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Effects of Humic Acids on Calorific Value and Chemical Composition of Maize Biomass in Iron-Contaminated Soil Phytostabilisation

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Abstract: An interesting feedstock for energy purposes is plant biomass due to its renewability, widespread availability and relatively low cost. One plant with a high and versatile use potential is maize. Plants used for energy production can be grown in polluted areas, e.g., with iron. The aim of the study was to determine the effect of humic acids (HAs) on the yield, calorific value and other energy parameters and chemical composition of maize biomass applied as a phytostabiliser on iron-contaminated soil. The soil was contaminated with iron at 0, 250, 500 and 750 mg kg^{-1}. The HAs were added to the soil in the following amounts: 0, 0.3, 0.6 and 0.9 g kg^{-1} of soil. Soil contamination with iron had relatively little effect on the heat of combustion and calorific value of biomass and very strongly reduced plant height (42%), dry matter yield (95%) and energy production of maize biomass (90%), the SPAD index at the fifth leaf unfolded stage (44%) (as opposed to the stem elongation stage), sodium, magnesium and phosphorus contents, and increased calcium, potassium and nitrogen contents of maize. The application of HAs to the soil had a positive and very large effect on both the height and biomass parameters studied, resulting in an increase in plant height (22%), dry matter yield (67%) and energy production from maize biomass (62%). Changes in the heat of combustion and calorific value of the biomass were minimal but positive. HAs contributed to a decrease in the value of the SPAD index during the stem elongation phase of maize and in the content of all macronutrients in maize biomass as a result of a reduction in the effect of iron on macronutrient content and to a significant increase in maize dry matter yield in plots with their application. The application of HAs appears to be an effective adjunct in the phytostabilisation of iron-contaminated soils by growing crops for energy purposes.

Keywords: Fe contamination; humic acids; maize biomass; yield; calorific value; SPAD; macronutrients

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1. Introduction

The world's fossil energy resources (oil, coal, cold gas) are limited and are gradually being depleted. For this reason, the diversification of energy sources and the widespread use of renewable energy sources should be pursued [1]. The need to diversify the energy generation mix is also strongly influenced by environmental considerations and the need to reduce the negative environmental impact of conventional technologies [2], as well as the need for economic independence from fossil fuel-supplying countries [3]. A promising feedstock for energy purposes is plant biomass due to its renewability, widespread availability and relatively low cost [4]. One plant with a high and versatile use potential is maize [5]. It provides a valuable source of raw materials for the food and chemical industries [6] and is an excellent animal feed [7]. A future direction for its use is production for energy purposes. The dry matter (DM) yield of maize is 12–15 Mg (tonnes) ha^{-1} [8]. Maize has high photosynthetic efficiency (1.5–2 times that of C3 plants), medium soil requirements and high adaptation to climate change [9,10].

Plant biomass can also be used to produce nanomaterials. Thangaraj et al. [11] used dry sugarcane (*Saccharum officinarum*) leaves, which they subjected to two-stage pyrolysis without a catalyst (or reducing agent) at different temperatures after adding acid to obtain reduced graphene oxide (rGO) with a multilayer graphitic structure. On the other hand, biomass from waste materials (sugarcane bagasse, rice husks or coconut shells) can be used to produce graphene oxide (GO) after the removal of silica [12]. In a subsequent study, Thangaraj et al. [13] obtained graphene oxide (GO) from dry sugarcane leaves using pyrolysis with the catalyst ferric citrate, followed by interaction with concentrated H_2SO_4. Low-temperature hydrothermal haracterized of biomass (isolated carbohydrates or raw plants) is another method that can be used to synthesise new carbon materials or composites from biomass. It is environmentally friendly and is widely used to produce carbon materials with significant microporosity or mesoporosity and high reactivity [14].

The primary form of energy use of agricultural biomass is direct combustion or co-firing in dedicated heating systems [15]. This biomass needs to be processed (e.g., by pelletisation) as it has a high bulk density and poorer energy properties when fresh [16]. The use of processed plant biomass for energy purposes in the form of briquettes or pellets also significantly reduces transport and storage costs and offers the possibility of fully automating the combustion process [16]. The calorific and physicochemical properties of biomass differ from those of traditional fuels. This mainly concerns the total moisture content, which reduces the calorific value of the fuel [17]. According to Wojcieszak [18], the average calorific value of fresh maize cobs is 7.62–10.79 MJ kg^{-1}, while after drying, it increases to 16.19–16.53 MJ kg^{-1}. In an experiment conducted by Magdziarz and Wilk [19], the calorific value of plant biomass (woody biomass—pellets and agricultural biomass—oats) was about 18 MJ kg^{-1}, while that of hard coal was about 24 MJ kg^{-1}. Undoubtedly, the advantage of plant biomass for energy purposes is the lower content of ash and sulphur, nitrogen and carbon compared to hard coal. This is reflected in lower emissions of dust and sulphur, nitrogen and carbon oxides into the environment during the combustion process [17].

The cultivation of energy crops allows the use of marginal land with reduced use value, including ecologically degraded land [20]. Soils contaminated with iron (Fe) are an example of such areas. This element enters the environment as a result of emissions from industrial and municipal facilities, transport routes and power plants (coal combustion) [21,22]. Wastewater from metallurgical industries and corrosion of old water distribution pipes are also considered sources of iron pollution [23].

Iron is an essential element for plant growth and development [24]. It acts as a cofactor for enzymes that mediate redox reactions in many important metabolic processes of plant cells [25]. It is an essential component of the photosynthetic apparatus, is involved in chlorophyll synthesis and is a component of ferredoxin [26], superoxide dismutase, catalase, peroxidase and nitrate reductase [27]. Consequently, iron plays an extremely important role in photosynthesis, cellular respiration, nitrogen fixation and metabolism, sulphur assimilation, and hormone and DNA synthesis [28]. Both iron deficiency and iron excess are detrimental to plants. Under iron deficiency conditions, chlorophyll synthesis and photosynthesis are reduced, resulting in chlorosis and stunted plant growth [25]. On the other hand, excess iron in plant tissues (>500 mg Fe kg^{-1} DM) [29] negatively affects photosynthesis, cell structural integrity, plant physiological traits, and polyphenol content and induces oxidative stress and reactive oxygen species production [24,30]. Excess soil iron also leads to reduced crop yield, reduced crop quality due to reduced nutrient content (mainly simple sugars, starch and protein nitrogen) [31] and inhibition of primary root growth through induction of H_2O_2 synthesis in the apical zone [32]. It also leads to chlorosis and necrosis of leaves, inhibition of tillering and reduced seed production, which negatively affects plant reproduction [33]. Iron phytotoxicity can be direct (accumulation of the element in plant tissues) [24] or indirect (deposition of an iron layer on the root surface, which affects the uptake of other nutrients by the plant) [34,35]. The high content of iron ions in the soil limits the solubility of phosphorus compounds and, thus, their availability to plants [36].

Iron is one of the most mobile elements in soil, and its bioavailability depends on environmental conditions. Organic compounds of iron generally increase its mobility, except for the adsorption process by soil humus [37]. Iron is well taken up from solution at low pH in the form of Fe^{2+} and Fe^{3+} cations and quite efficiently in the form of chelates [38]. One of the factors influencing the mobility and bioavailability of iron in soils is the content of organic matter, of which humic substances (HS) are an important component [39]. The presence of functional groups and the large specific surface area of the aforementioned substances make them involved in the haracterized of trace elements in soil, following complexation, adsorption and ion exchange [40]. The use of humic substances can, therefore, influence the content of bioavailable fractions of trace elements [41].

Large proper surface, inert nature, three-dimensional structure and amphiphilic properties [42], as well as the high cation exchange capacity and the presence of active functional groups (–OH, –COOH, $-NH_3$, $-OCH_3$) [40] in HS, make them capable of interacting with trace element ions [43]. Humic substances, especially humic acids (HAs) and fulvic acids (Fas), strongly influence the mobility, bioavailability and toxicity of trace elements through ion exchange phenomena, physical adsorption, complex/chelate formation or redox reactions [44,45]. These processes alter the mobility and local accumulation of trace elements in the soil and their transport to plant organs [46] or determine their partial detoxification [45]. Due to their unique physicochemical properties, humic substances are used as organic additives in the chemical haracterized processes of contaminated soils [42,47]. Their usefulness is confirmed by a study by Wu et al. [48], who recorded maximum reductions in the available fractions of copper, lead and cadmium of 57%, 28% and 7%, respectively, after the introduction of HAs (5%) into the soil, compared to the control series (without the addition of HAs). Also, in our other experiment [49], the application of humic substances reduced the content of many trace elements in the soil. The largest changes were observed for chromium, cadmium, lead and nickel, and smaller changes for copper and cobalt. Similar results were obtained by Rong et al. [41], who reported reductions in lead (by 39%), cadmium (by 37%), zinc (by 29%) and copper (by 18%) in soil relative to the control series, after HAs application (14.8 kg ha^{-1}).

As a result of human industrial and economic activities, the natural levels of trace elements in soils are repeatedly exceeded. They can adversely affect the biological properties of soil and groundwater, be toxic to plants and pose a threat to human health [50]. The physiological and molecular mechanisms of plant responses to iron deficiency have been extensively discussed in the literature. Less attention has been paid to the phytotoxic effects of excess iron on plants, especially maize. The above dependencies were the reason for the study in which the following research hypotheses were assumed: (1) iron soil contamination negatively affects yield, calorific value and other energy parameters and chemical composition of maize biomass; (2) HAs reduce the negative impact of excess iron on plants; (3) HAs favourably affected the formation of yield, heating value and other maize biomass parameters.

