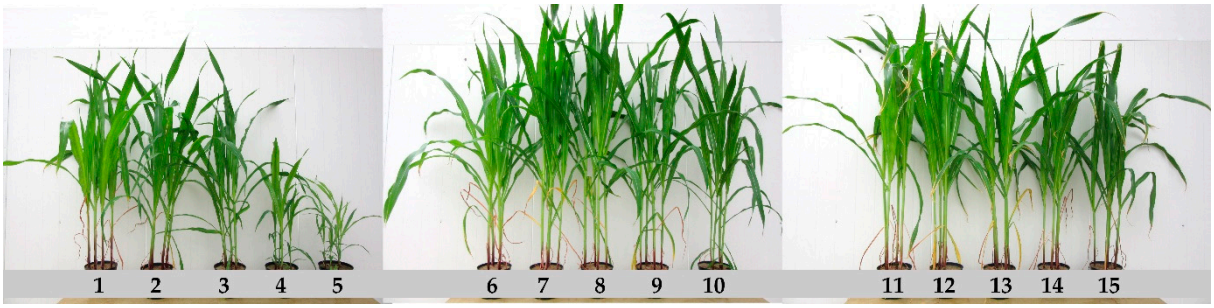


Figure 2. Maize on the day of harvest in BBCH phase 19 (50 days of vegetation). Series without additives (**a**), with compost (**b**), and with HumiAgra (**c**). Numbered samples 1, 6, 11—0 mg; 2, 7, 12—15 mg, 3, 8, 13—30 mg, 4, 9, 14—45 mg, and 5, 10, 15—60 mg Cr(VI) kg^{-1} soil d.m.

The toxic effect of Cr(VI) on the growth and development of *Zea mays* was demonstrated by the significant inhibition of the growth of the aerial organs of maize plants (Table S3, Figure 1). Under the highest dose of Cr(VI), in the experimental series without compost or HumiAgra, the height of *Zea mays* plants decreased from 138.8 cm to 70.5 cm. The application of compost and HumiAgra effectively reduced the negative effect of Cr(VI) on the height of *Zea mays* as well as the negative effect of the highest levels of contamination (45–60 mg Cr(VI) kg^{-1} d.m.) on the greenness index (Table S4, Figure 1). Despite the

negative effect of Cr(VI) on the growth and development of *Zea mays*, this element did not decrease the net calorific value (Table S5) and gross calorific value of the plants (Table S6), which is manifested by the low coefficients of the impact of Cr(VI), compost, and HumiAgra on the mentioned parameters (Figure 1). Because both Cr(VI) contamination and compost or HumiAgra fertilization changed the amounts of produced biomass, despite the stable net and gross calorific value of *Zea mays*, the energy of the biomass harvested per 1 kg of soil was varied (Table S7). The impact indices of Cr(VI) on the produced energy of biomass were negative and consistently lower at higher levels of soil contamination. In the series fertilized with compost or HumiAgra, these indices achieved positive values, which proves that both fertilizing substances are effective in alleviating the effects of soil contamination of Cr(VI), and as such they contribute to a higher harvest of energy from biomass.

3.2. Activity of Soil Enzymes in Soil Contaminated with Cr(VI)

Dehydrogenases demonstrated the highest activity in the soil uncontaminated with Cr(VI), in which their average activity was 3.871 µM TFF kg^{-1} soil d.m. h^{-1} (Table S8). As the level of chromium contamination increased (up to 60 mg Cr(VI)), their activity decreased to 0.682 µM TFF kg^{-1} soil d.m. h^{-1}. In the soil not fertilized with compost or HumiAgra, the index of the influence of chromium as a soil pollutant on dehydrogenases ranged from −0.595 to −0.891 (Figure 3), which means that Cr(VI) had a significant negative impact on these enzymes.

