agronomy

MDPI

Article

Mineral Fertilization and Maize Cultivation as Factors Which Determine the Content of Trace Elements in Soil

Marzena S. Brodowska [1,*], Mirosław Wyszkowski [2,*] and Barbara Bujanowicz-Haraś [3]

[1] Department of Agricultural and Environmental Chemistry, Faculty of Agrobioengineering, University of Life Sciences in Lublin, Akademicka 15 Str., 20-950 Lublin, Poland
[2] Department of Agricultural and Environmental Chemistry, Faculty of Agriculture and Forestry, University of Warmia and Mazury in Olsztyn, Łódzki 4 Sq., 10-727 Olsztyn, Poland
[3] Department of Management and Marketing, Faculty of Agrobioengineering, University of Life Sciences in Lublin, B. Dobrzańskiego 37 Str., 20-262 Lublin, Poland; barbara.bujanowicz-haras@up.lublin.pl
* Correspondence: marzena.brodowska@up.lublin.pl (M.S.B.); miroslaw.wyszkowski@uwm.edu.pl (M.W.)

Abstract: This study has been carried out in order to determine the effect of increasingly intensive fertilization with potassium, applied in combination with nitrogen, on the content of trace elements in soil after the harvest of maize (*Zea mays* L.). The soil content of trace elements depended on the fertilization with potassium and nitrogen. Potassium fertilization had a stronger effect on the content of trace elements in the pots fertilized with the lower nitrogen dose (130 mg N kg^{-1} of soil). The increasing doses of potassium led to a higher soil content of zinc (Zn), and especially of nickel (Ni). The impact of potassium fertilization on the content of the remaining trace elements in the soil was less unambiguous, and depended on the dose of potassium and nitrogen fertilization. Nitrogen fertilization resulted in a higher soil content of manganese (Mn), chromium (Cr), nickel (Ni) and cadmium (Cd), as well as a decreased soil content of lead (Pb). It needs to be underlined that changes in the soil content of Ni, Cd, and Pb, effected by nitrogen fertilization, were larger than in the cases of the other trace elements. The influence of potassium and nitrogen fertilization did not result in exceeding the current threshold amounts of trace elements set for agriculturally used soil. An increase in the contents of some trace elements in soil is beneficial from an agricultural point of view. Some of these elements are necessary for the correct growth and development of arable plants.

Keywords: mineral fertilization; maize; trace elements in soil

check for updates

Citation: Brodowska, M.S.; Wyszkowski, M.; Bujanowicz-Haraś, B. Mineral Fertilization and Maize Cultivation as Factors Which Determine the Content of Trace Elements in Soil. *Agronomy* **2022**, *12*, 286. https://doi.org/10.3390/agronomy12020286

Academic Editors: Gang Li, Dong-Xing Guan, Daniel Menezes-Blackburn and Fuyong Wu

Received: 7 October 2021
Accepted: 20 January 2022
Published: 23 January 2022

1. Introduction

The constantly growing human population requires an increased production of food and feeds. To secure food for people and to achieve high yields in agriculture, it is necessary to apply mineral fertilizers in plant production, as they will meet the nutritional requirements of crops while acting more rapidly than natural or organic fertilisers. Fertilisation with basic elements is a sufficient measure to achieve high crop yields, but they may not be of high quality. It is therefore recommended to supply cultivated plants with a larger array of macro- and micronutrients [1]. In recent years, multi-nutrient fertilizers, specifically designed for individual plant species by accounting for their nutritional requirements, have been gaining increasing interest. Meanwhile, eating habits have changed and a demand for high quality food products has been increasing, which is closely connected with the improved life comfort and wealth of the human population [2].