2. Materials and Methods

2.1. Pot Experiment

The research carried out was based on a vegetation hall pot experiment. The experiment investigated the effect of two factors. The first factor was soil contamination with iron at 0, 250, 500 and 750 mg kg^{-1} of soil. Iron was added to the soil in the form of $FeCl_3$. The second factor was the application of humic acids (HAs) in the following amounts: 0, 0.3, 0.6 and 0.9 g kg^{-1} of soil. Soil material taken from an arable layer of light soil with a granulometric composition of loamy sand [51] was used for the study. Humic acids were applied twice: during the establishment of the experiment and at the 5-leaf stage of the test plant. During the establishment phase, in addition to iron and HAs, basic macronutrients (160 mg N; 60 mg P; 170 mg K per kg soil) were applied to the soil in equal amounts to ensure the nutritional needs of the plants. Next, they were mixed with 9 kg of soil and placed in polyethylene pots. The height of the pot was 25 cm, the diameter at the top was 24 cm, and the diameter at the bottom was 19 cm. Maize (*Zea mays* L.) was used as the phytoremediation plant, as it is one of the staple crops and is haracterized by high biomass, significant elemental and contaminant uptake capacity and can be used for energy purposes. *Zea mays* L. was also used in this experiment because it is an annual plant, which is an advantage when conducting pot experiments. It is also of great economic importance worldwide. The study was carried out in 3 replicates. The experiment was carried out at a density of 6 plants per pot. During plant growth, the SPAD leaf greenness index was determined twice: at the fifth leaf unfolded stage and at the intensive stem elongation stage. Meteorological data during the maize vegetation were as follows (the averages per month): the air temperature ranged from 11.8 °C to 21.2 °C, the air humidity from 65% to 75%, and the insolation from 218.1 h to 335.6 h. Plants were harvested at panicle emergence to determine plant height and dry matter yield. At the same time, plant samples were taken. To take samples for laboratory analysis, we cut the above-ground parts of all plants at ground level.

2.2. Analytical Methods

The heat of combustion (Q) of the aerial parts of the maize was determined using a C-2000 calorimeter (IKA Works, Inc., Wilmington, NC, USA) according to the PN-EN ISO 18125:2017 IKA C2000 standard [52].

After determining the heat of combustion, the calorific value (Hv) of the maize biomass was calculated according to the following formula [53]:

$$\text{Cv} = (\text{Q}\ (100 - \text{Mc})\ 100^{-1}) - (\text{Mc}\ 0.0244)$$

where:

Cv—the calorific value of the biomass (MJ kg^{-1});
Q—the heat of combustion of the biomass;
Mc—moisture content of the biomass (%);
0.0244—water evaporation enthalpy correction factor (MJ kg^{-1} per 1% moisture).

The energy production from maize biomass per kg of soil was then calculated using the following formula [54]:

$$\text{BEP} = \text{Y Cv}$$

where:

BEP—biomass energy production (MJ);
Y—maize dry matter yield in kg per pot;
Cv—the calorific value of dried biomass (MJ kg^{-1}).

The SPAD leaf greenness index was determined using a Konica Minolta Optics SPAD-502Plus meter (Konica Minolta, Inc., Chiyoda, Japan) [55]. Plant samples were transferred to polyethylene containers after crushing, drying at a constant temperature of 60 °C and grinding. The plant samples prepared in this way were subjected to wet digestatition in sulphuric acid VI (analytical grade), and then the content of macronutrients was determined using standard methods: N—by the Kjeldahl method [56], P—by colourimetry [57], K, Na, Ca and Mg—by atomic absorption–emission spectrometry [57].

2.3. Statistical Methods

Two-factor ANOVA with Tukey's HSD test ($p \leq 0.01$) was used for statistical calculations. Pearson's simple correlation coefficients (r for ** $p \leq 0.01$ and * $p \leq 0.05$) and percentage of observed variability were also calculated. Statistical calculations were performed using Statistica 13.3 [58].

3. Results

Soil iron contamination and the HAs used to reduce its effect significantly affected both plant height and dry matter yield of maize (Table 1), its fuel properties (Table 2), the leaf greenness index SPAD (Figures 1 and 2) and plant macronutrient content (Tables 2 and 3).

Table 1. Height and dry matter (DM) yield of aerial parts of *Zea mays* L.

Fe Dose mg kg^{-1} of Soil	Humic Acids (HAs) Application in g kg^{-1} of Soil				
	0	0.3	0.6	0.9	Average
	Height (cm)				
0	139.9 ^{ef}	153.3 ^{fg}	154.7 ^{fg}	153.1 ^{fg}	150.3 ^{C}
250	152.1 ^{fg}	154.1 ^{fg}	158.8 ^{g}	152.7 ^{fg}	154.4 ^{D}
500	94.4 ^{ab}	131.4 ^{de}	148.8 ^{fg}	147.1 ^{f}	130.4 ^{B}
750	81.7 ^{a}	84.1 ^{a}	106.1 ^{bc}	119.6 ^{cd}	97.8 ^{A}
Average	117.0 ^{A}	130.7 ^{B}	142.1 ^{C}	143.1 ^{C}	133.2
r	−0.876 **	−0.906 **	−0.826 **	−0.861 **	−0.906 **
	Aerial parts dry matter yield (g pot^{-1})				
0	67.03 ^{g}	81.71 ^{i}	87.89 ^{j}	87.18 ^{j}	80.95 ^{D}
250	67.95 ^{g}	66.78 ^{g}	73.62 ^{h}	84.70 ^{ij}	73.26 ^{C}
500	18.38 ^{c}	31.23 ^{d}	45.52 ^{e}	56.93 ^{f}	38.02 ^{B}
750	3.37 ^{a}	8.89 ^{b}	18.45 ^{c}	32.30 ^{d}	15.75 ^{A}
Average	39.18 ^{A}	47.15 ^{B}	56.37 ^{C}	65.28 ^{D}	52.00
r	−0.934 **	−0.989 **	−0.991 **	−0.959 **	−0.976 **

r—coefficient of correlation, significant at ** $p \leq 0.01$. Different letters (homogeneous groups) to the right of the values (*a*–*j* for interactions between HAs and Fe dose, *A*–*D* for averages HAs and Fe doses) are significant at $p \leq 0.01$.

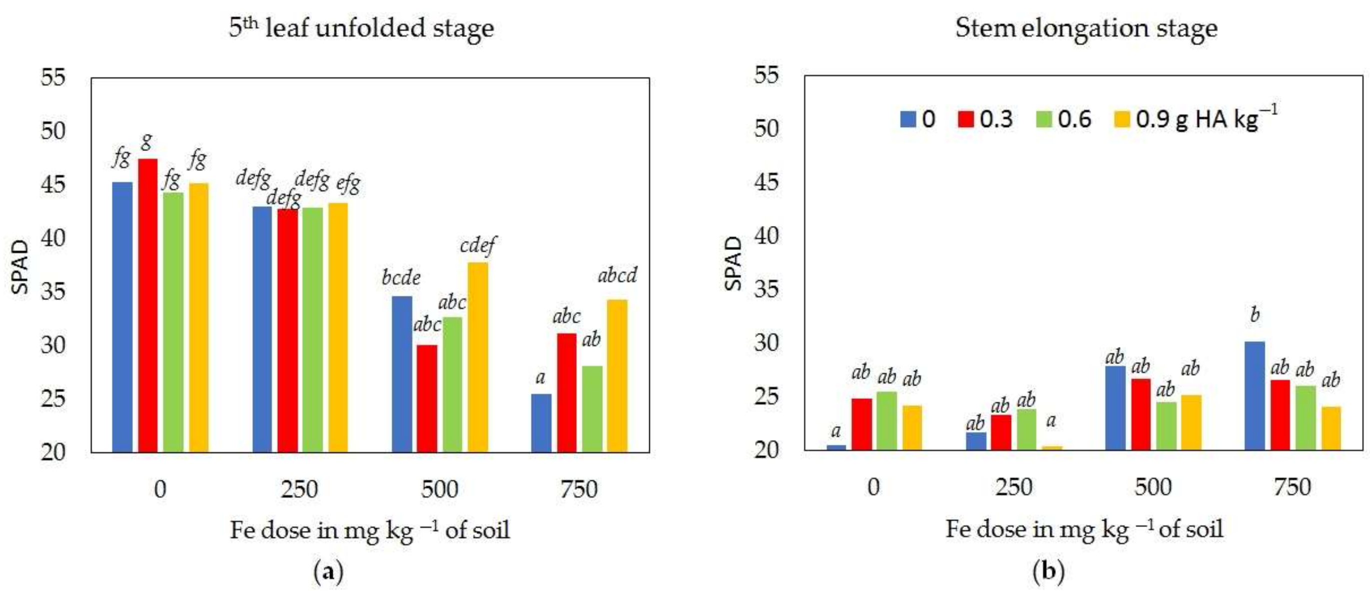

Figure 1. SPAD index in *Zea mays* L. vegetation stages of the fifth leaf unfolded (**a**) and stem elongation (**b**). Different letters (homogeneous groups) above the bars are significant at $p \leq 0.01$.

Table 2. The heat of combustion, calorific value and energy production from *Zea mays* L. biomass.

Fe Dose mg kg^{-1} of Soil	HAs Application in g kg^{-1} of Soil				
	0	**0.3**	**0.6**	**0.9**	**Average**
Heat of combustion, MJ kg^{-1} of plant					
0	18.03 ^{b}	18.33 ^{gh}	18.48 ^{i}	18.50 ^{i}	18.34 ^{D}
250	18.09 ^{bc}	18.19 ^{de}	18.24 ^{ef}	18.21 ^{ef}	18.18 ^{B}
500	18.38 ^{h}	18.12 ^{bc}	18.13 ^{cd}	18.31 ^{g}	18.23 ^{C}
750	17.89 ^{a}	18.27 ^{fg}	17.84 ^{a}	18.31 ^{g}	18.08 ^{A}
Average	18.10 ^{A}	18.23 ^{C}	18.17 ^{B}	18.33 ^{D}	18.21
r	−0.076	−0.357	−0.986 **	−0.521	−0.865 **
Calorific value, MJ kg^{-1} of plant					
0	15.48 ^{b}	15.74 ^{hi}	15.88 ^{j}	15.89 ^{j}	15.75 ^{D}
250	15.53 ^{c}	15.62 ^{de}	15.66 ^{ef}	15.64 ^{ef}	15.61 ^{B}
500	15.79 ^{i}	15.55 ^{c}	15.57 ^{cd}	15.72 ^{gh}	15.66 ^{C}
750	15.36 ^{a}	15.69 ^{fg}	15.31 ^{a}	15.72 ^{gh}	15.52 ^{A}
Average	15.54 ^{A}	15.65 ^{C}	15.60 ^{B}	15.74 ^{D}	15.63
r	−0.076	−0.357	−0.986 **	−0.521	−0.865 **
Energy production from maize biomass, MJ pot^{-1}					
0	0.913 ^{h}	1.081 ^{l}	1.102 ^{m}	1.146 ^{o}	1.061 ^{D}
250	0.979 ^{k}	0.975 ^{j}	1.106 ^{n}	1.158 ^{p}	1.054 ^{C}
500	0.361 ^{d}	0.416 ^{e}	0.769 ^{g}	0.939 ^{i}	0.621 ^{B}
750	0.088 ^{a}	0.164 ^{b}	0.304 ^{c}	0.533 ^{f}	0.272 ^{A}
Average	0.586 ^{A}	0.659 ^{B}	0.820 ^{C}	0.944 ^{D}	0.752
r	−0.924 **	−0.970 **	−0.931 **	−0.910 **	−0.950 **

r—coefficient of correlation, significant at ** $p \leq 0.01$. Different letters (homogeneous groups) to the right of the values (*a*–*p* for interactions between HAs and Fe dose, *A*–*D* for averages HAs and Fe doses) are significant at $p \leq 0.01$.