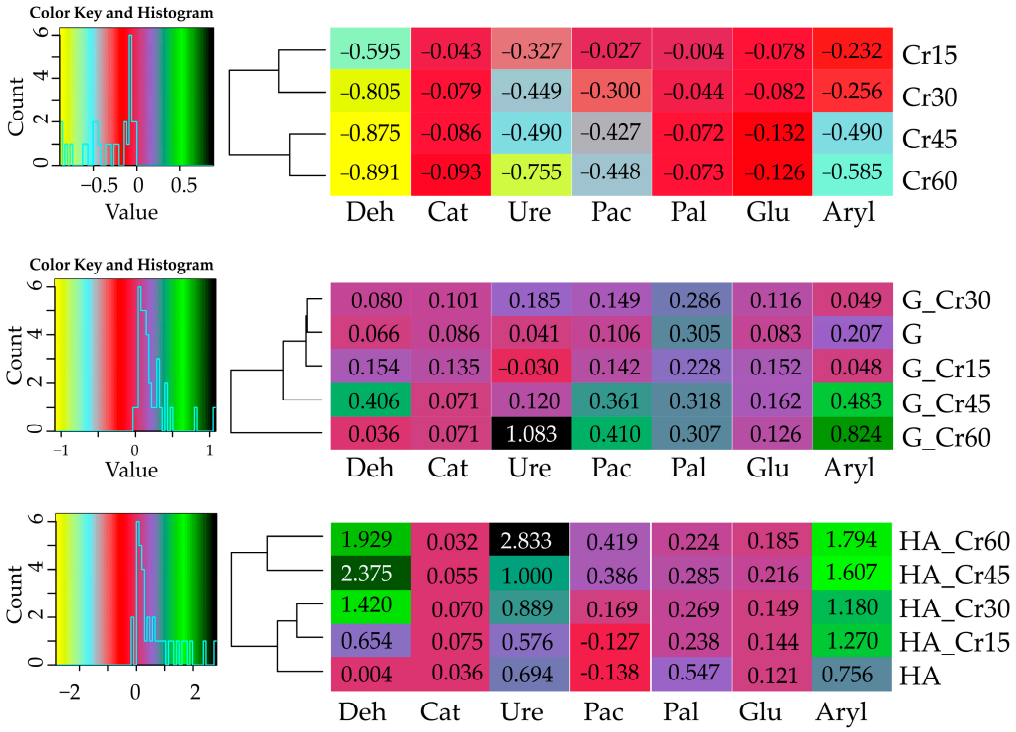


Figure 3. Index of the effect of Cr(VI), compost, and HumiAgra on the activity of soil enzymes: Deh—dehydrogenases, Cat—catalase, Pac—acid phosphatase, Pal—alkaline phosphatase, Glu—*β*-glucosidase, and Aryl—arylsulfatase.

The fertilization of soil with compost alleviated the effect of Cr(VI) on dehydrogenases, which was manifested by the positive indices of the influence of this treatment on the activity of dehydrogenases, ranging from 0.036 to 0.406. The impact of Cr(VI) on dehydrogenases was mollified even more distinctly by the application of HumiAgra. The value of the index of the influence of this preparation in contaminated objects varied from 0.654 to 2.375, which corresponded to an increase in the activity of dehydrogenases by 65.4% to 237.5% in soil contaminated with chromium in doses of 15 and 45 mg Cr(VI) kg^{-1} soil d.m.,

respectively. The activity of catalase was also inhibited by Cr(VI) in soil (Table S8). The average activity of this enzyme in the objects uncontaminated with Cr(VI) was 0.383 M O_2 kg^{-1} soil d.m. h^{-1}. It was the lowest in the soil with the highest contamination level (60 mg Cr(VI) kg^{-1} soil d.m.), in which it fell to 0.345 M O_2 kg^{-1} soil d.m. h^{-1}. The effect of Cr(VI) on the activity of catalase was much weaker than that on the activity of dehydrogenases (Table S9). The value of the influence index of this element on catalase ranged from −0.043 to −0.093 (Figure 3). The indices of the influence of compost and HumiAgra alleviating the impact of Cr(VI) achieved positive, albeit low, values, owing to the high tolerance of catalase to the soil presence of Cr(VI).

The average activity of urease in the uncontaminated objects was 1.014 mM N–NH_4 kg^{-1} soil d.m. h^{-1} (Table S10), and this decreased significantly as the Cr(VI) soil contamination level increased. The lowest activity of urease (0.460 mM N–NH_4 kg^{-1} soil d.m. h^{-1}) was found in soil contaminated with 60 mg Cr(VI) kg^{-1} soil d.m. Values of the index of influence of Cr(VI) on the activity of urease in soil unfertilized with compost or HumiAgra ranged from −0.327 in soil contaminated with 15 mg Cr(VI) to −0.755 in soil contaminated with 60 mg Cr(VI) kg^{-1} soil d.m. (Figure 3). Comparison of the values of the index of the influence of compost and HumiAgra mitigating the effects of Cr(VI) on the activity of this enzyme proves that HumiAgra was more effective than compost in alleviating the adverse impact of Cr(VI) on urease. Nevertheless, both fertilizing substances limited the inhibitory effect of chromium on the activity of urease to the highest degree in soil contaminated with 60 mg Cr(VI) kg^{-1} soil d.m., in which the index of the influence of compost reached 1.083, and that of HumiAgra was even higher, at 2.833.