While fertilization with basic macronutrients affects mainly the volume of yields, the application of trace elements decides about their quality. Small quantities of some trace elements (Cr, Cu, Ni, Zn, Mn, iron—Fe or cobalt—Co) are essential for the proper growth and development of plants and other living organisms [3,4]. On the other hand, little is known about the positive impact of other trace elements (such as Cd, Pb, Hg or As) on living organisms, and it is believed that these elements do not play a beneficial physiological role [5]. The influence of trace elements, however, depends on quantities in which they enter the plants' environment, mainly the soil [6]. In an uncontaminated soil environment, the main source of trace elements, which may become a potential threat to plants and other living organisms, are fertilizers, especially mineral ones [7]. Even mineral fertilizers which are not enriched with trace minerals added during their manufacturing process import some amounts of these elements, usually small ones, into the soil [8]. Under specific conditions, e.g., in areas with relatively severe air pollution, this additional dose of trace elements incorporated to soil might be the factor that will result in exceeding the permissible threshold amounts of these contaminants in soil [9]. A risk then arises that trace elements will migrate to subsequent links in the trophic chain [7]. They can become hazardous to the development of living organisms [10,11]. The literature data most often point to phosphate fertilizers as a source of trace elements in soil [12]. However, it should be emphasized that mineral fertilizers most polluted with trace elements can be placed as follows: phosphoric > calcium > potassium > nitrogen. The biggest impact on the degree of pollution of mineral fertilizers with trace elements has a raw material and technological process of their production [13]. Phosphorus fertilizers have a particularly large impact on the increase in the content of trace elements in soil [14]. The applied phosphorus fertilizers can be a significant source of soil contamination with heavy metals, mainly Cd, Cu, Pb, Ni and Zn. However, there is a significant variation in the content of trace elements depending on the form of the fertilizer [13]. According to Bracher et al. [15], the content of some trace elements in soil, mainly Cd, increases with an increasing dose of phosphorus fertilizers. Then, not only its total content in soil increases, but also the content of available forms for plants increases [16]. There are far fewer reports implicating potassium or nitrogen fertilizers in this regard [17]. Long-term mineral fertilization can raise the soil content of some trace elements, including Cd, Pb, Cu, Zn or Mn [18]. In their study, Zao et al. [19] found that a persistent application of fertilizers increased the content of trace elements in soil, with organic fertilizers having a stronger impact than mineral ones. It is worth drawing attention to several factors that determine the availability of trace elements for plants [20], such as soil acidity [21,22], or soil sorptivity, associated with the presence of organic matter, clay minerals [21], or hydrated iron and aluminium oxides [23,24], as well as soil microorganisms [25], which participate in the cycling of elements in nature [26].

In view of the above, this study has been carried out in order to determine the effect of increasingly intensive fertilization with potassium, applied in combination with nitrogen, on the content of trace elements in soil.

2. Materials and Methods

2.1. Methodological Design

An experiment was carried out in a greenhouse, with plants grown in polyethylene pots filled with soil from the humic horizon of proper brown soil (Eutric Cambisol) which, in terms of texture, was classified as loamy sand (sand > 0.05 mm—75.47%, silt 0.002–0.05 mm—21.30% and clay < 0.002 mm—3.23%) according to the taxonomy by the United States Department of Agriculture [27]. The basic soil properties were as follows: pH in 1 M KCl dm^{-3}—5.43; hydrolytic acidity—30.00 mM(+) kg^{-1}; total exchangeable bases—56.0 mM(+) kg^{-1}; cation exchange capacity—86.5 mM(+) kg^{-1}; base saturation—64.7%; content of total organic carbon (TOC)—5.386 g kg^{-1}; total nitrogen (total-N)—1.225 g kg^{-1}; available forms of phosphorus (P)—26.58 mg kg^{-1}; potassium (K)—125.36 mg kg^{-1}; magnesium (Mg)—27.97 mg kg^{-1}; sulphur (S) 12.86 mg S-SO_4 kg^{-1}; Cd—0.312 mg kg^{-1}; Pb—28.49 mg kg^{-1}; Cr—42.30 mg kg^{-1}; Co—5.741 mg kg^{-1}; Ni—16.05 mg kg^{-1}; Zn—36.18 mg kg^{-1}; Cu—6.658 mg kg^{-1}; Mn—318.9 mg kg^{-1}; Fe—11,906 mg kg^{-1} d.m. of soil. Increasing doses of potassium, 0, 140, 190 and 240 mg K_2O kg^{-1} of soil, were tested in combination with a lower and higher dose of nitrogen: 130 and 170 mg N kg^{-1} of soil. Potassium was applied as potassium sulphate (500 g K_2O kg^{-1} and 450 g S kg^{-1}), while nitrogen was added to soil as urea and ammonium nitrate solution (UAN) (280 g N kg^{-1}), with half the dose applied before sowing and the other half during the growth of plants. Same amounts of phosphorus, 85 mg P_2O_5 kg^{-1} of soil, and amounts of the micronutrients, 2.9 mg Zn [$ZnCl_2 \cdot 7H_2O$], 3.4 mg Cu [$CuSO_4 \cdot 5H_2O$], 1 mg B [H_3BO_3], 2.7 mg Mn [$MnCl_2 \cdot H_2O$], 0.02 mg Mo kg^{-1} of soil [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$], were added in soil in each pot. The influence of potassium and nitrogen fertilizers was tested on maize (*Zea mays* L.). A 9-kg batch of soil was carefully mixed with the mineral fertilizers and placed in a pot. Afterwards, maize was sown to grow 8 plants per pot. During the growth of the maize plants, at the 4–6-leaf stage, the second dose of potassium and nitrogen fertilizers was added to the soil. During the entire experiment, the soil moisture was maintained at a constant level of 60% of the water capillary capacity. Maize was harvested at the stage of the middle of tassel emergence (BBCH 55), which was also when soil samples for laboratory analyses were collected.