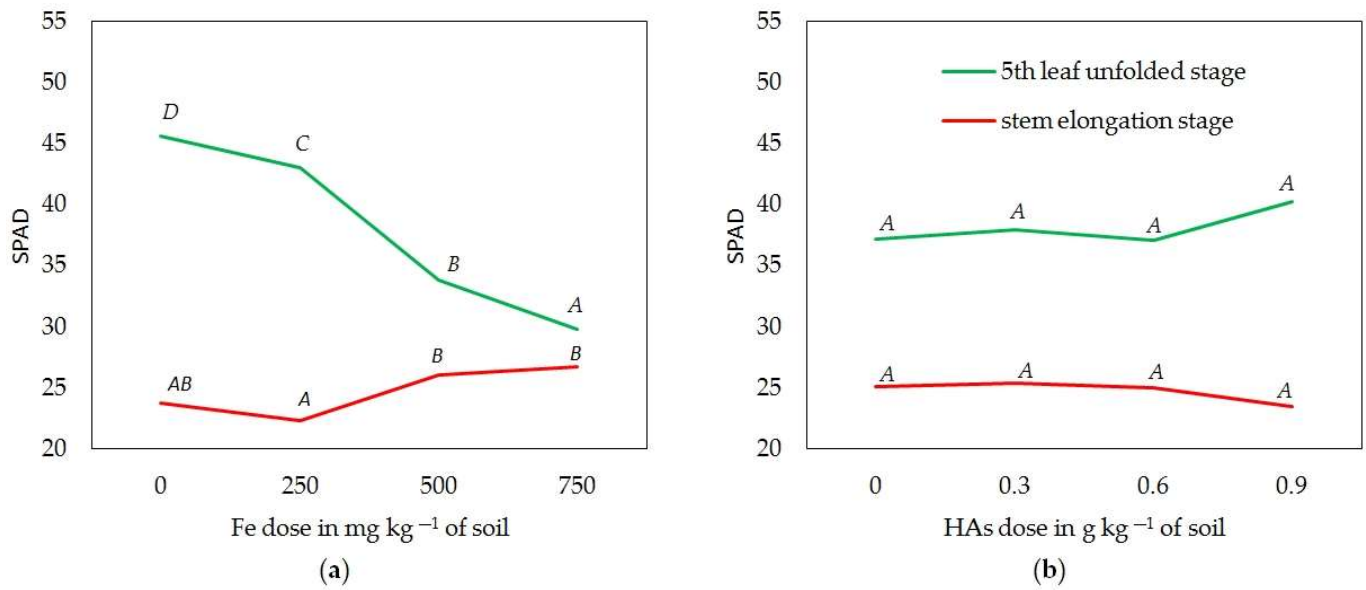

Figure 2. Effect of Fe dose (**a**) and HAs application (**b**) on SPAD index in *Zea mays* L. (averages from all series). Different letters (homogeneous groups) above the lines are significant at $p \leq 0.01$.

Table 3. Nitrogen, phosphorus and potassium content of aerial parts of *Zea mays* L., g kg^{-1} DM.

Fe Dose mg kg^{-1} of Soil	HAs Application in g kg^{-1} of Soil				
	0	0.3	0.6	0.9	Average
			Nitrogen		
0	14.93 ^{e}	11.20 ^{a}	11.29 ^{ab}	11.57 ^{ab}	12.25 ^{A}
250	16.80 ^{f}	15.21 ^{e}	11.95 ^{bc}	12.51 ^{c}	14.12 ^{B}
500	19.97 ^{h}	17.08 ^{f}	16.43 ^{f}	13.53 ^{d}	16.75 ^{C}
750	28.09 ^{j}	19.13 ^{g}	21.00 ^{f}	14.93 ^{e}	20.79 ^{D}
Average	19.95 ^{D}	15.66 ^{C}	15.17 ^{B}	13.14 ^{A}	15.98
r	0.947 **	0.982 **	0.962 **	0.995 **	0.985 **
			Phosphorus		
0	2.693 ^{h}	2.043 ^{f}	2.112 ^{f}	1.631 ^{bc}	2.120 ^{A}
250	2.730 ^{h}	2.243 ^{g}	1.898 ^{e}	1.619 $^{a–c}$	2.123 ^{A}
500	2.767 ^{h}	1.772 ^{de}	1.522 ^{ab}	1.717 ^{cd}	1.945 ^{C}
750	1.876 ^{e}	1.804 ^{de}	1.571 ^{ab}	1.496 ^{a}	1.687 ^{B}
Average	2.517 ^{D}	1.966 ^{C}	1.776 ^{B}	1.616 ^{A}	1.968
r	−0.728 **	−0.693 **	−0.924 **	−0.434	−0.928 **
			Potassium		
0	20.67 ^{f}	15.58 ^{c}	14.61 ^{b}	14.20 ^{a}	16.27 ^{A}
250	20.72 ^{f}	20.50 ^{f}	16.67 ^{d}	15.50 ^{c}	18.35 ^{B}
500	26.85 ^{j}	23.56 ^{h}	24.46 ^{i}	19.66 ^{e}	23.63 ^{C}
750	37.25 ^{m}	27.77 ^{k}	29.49 ^{l}	22.32 ^{g}	29.21 ^{D}
Average	26.37 ^{D}	21.85 ^{C}	21.31 ^{B}	17.92 ^{A}	21.86
r	0.923 **	0.996 **	0.980 **	0.983 **	0.983 **

r—coefficient of correlation, significant at ** $p \leq 0.01$. Different letters (homogeneous groups) to the right of the values (*a*–*m* for interactions between HAs and Fe dose, *A*–*D* for averages HAs and Fe doses) are significant at $p \leq 0.01$.

3.1. Plants Height and Dry Matter Yield

In the series without HAs, soil contamination with iron reduced plant height by 42% and maize dry matter yield by as much as 95% compared to the uncontaminated site (Table 1). However, it should be noted that the first dose of iron (250 mg kg^{-1} soil) had a positive effect on plant height. The application of HAs to the soil had a positive and very large effect on both the height and the dry matter yield of the aerial parts of the maize. It reduced the negative effect of iron to a maximum of 22% on plant height and 63% on maize dry matter yield. After the application of the highest dose of HAs, the average plant height was 22%, and maize dry matter yield was 67% higher than in the untreated series.

3.2. Heat of Combustion, Calorific Value and Energy Production

The fuel properties of maize biomass were determined using the following indices: heat of combustion, calorific value and energy production from biomass (Table 2). Soil iron contamination had little effect on the calorific value and heat of combustion of maize biomass. However, in the series without HAs, there was a slight tendency for these indicators to increase up to an application rate of 500 mg Fe kg^{-1} soil. In the same series, energy production increased by 7% under the influence of 250 mg Fe kg^{-1} of soil and then decreased by as much as 90% compared to the control (without Fe). Changes in the heat of combustion and calorific value of maize biomass under the influence of HAs were minimal but positive. As the dose of HAs increased, its positive effect on biomass energy production was noted—reducing the negative effect of soil iron contamination. The average increase in biomass energy production ranged from 12% after application of the lowest dose of

HAs to 62% after application of the highest dose of HAs to the soil, compared to the series without HAs.

3.3. SPAD Index

The value of the SPAD index in maize leaves was dependent on the vegetation stage, the iron contamination of the soil, and the application of HAs to the soil (Figures 1 and 2).

At the fifth leaf unfolded stage, soil contamination with iron resulted in a significant reduction in the SPAD index of up to 44% in the series without HAs compared to the HAs-free site. The application of HAs to the soil significantly reduced the effect of iron on the SPAD index in plant leaves, especially in the last series of trials. The reduction in the value of this parameter due to the effect of excess soil iron in the series with the highest dose of HAs was 24% compared to the control (without Fe). As vegetation progressed, there was a marked reduction in SPAD values in maize leaves (Table 1), which was related to plant maturity. Humic acids had a beneficial effect on plant maturation by reducing the SPAD index value in leaves during the stem elongation phase of maize. During this phase of maize vegetation, soil contamination with iron promoted leaf greenness, as the SPAD index in the site with the highest iron contamination was 47% higher than in the site without iron application. The addition of HAs to the soil strongly reduced the effect of iron during this phase of maize vegetation. At the same time, it should be emphasised that the value of the SPAD index in the leaves at the intensive maize stem elongation stage was 33% (series without HAs) to 42% (series with the highest HA dose) lower than at the fifth leaf unfolded stage.

3.4. Macronutrients

Soil iron contamination and HAs application acted significantly on the chemical composition of maize biomass (Tables 3 and 4). For most macronutrients, however, the changes in their content under the influence of iron contamination were greater than after the application of HAs to the soil. The series without HAs under the influence of soil contamination with iron showed a reduction in the content of sodium by a maximum of 6%, magnesium by 18%, phosphorus by 30% and an increase in the content of calcium by 33%, potassium by 80% and nitrogen by 88% in maize, compared to the object without contamination. However, an increase of several per cent in the content of some macronutrients was shown as a result of the effects of the first (Mg) and second (P, K and Na) doses of iron. The application of HAs to soil contributed to a reduction in the content of all macronutrients studied in maize biomass, on average from 6% (Ca) to 12–13% (Na and Mg) to 32–36% (K, N and P), compared to sites without HAs. This was mainly due to the smaller effect of iron on macronutrient content and a significant increase in maize dry matter yield in the objects to which HAs were applied, especially at their highest dose.

Table 4. Sodium, magnesium and calcium content of aerial parts of *Zea mays* L., g kg^{-1} DM.