The analyzed soil was characterized by a higher activity of acid phosphatase (Table S11) than that of alkaline phosphatase (Table S12). It was nearly 6.5-fold higher in the uncontaminated soil and 3.9-fold higher in the soil contaminated with 60 mg Cr(VI) kg^{-1} soil d.m. than the activity of alkaline phosphatase in these soils. In the unfertilized soil and in the soil fertilized with compost, the contamination with Cr(VI) did not significantly change the activity of acid phosphatase. In the soil fertilized with HumiAgra, Cr(VI) did not significantly change the activity of acid phosphatase, but it did depress the activity of alkaline phosphatase. These dependences were confirmed by the indices of the influence of Cr(VI) and compost as well as HumiAgra on the activity of phosphatases (Figure 3).

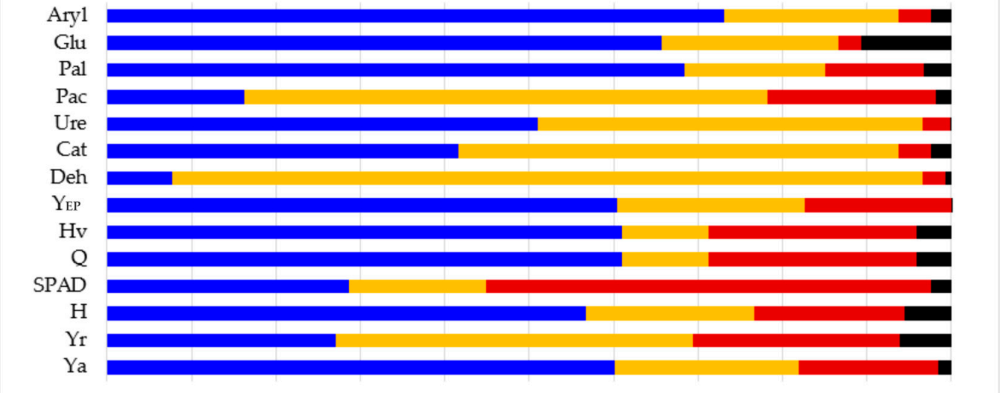
A relatively weak effect, compared to that observed in dehydrogenases and urease, was produced by Cr(VI) on the activity of β-glucosidase (Table S13). The activity of β-glucosidase decreased, although much less than the activity of the aforementioned enzymes, in the control series and in the soil fertilized with compost. No significant effect of Cr(VI) on the activity of β-glucosidase was observed in the soil treated with HumiAgra. However, the average results, regardless of the experimental series, indicate that the highest activity of β-glucosidase (0.637 mM PNP kg^{-1} soil d.m. h^{-1}) was achieved in the uncontaminated series, while the lowest one (0.575 mM PNP kg^{-1} soil d.m. h^{-1}) was found in the series contaminated with 60 mg Cr(VI) kg^{-1} soil d.m.. The indices of the influence of Cr(VI) on the activity of β-glucosidase ranged from −0.078 to −0.132, those of compost from 0.083 to 0.152, and of HumiAgra from −0.121 to 0.216 (Figure 3).

Arylsulfatase proved to be sensitive to the influence of Cr(VI) in both the control and the fertilized series (Table S14). The negative effect of this metal on arylsulfatase was detected already at the lowest contamination level of 15 mg Cr(VI) kg^{-1} soil d.m., while in the soil treated with HumiAgra, the activity of arylsulfatase was inhibited only by the higher concentrations of the pollutant, i.e., 45 and 60 mg Cr(VI) kg^{-1} of soil. The index of the influence of Cr(VI) on the activity of arylsulfatase scored negative values, lower as the level of chromium contamination of the soil increased (Figure 3), and ranged from −0.232 to −0.585. Both compost and HumiAgra added to soil improved the activity of arylsulfatase, which is evidenced by the index of the influence equaling 0.207 for compost and 0.756 for HumiAgra. The invariably positive effect of compost of the activity of arylsulfatase was determined in the soil contaminated with 45 and 60 mg Cr(VI) kg^{-1} of soil. The index of the influence of this compost scored 0.483 and 0.824, respectively. HumiAgra had an even

more beneficial effect on the activity of this enzyme. The index of its influence tended to reach higher values as the level of soil contamination with Cr(VI) increased and ranged from 1.270 to 1.794.

3.3. Interactions between the Yield of Zea mays and its Energy Yield and Soil Enzyme Activity

In the above experiment, a significantly higher impact on the dependent variable was produced by the fertilization of soil with compost and HumiAgra than by the soil contamination with Cr(VI) (Figure 4).