Fe Dose mg kg^{-1} of Soil	HAs Application in g kg^{-1} of Soil				
	0	**0.3**	**0.6**	**0.9**	**Average**
			Sodium		
0	0.348 $^{d–f}$	0.433 ^{g}	0.303 ^{ab}	0.287 ^{a}	0.343 ^{B}
250	0.361 ^{ef}	0.441 ^{g}	0.306 $^{a–c}$	0.299 $^{a–c}$	0.352 ^{AB}
500	0.373 ^{f}	0.442 ^{g}	0.310 $^{a–c}$	0.324 $^{b–d}$	0.362 ^{A}
750	0.328 $^{b–e}$	0.441 ^{g}	0.338 $^{c–e}$	0.322 $^{b–d}$	0.357 ^{A}
Average	0.353 ^{B}	0.439 ^{C}	0.314 ^{A}	0.308 ^{A}	0.354
r	−0.327	0.763 **	0.877 **	0.934 **	0.839 **

Table 4. *Cont.*

Fe Dose mg kg^{-1} of Soil	HAs Application in g kg^{-1} of Soil				
	0	**0.3**	**0.6**	**0.9**	**Average**
			Magnesium		
0	2.028 ^{fg}	1.797 ^{de}	1.732 $^{b–d}$	1.608 ^{a}	1.791 ^{B}
250	2.139 ^{h}	2.095 ^{gh}	2.010 ^{fg}	1.672 $^{a–c}$	1.979 ^{D}
500	2.003 ^{fg}	1.844 ^{e}	1.987 ^{f}	1.865 ^{e}	1.925 ^{C}
750	1.665 $^{a–c}$	1.778 ^{de}	1.648 ^{ab}	1.742 ^{cd}	1.708 ^{A}
Average	1.959 ^{D}	1.879 ^{C}	1.844 ^{B}	1.722 ^{A}	1.851
r	−0.773 **	−0.272	−0.195	0.697 **	−0.317
			Calcium		
0	5.057 ^{c}	4.899 ^{b}	4.609 ^{a}	4.558 ^{a}	4.781 ^{A}
250	6.635 ^{f}	6.785 ^{g}	6.694 ^{fg}	5.795 ^{d}	6.477 ^{B}
500	6.718 ^{fg}	6.798 ^{g}	6.797 ^{g}	6.820 ^{g}	6.783 ^{D}
750	6.731 ^{fg}	7.077 ^{h}	6.629 ^{f}	6.419 ^{e}	6.714 ^{C}
Average	6.285 ^{C}	6.390 ^{D}	6.182 ^{B}	5.898 ^{A}	6.189
r	0.804 **	0.843 **	0.757 **	0.864 **	0.832 **

r—coefficient of correlation, significant at ** $p \leq 0.01$. Different letters (homogeneous groups) to the right of the values (*a–h* for interactions between HAs and Fe dose, *A–D* for averages HAs and Fe doses) are significant at $p \leq 0.01$.

3.5. Relations between Variables

The relationships between the indicators studied were determined by calculating correlation coefficients (Table 5) and the strength of the effect of soil iron contamination and humic matter application in percentage terms (Figure 3).

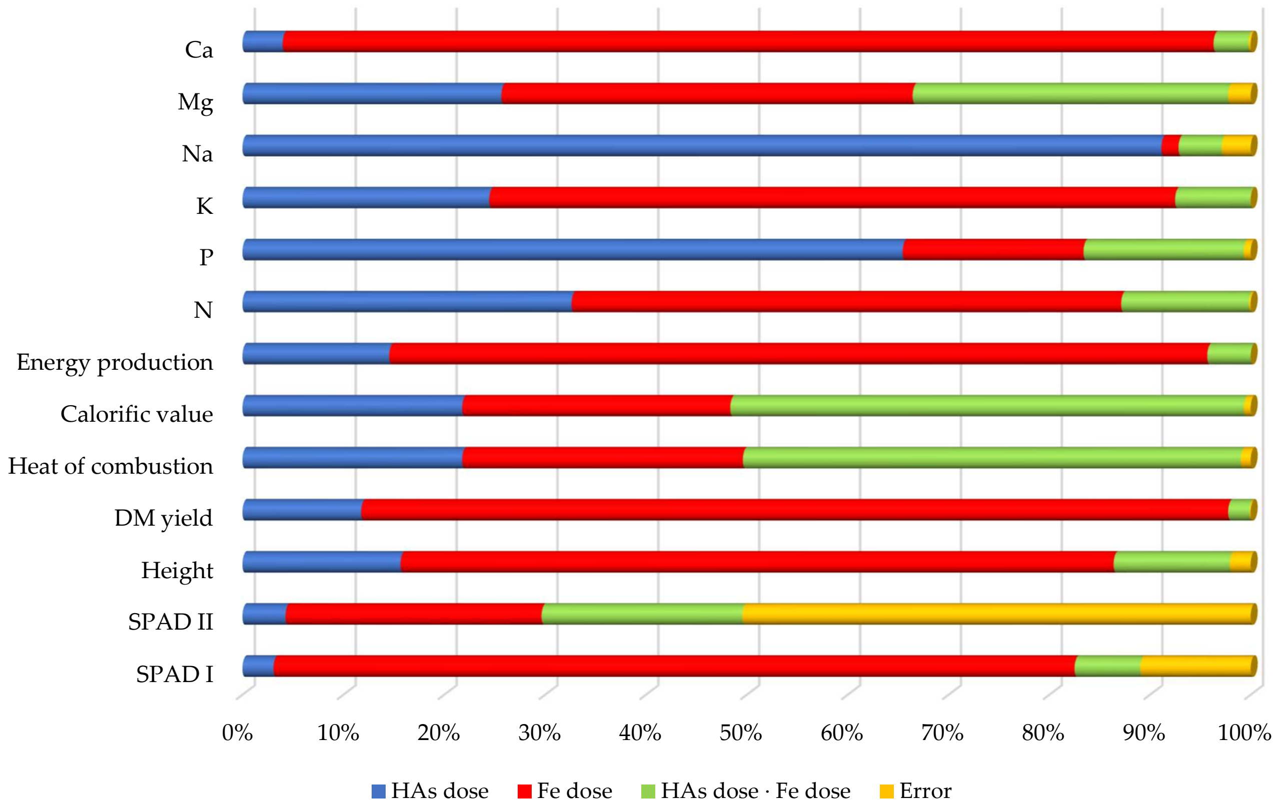

Figure 3. The relative effect of factors on yield and other parameters of *Zea mays* L. (in percentages). Key: SPAD I—SPAD at the fifth leaf unfolded stage; SPAD II—SPAD at the stem elongation stage.

Table 5. Correlation between variables in *Zea mays* L.

Variable	SPAD I	SPAD II	Height	DM Yield	Heat of Combustion	Calorific Value	Energy Production	N	P	K	Na	Mg
SPAD II	−0.516 **											
Height	0.750 **	−0.487 **										
DM yield	0.879 **	−0.499 **	0.907 **									
Heat of combustion	0.502 **	−0.047	0.332 *	0.481 **								
Calorific value	0.499 **	−0.051	0.333 *	0.481 **	0.998 **							
Energy production	0.867 **	−0.515 **	0.936 **	0.985 **	0.471 **	0.472 **						
N	−0.781 **	0.457 **	−0.837 **	−0.870 **	−0.672 **	−0.669 **	−0.875 **					
P	0.341 *	−0.124	0.015	0.119	0.007	0.008	0.108	0.064				
K	−0.838 **	0.476 **	−0.858 **	−0.933 **	−0.665 **	−0.665 **	−0.924 **	0.978 **	−0.025			
Na	−0.110	0.133	−0.227	−0.272	−0.101	−0.099	−0.307 *	0.160	0.283	0.188		
Mg	0.250	−0.254	0.295 *	0.123	−0.085	−0.081	0.211	−0.090	0.659 **	−0.082	0.290 *	
Ca	−0.645 **	0.235	−0.423 **	−0.682 **	−0.464 **	−0.451 **	−0.581 **	0.564 **	−0.110	0.625 **	0.275	0.322 *

Significant at ** $p \leq 0.01$; * $p \leq 0.05$.

The calculated correlation coefficients show highly significant positive correlations between heat of combustion, calorific value, biomass energy production, plant dry matter yield and SPAD index at the fifth leaf unfolded stage of maize and between plant height and dry matter yield, biomass energy production and SPAD index at the fifth leaf unfolded stage, and negative correlations between SPAD index at the stem elongation stage, plant height, dry matter yield and biomass energy production of maize (Table 5). There were also negative correlations between most of the indicators studied and nitrogen, potassium and calcium; SPAD index at the fifth leaf unfolded stage and SPAD index at the stem elongation stage; and positive relationships between nitrogen and potassium, calcium and SPAD index at the stem elongation stage; phosphorus and magnesium; potassium and calcium and SPAD index at the stem elongation stage.

The statistical contribution of the cumulative effect of soil iron contamination and HAs application on maize, expressed in %, is shown in Figure 3. Soil iron contamination had a greater effect than the application of HAs on the indicators studied in maize. Soil iron contamination had the greatest effect on calcium content (92.3%), dry matter yield (86.0%), biomass energy production (81.1%), SPAD index at the fifth leaf unfolded stage (79.4%), plant height (70.7%), content of potassium (68.0%), nitrogen (54.5%) and magnesium (40.8%). In contrast, soil application of HAs had a greater effect than iron on sodium (91.1%) and phosphorus (65.5%) content. The interaction of HAs with soil iron contamination had the greatest effect on the calorific value of maize biomass (51.0%) and the heat of combustion (49.4%). There was also a significant effect of iron on the SPAD index during the stem elongation phase (25.4%), the heat of combustion (27.8%) and the calorific value of maize biomass (26.6%), and of HAs on nitrogen (32.6%), magnesium (25.7%), potassium (24.5%) and the heat of combustion (21.8%) and the calorific value of maize biomass (21.8%).

4. Discussion

Soil physical properties, environmental conditions and agricultural practices influence plant growth and yield and, therefore, the results obtained in this study. In moist soils, temperature is usually the main determinant of germination and initial plant growth. Too low a soil temperature reduces solute solubility, ion diffusion and absorption, and soil enzyme activity, thereby reducing plant density [59]. In thermophilic maize, a reduction in temperature results in delayed seed germination, reduced growth rate and plant vigour [60]. Soil structure does not have a direct effect on plant vegetation, but it does have a significant effect on plant water and oxygen availability, temperature and the mechanical resistance the roots have to penetrate the soil medium [61]. The light soil with a granulometric composition of loamy sand used in our study has good permeability and aeration, warms quickly and is easy to cultivate. It also has better root penetration than other soils [62] due to good soil-seed contact and lower soil mechanical resistance within the plant root zone. Unfortunately, it is also characterised by lower water retention [63], so maintaining optimal soil moisture was particularly important during the period of intensive maize growth. It is important to provide plants with nutrients in the form of fertiliser, usually mineral fertiliser. Humic substances can be used as a type of organic fertiliser. We hypothesise that their positive effects on maize dry matter height and yield recorded in the present study were a consequence of the formation of a nodular soil structure and increased soil cohesion, altered soil pH and nutrient abundance, improved water holding capacity due to the porous nature and presence of hydrophilic functional groups in HS [45], and increased root growth potential that could bypass zones of high mechanical impedance in the altered soil compaction condition [61].

Humic acids are a major component of most organic fertilisers and an active component of composts and soil organic matter. Their use as biostimulants in crop production increases the availability of nutrients (e.g., nitrogen, phosphorus, sulphur) and improves the physical, biological and chemical properties of the soil [64]. However, the use of HAs has several drawbacks and limitations. These relate to the lack of standardised products and application guidelines. The quality and composition of products containing HAs can vary considerably depending on the manufacturer and the raw material used in production (e.g., peat, lignite, leonardite), making it difficult to determine optimal application rates and timing [64,65]. Over-application of HAs can disrupt the soil nutrient balance [66] and lead to leaching and contamination of groundwater or surface water, as well as eutrophication of water bodies [67]. The application of HAs does not always have the expected (positive) effects, both on crop growth and yield [65,68,69] and on the improvement of soil properties [70].

In our study, soil iron contamination and the HAs used to reduce its effect had a positive effect on the heat of combustion, calorific value and energy production of maize biomass used as a photostabiliser. The results obtained are comparable to those obtained by other authors [71–73]. In the experiment of Xiong et al. [71], the average calorific value of maize stalks and leaves was 18.92 MJ kg^{-1} and 17.99 MJ kg^{-1}, respectively. Similar results were obtained by Lizotte et al. [72], who recorded the highest calorific value of 17.72 MJ kg^{-1} for maize cobs and stalks. For leaves, the value was lower at 16.99 MJ kg^{-1}. In contrast, Wojcieszak et al. [73] reported the highest calorific value (18.2 MJ kg^{-1}) for leaves and the lowest (17.7 MJ kg^{-1}) for cobs and kernels.

In the present experiment, soil iron contamination negatively affected selected elements of maize yield quality, including height, dry matter yield and greenness index. It also resulted in a reduction in phosphorus, magnesium and sodium content in the aerial parts of the tested plant. In contrast, an inverse relationship was observed for nitrogen, potassium and calcium content. Similar observations were made by Ahmed et al. [74], who evaluated the effect of soil iron contamination (150–900 mg dm^{-3}) on rice yield. The authors showed that iron levels above 300 mg dm^{-3} had a negative effect on germination and growth of all plant genotypes tested. In addition, with increasing levels of soil contamination, progressive leaf browning and leaf damage, a reduction in 1000-grain weight, dry matter of roots and aerial parts, and a significant reduction in net photosynthetic rate and cell membrane stability factor were observed. The negative effects of soil contamination with iron (100 mg kg^{-1}) on wheat root and stem growth and yield reduction were reported by Setter et al. [75]. Dos Santos et al. [76] also showed negative effects of excess iron on rice productivity and photosynthesis. The authors conducted an experiment in which test plants were grown hydroponically in two groups depending on the level of iron contamination applied (25 µM or 5 mM). It was shown that the highest level of Fe contamination negatively affected the macronutrient content, especially calcium and magnesium in the leaves. It also contributed to a reduction in net photosynthetic rate, chlorophyll *a* fluorescence, stomatal conductance and electron transport rate, which in parallel resulted in a deterioration of yield structure-related traits. The authors found a reduction in total aerial parts biomass (by 27–32%) and roots (by 28–49%), grain biomass (by 32–41%), 1000 grain weight (by 3–21%), percentage of filled grains (by 16–23%) and number of grains per plant (by about 9%) compared to the group of plants grown in a less contaminated medium. An analogous effect of excess iron (concentration > 0.1 mM) on potato yield was reported by Chatterjee et al. [31]. Excess of this element resulted in leaf chlorosis, stunted growth, induced oxidative stress and significantly reduced plant biomass (up to 70%) compared to the control. In addition, the authors showed that excess iron reduced the activity of the Hill reaction (the first step of non-cyclic phosphorylation) and the concentration of chlorophyll *a* and *b*, which directly translated into photosynthetic rates and reduced productivity. This may explain the reduction in yield and leaf greenness index of maize grown on the soil with the highest level of iron contamination recorded in this study. The limiting effect of HAs on the trace element content of soils [77], therefore, has a beneficial effect on yield and its parameters, as well as modifying the chemical composition of plants.

High levels of iron in the soil lead to its precipitation on the root surface in the form of hydrated iron oxide [78], which hinders the uptake of phosphorus, potassium and zinc [38]. This may explain the reduction in phosphorus, magnesium and partly sodium content of maize aboveground biomass found in this study. A reduction in potassium, phosphorus and calcium contents in the aerial parts of rice grown in soil contaminated with iron (500 mg dm^{-3}) was also shown by da Silveira et al. [79]. The reduced levels of phosphorus, magnesium and sodium found in the present study may also be due to the competitive interaction of iron with a membrane transporter protein that facilitates the uptake and transport of these elements by the roots [33]. Excess iron can also lead to changes in the expression of genes involved in iron uptake, transport and homeostasis, which can exacerbate negative morphological and physiological changes in the plant [80], including chloroplastid pigmentation and greenness index. This is confirmed by the results of our study.

Iron deficiency and excess induce characteristic perturbations in plant metabolism. Under conditions of Fe excess, most genes involved in its uptake and transport are strongly repressed, especially in roots [81]. Genes involved in the synthesis of iron-specific complexing compounds (so-called phytosiderophores; PSs) are also reduced in transcription [82]. However, in response to excess Fe, genes encoding ferritin (a Fe storage protein), compounds that act as antioxidants (i.e., ascorbic acid and reduced glutathione) and enzyme proteins with antioxidant activity (i.e., superoxide dismutase, peroxidase and catalase) are increased in response to excess Fe [81]. Indeed, excess Fe leads to oxidative stress and the production of reactive oxygen species (ROS) in Fenton reactions in which Fe^{2+} acts as a catalyst [30,83]. ROS cause irreversible damage to DNA structure, cell cytoskeleton, lipids and membrane proteins, oxidises chlorophyll and inhibits cell division and signalling pathways [83]. Excessive Fe levels in plant tissues increase cytochrome b6/f content in thylakoids and sensitise photosystem II (PS II) to photoinhibition [84], reducing the rate of photosynthesis [82]. Morphological symptoms of iron toxicity are leaf browning from tip to base [85] and a reduction in shoot and root length and number of lateral roots [86]. Interestingly, leaf browning occurs first on older leaves with higher transpiration rates [82]. In contrast, under iron deficiency conditions, the expression of genes related to Fe uptake is increased. As reported by Ramírez et al. [87], the physiological and molecular changes observed in plants subjected to Fe deficiency stress are related to (1) activation of H^+-ATPase and induction of rhizosphere acidification by H^+ release; (2) increased expression and activity of Fe^{3+} chelate reductase (FRO); (3) increased expression of Fe^{2+} transporter (IRT); and (4) induction of trichome proliferation. In contrast, in certain plant species (cereals and grasses), there is increased transcription of genes responsible for the synthesis of PSs, including muginic acid (MA), which complexes Fe^{3+} ions and allows efficient uptake [88]. Fe deficiency also results in inhibition of electron transport in both PSII and PSI and a change in the function of the light-harvesting antenna complex I (LHCI) to a more diffuse one [89], which significantly reduces the efficiency of photosynthesis, thereby limiting plant growth and development and yield quality. Symptoms of iron deficiency in plants include interveinal chlorosis of young leaves due to reduced chlorophyll synthesis. The leaves then turn yellow, while the vascular bundles remain green. Morphological changes also include an increase in root area due to the formation of lateral roots and trichomes and swelling of root tips [88].

In our study, the application of HAs had a positive effect on the reduction in iron toxicity, maize dry matter yield and energy production from maize biomass. However, the opposite trend was observed for the macronutrient content of aerial parts of biomass. Similar results were presented by Eryiğit and Husamalddin [90], who evaluated the effect of soil application of HAs (0–180 kg ha^{-1}) on maize growth and yield. The authors obtained the best results when HAs were applied at a dose of 180 kg ha^{-1}. It had a positive effect on all vegetative parameters (except germination time, cob diameter, oil and protein content) and yield of the plant, increasing it by 53–72% compared to the control object (without the additive). Significant increases in maize grain yield (by 15% compared to the conventional crop, including NPK fertiliser treatments) following the application of HAs were reported by Baldotto et al. [91]. According to the authors, HAs benefit maize development and yield by increasing the assimilability of nutrients, especially nitrogen. Khaled and Fawy [92] also showed a significant increase in maize dry matter (by 23%) compared to the control object after foliar application of HAs (0.1%). However, under these conditions they recorded an increase in the assimilation of N, P, K, Ca, Mg and Na by the plants, which is a different relationship to that obtained in the present study. The reason for these differences could be the different source (origin) of the HAs, the dose applied and the different soil types in the two experiments, as well as a different plant response due to the negative effect of excess iron on plants. In another study [93] carried out on iron-free soil (loamy sand), HAs caused an increase in P, K, Ca and Mg contents in plants classically fertilised with urea. On weaker soil (sandy loam), changes in the macronutrient content of maize were inconclusive, but a reduction in the P and Na content of maize was observed in some sites.

The limiting effect of humic substances on the Fe content of soils contaminated with this element was confirmed by Ifansyah [94], who reported a 49% reduction in available Fe content after the application of HAs (0.5 g pot^{-1}) to the soil compared to the control (no addition). The reduced bioavailable Fe content in the soil solution as a result of HA application was a consequence of the formation of highly stable complexes between Fe(III) and the hydroxyl and carboxyl groups of HAs. The introduction of HAs also resulted in a significant increase in soil pH, which further reduced the mobility and bioavailability of iron. Similar results were reported by Herviyanti et al. [95], who evaluated the effect of HAs applications (200–600 mg kg^{-1}) on the iron content of flooded soils and the yield quality of rice. They obtained the best results in the series with the highest HA dose. Under these conditions, soil iron content decreased almost nine-fold (180 mg kg^{-1} versus 1614 mg kg^{-1}) and grain dry matter increased 3-fold (16.73 g pot^{-1} versus 5.15 g pot^{-1}) compared to the control (no HAs addition). Soil organic matter, of which HAs are a major component, contains a number of active functional groups (including -OH, -COOH, -NH_2, -Ar-OH) and has a negative charge after deprotonation in a weakly acidic to alkaline environment [96]. These functional groups can combine with trace element cations to form complexes called chelates [40,97] or complex organometallic compounds [94]. The formation of these combinations in the soil leads to partial detoxification of toxic forms of trace elements, limiting their uptake by plants [97], which may explain the positive effect of HAs on the height and dry matter yield of maize grown in iron-polluted soils found in this study. The stimulating effect of HAs on plant yield is also related to their effect on photosynthetic efficiency by improving electron transport in photosystem II [98] and increasing chlorophyll synthesis [99].