	Ya	Yr	H	SPAD	Q	Hv	Y_{EP}	Deh	Cat	Ure	Pac	Pal	Glu	Aryl
F	60.18	27.07	56.78	28.7	61.01	61.01	60.44	7.77	41.64	50.96	16.23	68.43	65.64	73.14
Cr	21.69	42.33	19.82	16.25	10.20	10.20	22.14	88.75	52.07	45.68	61.96	16.68	21.02	20.61
F × Cr	16.55	24.43	17.84	52.62	24.63	24.63	17.41	2.71	3.84	3.16	19.93	11.59	2.66	3.84
Error	1.58	6.17	5.57	2.43	4.15	4.15	0.01	0.77	2.44	0.19	1.89	3.30	10.67	2.41

Figure 4. The contribution of independent variables (η^2) in influencing the dependent variables. F—fertilization, Cr—Cr(VI) contamination, Ya—yield of aerial parts, Yr—yield of roots, H—plant height, SPAD—greenness index, Q—heat of combustion, Hv—calorific value, Y_{EP}—energy yield, Deh—dehydrogenases, Cat—catalase, Pac—acid phosphatase, Pal—alkaline phosphatase, Glu—*β*-glucosidase, and Aryl—arylsulfatase.

The load of the impact of the fertilization was very high and varied from 7.77% of the effect on dehydrogenases to 73.14% on arylsulfatase. The impact of the fertilization on the parameters assigned to the growth and development of plants varied from 27.07% (yield of roots) to 60.18% (yield of aerial parts). Fertilization of soil affected the net calorific value, gross calorific value, and energy production in the range of 60.44% to 61.01%. Fertilization also had a significant effect on the activity of alkaline phosphatase (68.43%), *β*-glucosidase (65.6%), urease (50.96%), and catalase (41.64%). While the considerable impact of soil fertilization with compost and HumiAgra on the analyzed parameters should be considered as a positive finding, the high impact of Cr(VI) on dehydrogenases (88.75%), acid phosphatase (61.96%), catalase (52.07%), urease (45.65), and the yield of *Zea mays* (42.33%) is an undesirable outcome. The interaction of the two independent variables (F and Cr) was the highest with respect to the growth and development of *Zea mays*, ranging from 16.55% on the yield of the aerial parts to 52.62% on the SPAD greenness index. The F × Cr interaction had a relatively strong effect on the net and gross calorific value of *Zea mays* (24.63%) and on the production of energy from biomass (17.41%).

The gross calorific value and the net calorific value of *Zea mays* (Figure 5) were not significantly correlated with the level of soil contamination with Cr(VI), while the biomass of maize, quantity of energy obtained from biomass, and the activity of all soil enzymes were significantly negatively correlated with the soil contamination of this metal.

Variable	Cr	Y_a	Y_r	H	SPAD	Q	Hv	Y_{ep}	Deh	Cat	Ure	Pac	Pal	Glu	Aryl
Cr	1.000														
Y_a	-0.457	1.000													
Y_r	-0.641	0.866	1.000												
H	-0.416	0.941	0.804	1.000											
SPAD	0.106	0.633	0.445	0.691	1.000										
Q	0.138	-0.405	-0.362	-0.336	0.067	1.000									
Hv	0.138	-0.405	-0.362	-0.336	0.067	1.000	1.000								
Y_{ep}	-0.461	0.991	0.886	0.941	0.649	-0.373	-0.373	1.000							
Deh	-0.847	0.509	0.687	0.438	-0.182	-0.465	-0.465	0.503	1.000						
Cat	-0.706	0.748	0.725	0.650	0.141	-0.282	-0.282	0.757	0.671	1.000					
Ure	-0.604	0.619	0.635	0.627	0.091	-0.632	-0.632	0.604	0.799	0.506	1.000				
Pac	-0.736	0.739	0.819	0.626	0.253	-0.189	-0.189	0.752	0.690	0.813	0.426	1.000			
Pal	-0.361	0.730	0.585	0.742	0.311	-0.444	-0.444	0.730	0.494	0.691	0.714	0.416	1.000		
Glu	-0.437	0.840	0.731	0.786	0.352	-0.568	-0.568	0.832	0.616	0.745	0.751	0.566	0.845	1.000	
Aryl	-0.447	0.625	0.544	0.660	0.211	-0.730	-0.730	0.601	0.643	0.470	0.891	0.326	0.677	0.760	1.000