In our study, the application of HAs reduced the levels of all macronutrients analysed in the aerial parts of maize. Similar results were obtained by Eyheraguibel et al. [100]. In their experiment, the application of HLS (humic-like substances; 50 mg C dm^{-3}) resulted in a reduction of S (by 68%), Mg (by 43%), P (by 39%) and K (by 24%) in maize stems and of Mg (by 42%), S (by 55%), K (by 16%), Ca (by 13%) and P (by 13%) in its leaves. Similar to the present study, the authors reported a beneficial effect of HLS on maize growth and development. In the series with the addition of the biostimulant, the amount of dry matter obtained was 85% higher than in the control object. No effect of different doses of HAs (0, 100, 200, 300 kg ha^{-1}) on the content of macronutrients (K, Ca, Mg) in lettuce was shown by Cimrin and Yilmaz [101]. Humic acids may not only influence macronutrient content but also micronutrient accumulation in plants [102].

The thermal treatment of agricultural residues is part of a circular economy. In addition, it can provide farmers with an additional income, and the cultivation of crops for this purpose (used at the same time as phytostabilisers on contaminated soils) offers a way of managing poor or partially degraded soils. The cultivation of annual crops, such as maize, also allows a rapid change in production profile in the event of unprofitability or the emergence of new energy trends. Maize is a crop with great potential for thermal energy production due to its yield, fuel properties and ecological aspects. Research in this area is therefore necessary and remains relevant.

5. Conclusions

In the series without HAs, soil iron contamination had relatively little effect on the heat of combustion and calorific value of biomass and very strongly reduced plant height

(42%), dry matter yield (95%), energy production from maize biomass (90%), the SPAD index at the fifth leaf unfolded stage (44%) and promoted an increase in SPAD at the maize stem elongation stage (47%). However, the first dose of iron (250 mg kg^{-1} soil) had a positive effect on plant height and biomass energy production. Soil iron contamination reduced sodium, magnesium and phosphorus contents and increased calcium, potassium and nitrogen contents of maize compared to a site without Fe contamination. A reduction in SPAD index values was observed during the growing season.

The application of HAs to the soil had a positive and very strong effect on both the height and the maize biomass parameters. The effects showed an increase in plant height (22%), dry matter yield (67%) and energy production (62%) from maize biomass. Changes in the heat of combustion and calorific value of the biomass were minimal but positive. HAs contributed to a reduction in the SPAD index in plant leaves at the stem elongation phase and in the content of all macronutrients in maize biomass, which was associated with a reduction in the effect of iron on macronutrient content and a significant increase in the dry matter yield of this plant in objects with their application.

The application of HAs seems to be an effective supplement for the phytostabilisation of ferric soils by growing crops for energy purposes.

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References

1. Martins, F.; Felgueiras, C.; Smitkova, M.; Caetano, N. Analysis of fossil fuel energy consumption and environmental impacts in European countries. *Energies* **2019**, *12*, 964. [CrossRef]
2. Karimi, S.; Karri, R.R.; Tavakkoli Yaraki, M.; Koduru, J.R. Processes and separation technologies for the production of fuel-grade bioethanol: A review. *Environ. Chem. Lett.* **2021**, *19*, 2873–2890. [CrossRef]
3. Cirovic, M.; Makajic-Nikolic, D.; Petrovic, N.; Vujosevic, M.; Kuzmanovic, M. European Union oil import dependency risk analysis. *Pol. J. Environ. Stud.* **2015**, *24*, 75–81. [CrossRef] [PubMed]
4. Sarkar, N.; Gosh, S.K.; Bannerjee, S.; Aikat, K. Bioethanol production from agricultural wastes: An overview. *Renew. Energ.* **2012**, *37*, 19–27. [CrossRef]
5. Erenstein, O.; Jaleta, M.; Sonder, K.; Mottaleb, K.; Prasanna, B.M. Global maize production, consumption and trade: Trends and R&D implications. *Food Sec.* **2022**, *14*, 1295–1319. [CrossRef]
6. Jiao, Y.; Chen, H.-D.; Han, H.; Chang, Y. Development and utilization of corn processing by-products: A review. *Foods* **2022**, *11*, 3709. [CrossRef]
7. Klopfenstein, T.J.; Erickson, G.E.; Berger, L.L. Maize is a critically important source of food, feed, energy and forage in the USA. *Field Crops Res.* **2013**, *153*, 5–11. [CrossRef]
8. Zbytek, Z.; Dach, J.; Pawłowski, T.; Smurzyńska, A.; Czekała, W.; Janczak, D. Energy and economic potential of maize straw used for biofuels production. *MATEC Web Conf.* **2016**, *60*, 04008. [CrossRef]
9. Wyszkowska, J.; Boros-Lajszner, E.; Kucharski, J. 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. *Energies* **2024**, *17*, 1156. [CrossRef]
10. Konieczna, A.; Roman, K.; Roman, M.; Śliwiński, D.; Roman, M. Energy efficiency of maize production technology: Evidence from Polish farms. *Energies* **2021**, *14*, 170. [CrossRef]

11. Thangaraj, B.; Solomon, P.R.; Wongyao, N.; Helal, M.I.; Abdullah, A.; Abedrabbo, S.; Hassan, J. Synthesis of reduced graphene oxide nanosheets from sugarcane dry leaves by two-stage pyrolysis for antibacterial activity. *Nano Mat. Sci.* **2024**, 1–10. [CrossRef]
12. Supriyanto, G.; Rukman, N.K.; Nisa, A.K.; Jannatin, M.; Piere, B.; Abdullah, A.; Fahmi, M.Z.; Kusuma, H.S. Graphene oxide from Indonesian biomass: Synthesis and characterization. *BioResources* **2018**, *13*, 4832–4840. [CrossRef]
13. Thangaraj, B.; Mumtaz, F.; Abbas, Y.; Anjum, D.H.; Solomon, P.R.; Hassan, J. Synthesis of graphene oxide from sugarcane dry leaves by two-stage pyrolysis. *Molecules* **2023**, *28*, 3329. [CrossRef] [PubMed]
14. Hu, B.; Wang, K.; Wu, L.; Yu, S.H.; Antonietti, M.; Titirici, M.M. Engineering carbon materials from the hydrothermal carbonization process of biomass. *Adv. Mater.* **2010**, *22*, 813–828. [CrossRef] [PubMed]
15. Caputo, A.; Palumbo, M.; Pelagagge, P.M.; Scacchia, F. Economics of biomass energy utilization in combustion and gasification plants: Effects of logistic variables. *Biomass Bioenergy* **2005**, *28*, 35–51. [CrossRef]
16. Dujmović, M.; Šafran, B.; Jug, M.; Radmanović, K.; Antonović, A. Biomass pelletizing process: A review. *Drv. Ind.* **2021**, *73*, 99–106. [CrossRef]
17. Nowak, K.; Rabczak, S. Co-combustion of biomass with coal in grate water boilers at low load boiler operation. *Energies* **2021**, *14*, 2520. [CrossRef]
18. Wojcieszak, D.; Przybył, J.; Czajkowski, Ł.; Majka, J.; Pawłowski, A. Effects of harvest maturity on the chemical and energetic properties of corn stover biomass combustion. *Materials* **2022**, *15*, 2831. [CrossRef] [PubMed]
19. Magdziarz, A.; Wilk, M. Thermogravimetric study of biomass, sewage sludge and coal combustion. *Energy Convers. Manag.* **2013**, *75*, 425–430. [CrossRef]
20. Cervelli, E.; di Perta, E.S.; Pindozzi, S. Energy crops in marginal areas: Scenario-based assessment through ecosystem services, as support to sustainable development. *Ecol. Indic.* **2020**, *113*, 106180. [CrossRef]
21. Strezov, V.; Chaudhary, C. Impacts of iron and steelmaking facilities on soil quality. *J. Environ. Manag.* **2017**, *203*, 1158–1162. [CrossRef] [PubMed]
22. Akhtar, S.; Luqman, M.; Farooq Awan, M.U.; Saba, I.; Khan, Z.I.; Ahmad, K.; Muneeb, A.; Nadeem, M.; Batool, A.I.; Shahzadi, M.; et al. Health risk implications of iron in wastewater soil-food crops grown in the vicinity of peri urban areas of the District Sargodha. *PLoS ONE* **2022**, *17*, e0275497. [CrossRef] [PubMed]
23. Sarkar, A.; Shekhar, S. Iron contamination in the waters of Upper Yamuna basin. *Groundw. Sustain. Dev.* **2018**, *7*, 421–429. [CrossRef]
24. Siqueira-Silva, A.I.; Rios, C.O.; Pereira, E.G. Iron toxicity resistance strategies in tropical grasses: The role of apoplastic radicular barriers. *J. Environ. Sci.* **2019**, *78*, 257–266. [CrossRef] [PubMed]
25. Sun, J.; Xiao, S.; Xue, C. The tug-of-war on iron between plant and pathogen. *Phytopathol. Res.* **2023**, *5*, 61. [CrossRef]
26. Rai, S.; Singh, P.K.; Mankotia, S.; Swain, J.; Satbhai, S.B. Iron homeostasis in plants and its crosstalk with copper, zinc, and manganese. *Plant Stress* **2021**, *1*, 100008. [CrossRef]
27. Mehrotra, R.; Verma, R.K.; Pal, A. Iron deficiency chlorosis in aromatic grasses—A review. *Environ. Chall.* **2022**, *9*, 100646. [CrossRef]
28. Lapaz, A.M.; Yoshida, C.H.P.; Gorni, P.H.; de Freitas-Silva, L.; Araújo, T.O.; Ribeiro, C. Iron toxicity: Effects on the plants and detoxification strategies. *Acta Bot. Bras.* **2022**, *36*, e2021abb0131. [CrossRef]
29. Adamski, J.M.; Peters, J.A.; Danieloski, R.; Bacarin, M.A. Excess iron-induced changes in the photosynthetic characteristics of sweet potato. *J. Plant Physiol.* **2011**, *168*, 2056–2062. [CrossRef]
30. Müller, C.; Silveira, S.F.d.S.; Daloso, D.d.M.; Mendes, G.C.; Merchant, A.; Kuki, K.N.; Oliva, M.A.; Loureiro, A.E.; Almeida, A.M. Ecophysiological responses to excess iron in lowland and upland rice cultivars. *Chemosphere* **2017**, *189*, 123–133. [CrossRef]
31. Chatterjee, C.; Gopal, R.; Dube, B.K. Impact of iron stress on biomass, yield, metabolism and quality of potato (*Solanum tuberosum* L.). *Scientia Horticulturae* **2006**, *108*, 1–6. [CrossRef]
32. Reyt, G.; Boudouf, S.; Boucherez, J.; Gaymard, F.; Briat, J.F. Iron and ferritin dependent ROS distribution impact *Arabidopsis* root system architecture. *Mol. Plant* **2015**, *8*, 439–453. [CrossRef] [PubMed]
33. Harish, V.; Aslam, S.; Chouhan, S.; Pratap, Y.; Lalotra, S. Iron toxicity in plants: A Review. *Int. J. Environ. Clim. Chang.* **2023**, *13*, 1894–1900. [CrossRef]
34. Siqueira-Silva, A.I.; Silva, L.C.; Azevedo, A.A.; Oliva, M.A. Iron plaque formation and morphoanatomy of roots from species of restinga subjected to excess iron. *Ecotoxicol. Environ. Saf.* **2012**, *78*, 265–275. [CrossRef] [PubMed]
35. Araújo, T.O.; Freitas-Silva, L.; Santana, B.V.N.; Kuki, K.N.; Pereira, E.G.; Azevedo, A.A.; da Silva, L.C. Tolerance to iron accumulation and its effects on mineral composition and growth of two grass species. *Environ. Sci. Pollut. Res.* **2014**, *21*, 2777–2784. [CrossRef] [PubMed]
36. Johan, P.D.; Ahmed, O.H.; Omar, L.; Hasbullah, N.A. Phosphorus transformation in soils following co-application of charcoal and wood ash. *Agronomy* **2021**, *11*, 2010. [CrossRef]
37. Jansen, B.; Nierop, K.G.J.; Verstraten, J.M. Mobility of Fe(II), Fe(III) and Al in acidic forest soils mediated by dissolved organic matter: Influence of solution pH and metal/organic carbon ratios. *Geoderma* **2003**, *113*, 323–340. [CrossRef]
38. Krohling, C.A.; Eutrópio, F.J.; Bertolazi, A.A.; Dobbss, L.B.; Campostrini, E.; Dias, T.; Ramos, A.C. Ecophysiology of iron homeostasis in plants. *Soil Sci. Plant Nutr.* **2016**, *62*, 39–47. [CrossRef]