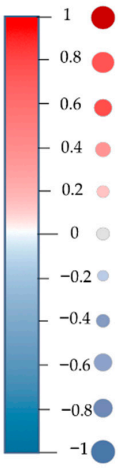
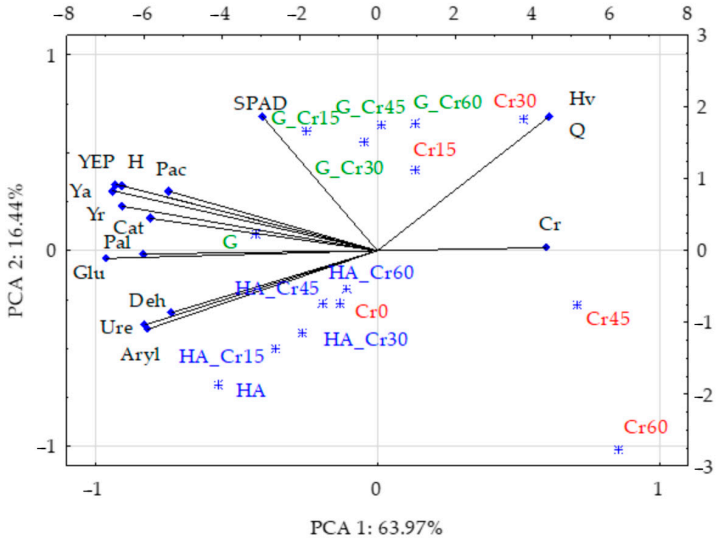


Figure 5. Pearson's simple correlation coefficients; $p = 0.05$, $n = 45$. * significant correlation coefficient, Ya—yield of aerial parts, Yr—yield of roots, H—plant height, SPAD—greenness index, Q—heat of combustion, Hv—calorific value, Y_{EP}—energy yield, Deh—dehydrogenases, Cat—catalase, Pac—acid phosphatase, Pal—alkaline phosphatase, Glu—*β*-glucosidase, and Aryl—arylsulfatase.

There was also a negative correlation between the gross and net calorific values and the biomass of *Zea mays* as well as the activity of dehydrogenases, urease, alkaline phosphatase, *β*-glucosidase, and arylsulfatase. The positive correlation between the energy acquired from the biomass of *Zea mays* and the activity of all analyzed soil enzymes is a valuable finding. This correlation value resulted from the positive effect of soil enzymatic activity on the growth and development of *Zea mays*. The PCA results (Figure 6) show that the strongest correlation appeared between the activities of: *β*-glucosidase and alkaline phosphatase; dehydrogenases, urease, and arylsulfatase; and acid and alkaline phosphatase.



Variable	PCA 1	PCA 2
Ya	−0.937	0.306
Yr	−0.905	0.228
H	−0.905	0.333
SPAD	−0.410	0.688
Q	0.605	0.682
Hv	0.605	0.682
YEP	−0.927	0.340
Deh	−0.729	−0.316
Cat	−0.805	0.165
Ure	−0.824	−0.380
Pac	−0.738	0.304
Pal	−0.830	−0.017
Glu	−0.962	−0.039
Aryl	−0.815	−0.401

Figure 6. Test results presented using the PCA method. Ya—yield of aerial parts, Yr—yield of roots, H—plant height, SPAD—greenness index, Q—heat of combustion, Hv—calorific value, Y_{EP}—energy yield, Deh—dehydrogenases, Cat—catalase, Pac—acid phosphatase, Pal—alkaline phosphatase, Glu—*β*-glucosidase, and Aryl—arylsulfatase, ⁜ — cases.

4. Discussion

4.1. Yield of Zea mays in Soil Contaminated with Cr(VI) and its Energy Efficiency

It has been demonstrated that heavy metals, including Cr, permeate into plant cells via the apoplastic (extracellular) or symplastic (intracellular) pathway or else through the competitive absorption of elements [67]. Nevertheless, their accumulation in plants is a

more complex process, dependent on the species and varieties of plants as well as the temperature, moisture, content of organic matter, and pH of the soil [68]. Thus, despite numerous reports on the toxicity of Cr(VI) towards plants, it is worthwhile to estimate the extent of the negative impact of this element on *Zea mays* through the prism of a wider array of parameters. The inhibited production of the aerial and root yields of maize, evidenced by the coefficients of the correlation between the dose of Cr(VI) and the yield of aerial organs ($r = -0.984$) and roots ($r = -0.985$), has been verified by other scholars, for example Mohammed et al. [69], who observed that oxyanions not only diminished the biomass of the plant's roots but also decreased the rate of its germination, or Poltis [70], who showed that exposure to Cr(VI) contributed to a decrease in the length of roots and aerial parts of the plant by 25% and 75%, respectively. Wyszkowska et al. [26] demonstrated in their study that Cr(VI) was just as toxic to *Zea mays*. The inhibitory effect of this element escalated when supplied at a dose of 60 mg Cr kg^{-1} soil d.m., which depressed the yield of aerial parts by 90% and that of roots by 92%. Several mechanisms are responsible, and many are activated already at the stage of Cr translocation from the endoderm to the xylem of the roots. This is when Cr ions undergo chelation, a translocation jest process facilitated by the CPx-ATPase trans-porters [71]. In our study, the response of the *Zea mays* aerial parts was similar to that of its roots, which may seem puzzling because Shanker et al. [72] maintain that—as part of the plant's protection mechanism—Cr is accumulated to a greater extent in the vacuoles of root cells, thereby retarding the root growth by inhibiting the mitotic divisions of cells due to chromosome aberrations [73]. In our experiment, there was also a significant retardation of the growth and development of *Zea mays* aerial parts. This can be attributed to the overproduction of reactive oxygen species (ROS), causing such oxidative damage as retardation of the growth of plants due to the decreased content of pigment, promoting genetic mutations and DNA fragmentation [74]. They include hydroxyl radicals (OH^-), hydrogen peroxide (H_2O_2), peroxynitrite ion ($OONO^-$), or paramagnetic singlet oxygen ($^1O_2$) [75,76]. The negative effects of this phenomenon arise from the Haber–Weis reaction and the Fenton reaction, both of which induce an increase in ROS [77]. The accumulation of H_2O_2 in maize roots is particularly tightly connected with the toxicity of Cr [39]. This compound is synthesized in the process of dismutation of the superoxide ion in the presence of superoxide dismutase (SOD), whose potential lies in the location of the enzyme in chloroplasts, cytosol, apoplasts, mitochondria, and peroxisomes [78]. A significant increase in ROS is additionally positively correlated with the content of malonic dialdehyde (MDA) [79]. However, it was reasonable to expect a milder negative impact of Cr(VI) in light of several facts. First, there is a high probability that the conversion of Cr(VI) into Cr(III) has occurred, which binds to cell walls, thereby hindering the transport of Cr in plant cells. Cr(III) is transported from the roots to the shoots or aerial parts of plants. This process results from the reduction of Cr(VI) to Cr(III) induced during the transport of this metal to the xylem. Although there is a small concentration of Cr(III) in the aerial parts of plants, which is the result of precipitation of its excess in the cell and the formation of complexes with ligands, it does not protect the plant against chromium toxicity. It leads to DNA strand breaks, excessive ROS production, or disturbances in chromosome aberrations that ultimately reduce the yield of crops [80,81]. Secondly, there is competition between the metals Fe and Cr during the translocation of Cr(VI) from the roots to aerial organs of plants [82,83]. Noteworthy is the role of glutathione, both in its reduced (GSH) and oxidized (GSSG) forms, in the ascorbate–glutathione cycle, where it eliminates harmful peroxides [84]. Interestingly, the defense strategies were not reinforced by the interaction of the ABA gene biosynthesis (*OsNCED2* and *OsNCED3*) with salicylic acid [85].

It is also worth considering the response of *Zea mays* to the toxicity of Cr(VI) as reflected by a decline in the greenness index under the pressure of the highest Cr(VI) doses (45–60 mg kg^{-1} soil d.m.). The results reported by Wyszkowska et al. [26], which showed that chromium decreased the SPAD greenness index by 47% and 28% in the 4th and 7th leaf development stages, respectively, attest to the tendencies observed in our study. Complete membranes of chloroplasts are necessary to maintain the photosynthetic activity of plants.

Changes in their ultrastructure include a decrease in the amount of such lipid components as monogalactosylglycerol or phosphatidylglycerol [86], disorder in the development of the lamellar system, and disorganization of the mesophyll cells. Moreover, a decreased conductivity of stomata has been observed in plants exposed to Cr, which is due to the modification of the cellular structure of spongy parenchyma, and leads to a smaller size of the mesophyll stomata, ultimately inhibiting photosynthesis, transpiration, and gas exchange [31,87]. The disturbance of chlorophyll synthesis is also explained by Cr(VI) inhibiting the activity of δ-aminolevulinate dehydratase (ALAD), which catalyzes this process [87].

In this experiment, the application of compost or HumiAgra alleviated the toxic effect of Cr(VI) on the aerial parts and roots of maize, and on the greenness index of *Zea mays*, although humic acid proved to be more effective. The reason was that it is humic acids that are responsible for the diminishing of the content of extractable heavy metals in compost [88]. Such satisfying effects of the application of either biostimulant tested were to be expected because compost, as a source of dissolved organic carbon (DOC), has a decisive influence on the soil's sorption capacity and retention of heavy metals [89]. Owing to this, both compost and HumiAgra could improve the synthesis of chlorophyll, and the activity of the PS1 and PS2 photosystems [90], by regulating the activity of such antioxidants as glutathione (GSH), peroxidase (POD), and superoxide dismutase (SOD), or by eliminating the risk of lipid peroxidation [91]. The stability and maturity of the compost are also evidenced by the percentage gain in total nitrogen or the loss in the carbon content during the progress of composting. A valuable indicator of compost maturity is thus a C/N ratio of 10–15:1. The decreasing C/N ratio is the result of the consumption of organic compounds by microorganisms [92]. In our research, the compost was characterized by a C_{org} to N_{tot} ratio of 7.27, which probably contributed to the lower effectiveness of the compost in alleviating the adverse impact of Cr(VI) on *Zea mays* biomass.