39. Ukalska-Jaruga, A.; Bejger, R.; Debaene, G.; Smreczak, B. Characterization of soil organic matter individual fractions (fulvic acids, humic acids, and humins) by spectroscopic and electrochemical techniques in agricultural soils. *Agronomy* **2021**, *11*, 1067. [CrossRef]
40. Piccolo, A.; Spaccini, R.; De Martino, A.; Scognamiglio, F.; di Meo, V. Soil washing with solutions of humic substances from manure compost removes heavy metal contaminants as a function of humic molecular composition. *Chemosphere* **2019**, *225*, 150–156. [CrossRef]
41. Rong, Q.; Zhong, K.; Huang, H.; Li, C.; Zhang, C.; Nong, X. Humic acid reduces the available cadmium, copper, lead, and zinc in soil and their uptake by tobacco. *Appl. Sci.* **2020**, *10*, 1077. [CrossRef]
42. Mosa, A.; Taha, A.A.; Elsaeid, M. In-situ and ex-situ remediation of potentially toxic elements by humic acid extracted from different feedstocks: Experimental observations on a contaminated soil subjected to long-term irrigation with sewage effluents. *Environ. Technol. Innov.* **2021**, *23*, 101599. [CrossRef]
43. Boguta, P.; D'Orazio, V.; Senesi, N.; Sokołowska, Z.; Szewczuk-Karpisz, K. Insight into the interaction mechanism of iron ions with soil humic acids. The effect of the pH and chemical properties of humic acids. *J. Environ. Manag.* **2019**, *245*, 367–374. [CrossRef] [PubMed]
44. Havelcov, M.; Mizera, J.; Skorov, I.; Pekař, M. Sorption of metal ions on lignite and the derived humic substances. *J. Hazard. Mater.* **2009**, *161*, 559–564. [CrossRef] [PubMed]
45. Yang, F.; Tang, C.; Antonietti, M. Natural and artificial humic substances to manage minerals, ions, water, and soil microorganisms. *Chem. Soc. Rev.* **2021**, *50*, 6221–6239. [CrossRef] [PubMed]
46. Ondurasek, G.; Rengel, Z.; Romic, D. Humic acids decrease uptake and distribution of trace metals, but not the growth of radish exposed to cadmium toxicity. *Ecotoxicol. Environ. Saf.* **2021**, *151*, 55–61. [CrossRef] [PubMed]
47. Perelomov, L.; Sarkar, B.; Pinsky, D.; Atroshchenko, Y.; Perelomova, I.; Mukhtorov, L.; Mazur, A. Trace elements adsorption by natural and chemically modified humic acids. *Environ. Geochem. Health* **2021**, *43*, 127–138. [CrossRef] [PubMed]
48. Wu, S.; Li, R.; Peng, S.; Liu, Q.; Zhu, X. Effect of humic acid on transformation of soil heavy metals. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, *207*, 012089. [CrossRef]
49. Wyszkowski, M.; Kordala, N.; Brodowska, M.S. Trace element content in soils with nitrogen fertilisation and humic acids addition. *Agriculture* **2023**, *13*, 968. [CrossRef]
50. Varol, M.; Sünbül, M.R.; Aytop, H.; Yilmaz, C.H. Environmental, ecological and health risks of trace elements, and their sources in soils of Harran Plain, Turkey. *Chemosphere* **2020**, *245*, 125592. [CrossRef]
51. IUSS Working Group WRB. *World Reference Base for Soil Resources 2014*; International Soil Classification System for Naming Soils and Creating Legends for Soil Maps. Update 2015; In World Soil Resources Reports No. 106; FAO: Rome, Italy, 2015; p. 182. Available online: https://www.fao.org/3/i3794en/I3794en.pdf (accessed on 14 April 2023).
52. *Solid Biofuels—Determination of Calorific Value*; European Committee for Standardization: Brussels, Belgium, 2017. Available online: https://pkn.pl/pn-en-iso-18125-2017-07 (accessed on 12 December 2023).
53. Kopetz, H.; Jossart, J.; Ragossnig, H.; Metschina, C. *European Biomass Statistics*; European Biomass Association: Brussels, Belgium, 2007.
54. Wyszkowska, J.; Borowik, A.; Zaborowska, M.; Kucharski, J. Calorific Value of *Zea mays* biomass derived from soil contaminated with chromium (VI) disrupting the soil's biochemical properties. *Energies* **2023**, *16*, 3788. [CrossRef]
55. Konica Minolta Optics. Chlorophyll Meter SPAD-502Plus Instruction Manual. Available online: https://www.konicaminolta.com/instruments/download/instruction_manual/color/pdf/spad-502plus_instruction_eng.pdf (accessed on 25 June 2023).
56. Bremner, J.M. Nitrogen—Total. In *Methods of Soil Analysis. Part 3. Chemical Methods*; Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E., Eds.; Soil Science Society of America, Inc.: Madison, WI, USA; American Society of Agronomy Inc.: Madison, WI, USA, 1996; pp. 1087–1123.
57. Ostrowska, A.; Gawliński, S.; Szczubiałka, Z. *Methods of Analysis and Assessment of Soil and Plants Properties*, 1st ed.; Institute of Environmental Protection: Warsaw, Poland, 1991; pp. 1–334.
58. TIBCO Software Inc. Statistica (Data Analysis Software System), Version 13.3. 2017. Available online: http://statistica.io (accessed on 20 February 2024).
59. Lipiec, J.; Nosalewicz, J.; Pietrusiewicz, J. Crop response to soil physical conditions. In *Encyclopedia of Agrophysics*; Gliński, J., Horabik, J., Lipiec, J., Eds.; Springer: Dordrecht, The Netherlands; Heidelberg, Germany; London, UK; New York, NY, USA, 2011. [CrossRef]
60. Walne, C.H.; Reddy, K.R. Temperature effects on the shoot and root growth, development, and biomass accumulation of corn (*Zea mays* L.). *Agriculture* **2022**, *12*, 443. [CrossRef]
61. Blake, G.R.; Steinhardt, G.C.; Pombal, X.P.; Muñoz, J.C.N.; Cortizas, A.M.; Arnold, R.W.; Schaetzl, R.J.; Stagnitti, F.; Parlange, J.-Y.; Steenhuis, T.S.; et al. Plant roots and soil physical factors. In *Encyclopedia of Soil Science*; Chesworth, W., Ed.; Encyclopedia of Earth Sciences Series; Springer: Dordrecht, The Netherlands, 2008. [CrossRef]
62. Atkinson, B.S.; Sparkes, D.L.; Mooney, S.J. Effect of seedbed cultivation and soil macrostructure on the establishment of winter wheat (*Triticum aestivum*). *Soil Tillage Res.* **2009**, *103*, 291–301. [CrossRef]
63. Abdelfattah, M.A.; Rady, M.M.; Belal, H.E.E.; Belal, E.E.; Al-Qthanin, R.; Al-Yasi, H.M.; Ali, E.F. Revitalizing Fertility of Nutrient-Deficient Virgin Sandy Soil Using Leguminous Biocompost Boosts *Phaseolus vulgaris* Performance. *Plants* **2021**, *10*, 1637. [CrossRef]