Diversification of the energy matrix is also achievable by selecting plant biomass that has been produced in unfavorable natural conditions [93]. However, the results of this study do not seem to support this option, as one of the findings was that the decreasing biomass of *Zea mays* due to Cr(VI) soil contamination entailed lower energy harvest. Nonetheless, chromium did not have a negative effect on the net calorific value or the gross calorific value of the dry matter of maize straw. It also needs to be emphasized that the calorific value of the dry matter of maize straw (18.2 MJ kg^{-1}) [94] and (18.5 MJ kg^{-1}) [95] is higher than that of oilseed rape straw (15.3 MJ kg^{-1}) [96] or barley straw (15.7 MJ kg^{-1}) [97]. Calorific value of various biomass types is presented in Table 1.

Table 1. Calorific values of various biomass types.

Plant	Calorific Value MJ kg^{-1}	Reference
Bromus inermis Leyss.	17.231	[98]
Calamagrostis epigejos L. (Roth)	18.037	[98]
Camelina sativa	18.500	[99]
Crambe abyssinica	17.940	[99]
Euphorbia nerrifolia	21.487	[100]
Elymus elongatus	15.052	[12]
Festuca rubra	16.306	[13]
Holcus lanatus L.	16.029	[98]
Mimusops elengi L.	19.217	[100]
Miscanthus sinensis	17.840	[101]
Nerium indicum	18.443	[100]
Populus × *euramericana*	17.980	[102]
Robinia pseudoacacia L.	17.550	[102]
Salix trianda L. × *Salis viminalis* L.	17.930	[102]
Salix viminalis L. *	8.600–19.500	[103]
Sida hermaphrodita	17.430	[101]
Silphium perfoliatum L.	16.610	[104]
Zea mays—corn cob cores	16.190–16.530	[105]
Zea mays—BBCH 51 phase	14.799	Own research

* Three varieties and three clones of willow (*Salix* spp.) cultivated in the Eco-Salix system.

To raise the energy value by increasing the biomass of plants grown in soils contaminated with Cr(VI), humic acids should be applied to the soil, as suggested by this study. Other important techniques regulating the production of plant biomass grown under the pressure of heavy metals are the manipulation of the content of plant hormones [106] or phytomining, which consists of the recovery of the target metal after harvesting, drying, and incinerating the plant biomass [107].

4.2. Activity of Soil Enzymes in Soil Contaminated with Cr(VI)

The biggest challenge in research on the activity of soil enzymes is to gain an in-depth understanding how they overcome the inhibitory and competitive properties of the soil matrix [108]. The first step in diagnosing the response of soil enzymes to the increase in soil contaminated with Cr(VI) is to achieve a better insight into the complexity of the forms in which enzymes occur in soil, which was reflected by the diverse responses of the seven enzymes analyzed in this study. While it was true that the activity of all these enzymes was inhibited, dehydrogenases, urease, and arylsulfatase proved to be the most sensitive to Cr(VI). It would be rather difficult to question these results as they are confirmed by reports from many other studies [26,109,110]. However, the response of alkaline phosphatase, which was determined in this study as the most tolerant to Cr(VI), seems puzzling because it is contrary to the research results showing that chromium inhibited the activity of hydrolase as effectively as the activity of the other enzymes [111,112]. It is known that, apart from the type and speciation of metals, soil enzymatic activity is significantly affected by the bioavailability of metals, which depends on the soil pH and organic matter (OM) content [113,114]. Extracellular enzymes are complexed with organic matter through copolymerization or adsorption, which reduces the availability of the substrate and causes their conformation modifications [115], while simultaneously turning them into signal molecules for the microbial community [116]. In our study, the response of dehydrogenases to Cr(VI) toxicity can be explained by the fact that they are an integral element of the enzymatic system of all living microorganisms, responsible for the transport of electrons in oxygen metabolism [117]. Cr(III) may also be responsible for inhibiting the activity of enzymes, mainly that of dehydrogenases. The effects of the pressure of this form of chromium in the amount of 80 mg Cr(III) kg^{-1} soil d.m. on the activity of dehydrogenases and the value of the biochemical soil fertility index, which also accounts for the activity of urease, acid phosphatase, and alkaline phosphatase, was observed by Wyszkowska et al. [111]. Chromium is cytotoxic and genotoxic towards microorganisms by binding thiol groups of proteins or inhibiting DNA transcription and replication, which leads to the loss of their functionality and hence the inhibition of dehydrogenases [118,119]. Interestingly, Schimel and Weintrub [120] maintain that microorganisms use 2% of their assimilated carbon to synthesize enzymes.

The moderating effect of soil pH is also significant because higher pH is responsible for breaking down the ionic and hydrogen bonds in the active center of dehydrogenases [121], while catalase is active in a broad range of pH levels above the value of 3.5 [122]. The reason why the activity of urease is inhibited can be sought in some changes in the enzyme's molecular structure under the pressure of Cr(VI). The toxicity of this element may have resulted from Cr(VI) forming bonds with sulfhydryl groups (SH), cysteines, and carbonyl groups [123,124]. The fact that the contribution of intracellular urease to the total activity of this enzyme in soil varies from 37.1% to 73.1% should not be neglected [125]. Similarly to phosphatase, urease is not, strictly speaking, an extracellular enzyme, but rather assumes its status as a result of lysis and eventually the death of a maternal cell [107]. In our study, both compost and HumiAgra were effective in alleviating the negative effect of Cr(VI) on the activity of soil enzymes, but humic acids unquestionably had primacy in the biostimulation of dehydrogenases, urease, β-glucosidase, and arylsulfatase. The tendencies detected in this study most probably arose from the fact that metals, including Cr(VI), undergo chelation via the functional groups of humic substances [48]. Although fulvic acids have more carboxyl groups, humate acids, which make up 50% of the composition of HumiAgra,

are more effective in the formation of metal–humate complexes because they provide more binding sites owing to their more complex structure and larger molecules [126]. Nevertheless, compost is also an attractive biostimulating substance, which, in another study by Wyszkowska et al. [13], induced the activity of dehydrogenases, catalase, urease, acid phosphatase, and alkaline phosphatase. It is worth underlining that the application of compost stimulates the release of exudates from plant roots, mainly organic acids, amino acids, and fatty acids [127] and—similarly to humic acids—changes the chemical speciation of Cr(VI) through adsorption and complexing [128].

5. Conclusions

Excessively large quantities of chromium (VI) distort the biochemical balance of soil, which results in decreased biomass production by *Zea mays* and, consequently, lower energy output. Energy crops, for example *Zea mays*, can be grown in soil contaminated with Cr(VI) provided that the soil enzyme activity is compensated for by fertilization with compost or HumiAgra. The preparation HumiAgra proved to be more effective than compost in alleviating the adverse impact of Cr(VI) on *Zea mays* biomass. Thus, the preparation HumiAgra or other treatments contributing to the increase in the content of humic acids in soils should be recommended if an adequate amount of biomass is to be harvested from energy crops cultivated on soil contaminated with Cr(VI).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en16093788/s1, Table S1. Yield aerial parts of *Zea mays* (g d.m. pot^{-1}); Table S2. Yield roots of *Zea mays* (g d.m. pot^{-1}); Table S3. Plant *Zea mays* height (cm); Table S4. Greenness index (SPAD) of *Zea mays*; Table S5. Heat of combustion (Q) *Zea mays*, MJ kg^{-1} air-dried plant matter; Table S6. Calorific value of *Zea mays*, MJ kg^{-1} air-dried matter plants; Table S7. Energy yield (Y_{EP}), MJ kg^{-1}; Table S8. Dehydrogenase activity, μM TFF kg^{-1} soil d.m. h^{-1}; Table S9. Catalase activity, M O_2 kg^{-1} soil d.m. h^{-1}; Table S10. Urease activity, mM N-NH_4 kg^{-1} soil d.m. h^{-1}; Table S11. Acid phosphatase activity, mM PNP kg^{-1} soil d.m. h^{-1}; Table S12. Alkaline phosphatase activity, mM PNP kg^{-1} soil d.m. h^{-1}; Table S13. β-glucosidase activity, mM PNP kg^{-1} soil d.m. h^{-1}; Table S14. Arylsulfatase activity, mM PNS kg^{-1} soil d.m. h^{-1}.

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Abbreviations

The following abbreviations are used in this manuscript: F—fertilization; Cr—Cr(VI) contamination; Ya—yield of aerial parts; Yr—yield of roots; H—plant height; SPAD—greenness index; Q—heat of combustion; Hv—calorific value; YEP—energy yield; Deh—dehydrogenases; Cat—catalase; Ure—urease; Pac—acid phosphatase; Pal—alkaline phosphatase; Aryl—arylsulfatase; Glu—β-glucosidase.

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