64. Ampong, K.; Thilakaranthna, M.S.; Gorim, L.Y. Understanding the role of humic acids on crop performance and soil health. *Front. Agron.* **2022**, *4*, 848621. [CrossRef]
65. Lodhi, A.; Tahir, S.; Iqbal, Z.; Mahmood, A.; Akhtar, M.; Qureshi, T.M.; Yaqub, M.; Naeem, A. Characterization of Commercial Humic Acid Samples and Their Impact on Growth of Fungi and Plants. *Soil Environ.* **2013**, *32*, 63–70. Available online: https://www.academia.edu/download/85951909/File-Download.pdf (accessed on 26 January 2024.).
66. Duary, S. Humic Acid. A Critical Review. *Int. J. Curr. Microbiol. App. Sci.* **2020**, *9*, 2236–2241. [CrossRef]
67. Yigit, F.; Dikilitas, M. Effect of humic acid applications on the root-rot disease caused by *Fusarium* Spp. on tomato. *Plant Pathol. J.* **2008**, *7*, 179–182. [CrossRef]
68. Delfine, S.; Tognetti, R.; Desiderio, E.; Alvino, A. Effect of foliar application of N and humic acids on growth and yield of durum wheat. *Agron. Sustain. Dev.* **2005**, *25*, 183–191. [CrossRef]
69. Turan, M.A.; Asik, B.B.; Katkat, A.V.; Celik, H. The effects of soil-applied humic substances to the dry weight and mineral nutrient uptake of maize plants under soil-salinity conditions. *Not. Bot. Horti Agrobot. Cluj-Napoca* **2011**, *39*, 171–177. [CrossRef]
70. Albiach, R.; Canet, R.; Pomares, F.; Ingelmo, F. Organic matter components and aggregate stability after the application of different amendments to a horticultural soil. *Bioresour. Technol.* **2001**, *76*, 125–129. [CrossRef] [PubMed]
71. Xiong, S.; Zhang, Y.; Zhuo, Y.; Lestander, T.; Geladi, P. Variations in fuel characteristics of corn (*Zea mays*) stovers: General spatial patterns and relationships to soil properties. *Renew. Energy* **2010**, *35*, 1185–1191. [CrossRef]
72. Lizotte, P.-L.; Savoie, P.; De Champlain, A. Ash content and calorific energy of corn stover components in Eastern Canada. *Energies* **2015**, *8*, 4827–4838. [CrossRef]
73. Wojcieszak, D.; Pawłowski, A.; Przybył, J. Energy comparison of corn stover fraction. In *Farm Machinery and Processes Management in Sustainable Agriculture. FMPMSA 2022. Lecture Notes in Civil Engineering, 289*; Pascuzzi, S., Santoro, F., Eds.; Springer: Cham, Switzerland, 2023. [CrossRef]
74. Ahmed, S.F.; Ullah, H.; Aung, M.Z.; Tisarum, R.; Cha-Um, S. Iron toxicity tolerance of rice genotypes in relation to growth, yield and physiochemical characters. *Rice Sci.* **2023**, *30*, 321–334. [CrossRef]
75. Setter, T.L.; Waters, I.; Sharma, S.K.; Singh, K.N.; Kulshreshtha, N.; Yaduvanshi, N.P.; Ram, P.C.; Singh, B.N.; Rane, J.; McDonald, G.; et al. Review of wheat improvement for waterlogging tolerance in Australia and India: The importance of anaerobiosis and element toxicities associated with different soils. *Ann. Bot.* **2009**, *103*, 221–235. [CrossRef] [PubMed]
76. Dos Santos, M.S.; Sanglard, L.M.V.P.; Barbosa, M.L.; Namorato, F.A.; de Melo, D.C.; Franco, W.C.G.; Pérez-Molina, J.P.; Martins, S.C.V.; DaMatta, F.M. Silicon nutrition mitigates the negative impacts of iron toxicity on rice photosynthesis and grain yield. *Ecotoxicol. Environ. Saf.* **2020**, *189*, 110008. [CrossRef] [PubMed]
77. Brodowska, M.S.; Wyszkowski, M.; Kordala, N. Use of organic materials to limit the potential negative effect of nitrogen on maize in different soils. *Materials* **2022**, *15*, 5755. [CrossRef]
78. Hansel, C.M.; Fendorf, S.; Sutton, S.; Newville, M. Characterization of Fe plaque and associated metals on the roots of mine-waste impacted aquatic plants. *Environ. Sci. Technol.* **2001**, *35*, 3863–3868. [CrossRef] [PubMed]
79. da Silveira, V.C.; de Oliveira, A.P.; Sperotto, R.A.; Espindola, L.S.; Amaral, L.; Dias, J.F.; da Cunha, J.B.; Fett, J.P. Influence of iron on mineral status of two rice (*Oryza sativa* L.) cultivars. *Braz. J. Plant Physiol.* **2007**, *19*, 127–139. [CrossRef]
80. Thomine, S.; Vert, G. Iron transport in plants: Better be safe than sorry. *Curr. Opin. Plant Biol.* **2013**, *16*, 322–327. [CrossRef]
81. Aung, M.S.; Masuda, H. How Does Rice Defend Against Excess Iron?: Physiological and Molecular Mechanisms. *Front. Plant Sci.* **2020**, *11*, 1102. [CrossRef]
82. Aung, M.S.; Masuda, H.; Kobayashi, T.; Nishizawa, N.K. Physiological and transcriptomic analysis of responses to different levels of iron excess stress in various rice tissues. *Soil Sci. Plant Nutr.* **2018**, *64*, 370–385. [CrossRef]
83. Onaga, G.; Dramé, K.N.; Ismail, A.M. Understanding the regulation of iron nutrition: Can it contribute to improving iron toxicity tolerance in rice? *Funct. Plant Biol.* **2016**, *43*, 709–726. [CrossRef] [PubMed]
84. Suh, H.J.; Kim, C.S.; Lee, J.Y.; Jung, J. Photodynamic effect of iron excess on photosystem II function in pea plants. *Photochem. Photobiol.* **2002**, *75*, 513–518. [CrossRef] [PubMed]
85. Becker, M.; Asch, F. Iron toxicity in rice—Conditions and management concepts. *J. Plant Nutr. Soil Sci.* **2005**, *168*, 558–573. [CrossRef]
86. Onyango, D.A.; Entila, F.; Dida, M.M.; Ismail, A.M.; Drame, K.N. Mechanistic understanding of iron toxicity tolerance in contrasting rice varieties from Africa: 1. Morpho-physiological and biochemical responses. *Funct Plant Biol.* **2019**, *46*, 93–105. [CrossRef] [PubMed]
87. Ramírez, L.; Graziano, M.; Lamattina, L. Decoding plant responses to iron deficiency: Is nitric oxide a central player? *Plant Signal Behav.* **2008**, *3*, 795–797. [CrossRef] [PubMed]
88. Hindt, M.N.; Guerinot, M.L. Getting a sense for signals: Regulation of the plant iron deficiency response. *Biochim. Biophys. Acta Mol. Cell Res.* **2012**, *1823*, 1521–1530. [CrossRef] [PubMed]
89. Wang, Y.; Xu, C.; Li, K.; Cai, X.; Wu, M.; Chen, G. Fe deficiency induced changes in rice (*Oryza sativa* L.) thylakoids. *Environ. Sci. Pollut. Res.* **2017**, *24*, 1380–1388. [CrossRef]
90. Eryiğit, T.; Husamalddin, A.H. Effects of different humic acid doses on yield and quality properties of corn (*Zea mays* L.) in Iraq-Sulaymaniyah conditions. *J. Inst. Sci. Technol.* **2023**, *13*, 1377–1393. [CrossRef]
91. Baldotto, M.A.; Melo, R.O.; Baldotto, L.B. Field corn yield in response to humic acids application in the absence or presence of liming and mineral fertilization. *Semin. Cienc. Agrar.* **2019**, *40*, 3299–3304. [CrossRef]

92. Khaled, H.; Fawy, H.A. Effect of different levels of humic acids on the nutrient content, plant growth, and soil properties under conditions of salinity. *Soil Water Res.* **2011**, *6*, 21–29. [CrossRef]
93. Wyszkowski, M.; Kordala, N.; Brodowska, M. Role of humic acids-based fertilisers and nitrogen fertilisers in the regulation of the macroelement content in maize biomass. *J. Elem.* **2023**, *28*, 1289–1309. [CrossRef]
94. Ifansyah, H. Soil pH and solubility of aluminum, iron, and phosphorus in ultisols: The roles of humic acid. *J. OF Trop. Soils* **2013**, *18*, 203–208. [CrossRef]
95. Herviyanti; Prasetyo, T.B.; Ahmad, F.; Saidi, A. Humic acid and water management to decrease ferro (Fe^{2+}) solution and increase productivity of established new. *J. Trop Soils* **2012**, *17*, 9–17. [CrossRef]
96. Evangelou, V.P.; Marsi, M.; Chappel, M.A. Potentiometric-spectroscopic evaluation of metal-ion complexes by humic fractions extracted from corn tissue. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2002**, *58*, 2159–2175. [CrossRef] [PubMed]
97. Kwiatkowska-Malina, J. Functions of organic matter in polluted soils: The effect of organic amendments on phytoavailability of heavy metals. *Appl. Soil Ecol.* **2017**, *123*, 542–545. [CrossRef]
98. Abros'kin, D.P.; Fuentesb, M.; Garcia-Minab, J.M.; Klyainc, O.I.; Senikd, S.V.; Volkova, D.S.; Perminovaa, I.V.; Kulikova, N.A. The effect of humic acids and their complexes with iron on the functional status of plants grown under iron deficiency. *Eurasian Soil Sci.* **2016**, *49*, 1099–1108. [CrossRef]
99. Rasouli, F.; Nasiri, Y.; Asadi, M.; Hassanpouraghdam, M.B.; Golestaneh, S.; Pirsarandib, Y. Fertilizer type and humic acid improve the growth responses, nutrient uptake, and essential oil content on *Coriandrum sativum* L. *Sci. Rep.* **2022**, *12*, 7437. [CrossRef]
100. Eyheraguibel, B.; Silvestre, J.; Morard, P. Effects of humic substances derived from organic waste enhancement on the growth and mineral nutrition of maize. *Bioresour. Technol.* **2008**, *99*, 4206–4212. [CrossRef]
101. Cimrin, K.M.; Yilmaz, I. Humic acid applications to lettuce do not improve yield but do improve phosphorus availability. *Acta Agric. Scand. B Soil Plant Sci.* **2005**, *55*, 58–63. [CrossRef]
102. Wyszkowski, M.; Brodowska, M.S.; Kordala, N. Trace element contents in maize following the application of organic materials to reduce the potential adverse effects of nitrogen. *Materials* **2023**, *16*, 215. [CrossRef] [PubMed]