2.2. Methods of Laboratory and Statistical Analyses

Soil was prepared for laboratory analyses by drying and sifting through a sieve with the mesh opening size of 1 mm. Then, each soil sample was wet-digested in a mixture of concentrated hydrochloric acid (HCl AR—1.18 g cm^{-3}) and nitric (HNO_3 AR—1.40 g cm^{-3}) in a MARS 6 microwave digestion system (CEM Corporation, Matthews, NC, USA), in Xpress Teflon vessels (CEM Corporation, Matthews, NC, USA), according to the method US-EPA3051 [28]. The digested soil samples were analysed to determine the total content of Cd, Pb, Cr, Co, Ni, Zn, Mn and Fe using flame atomic absorption spectrometry (FAAS) with an air–acetylene flame [29]. Correctness of the laboratory analyses was verified against reference solutions by Fluka denoted as: Cd 51994, Pb 16595, Cr 02733, Co 119785.0100, Ni 42242, Zn 188227, Cu 38996, Mn 63534 and Fe 16596, and Certified Analytical Soil Reference Material from the AGH University of Science and Technology in Kraków, Poland.

Before starting the experiment, soil underwent the following determinations: the textural composition by the aerometric method [30] and laser diffraction, pH in 1 M KCl with the potentiometric method [31], TOC on a total organic analyser coupled with a solids analyser Shimadzu TOC-L (Shimadzu Corporation, Kyoto, Japan) [32], total-N by the Kjeldahl method [33], available forms of P and K by the Egner–Riehm method [34,35], Mg by the Schachtschabel method [36], and S by nephelometry according to the procedure by Bardsley and Lancaster [37]. The results were submitted to statistical verification, using a two-factorial analysis of variance ANOVA, principal component analysis PCA, Pearson's simple correlation coefficients and the η2 coefficient, calculating the observed variance percentages according to the ANOVA method in Statistica (StatSoft, Inc., Tulsa, OK, USA) [38].

3. Results and Discussion

The content of trace elements in soil is essential for the proper growth and development of plants [3]. In uncontaminated soils, the most common source of trace elements are fertilizers, including minerals, especially multi-nutrient ones [1]. Single-nutrient fertilizers are also a source of micronutrients found in ballast, but their amounts are much smaller than in multi-nutrient fertilizers [8]. The uptake of fertilizers by plants is affected by soil properties, as well as the type of a crop, and even its cultivar [20]. The uptake of trace elements, and other macronutrients, by plants results in the depletion of soils, which must be enriched each year through the application of fertilizers. This is a prerequisite for high and good-quality yields of crops [39].

Consistent application of fertilizers tends to satisfy the demand of crops for micronutrients [40]. However, it is worth emphasising that the use of fertilizers containing basic macronutrients may have an antagonistic effect on the availability of some trace elements to plants. According to Symanowicz [41], excessively high doses of potassium fertilizers can trigger ionic antagonism between potassium and some trace elements.

In our experiment, the content of trace elements in soil proved to be statistically significantly dependent on the potassium and nitrogen fertilization (Tables 1 and 2). The effect of potassium fertilization on the content of trace elements in soil was stronger in the series in the lower (130 mg N kg^{-1} of soil) than in the higher dose of nitrogen (170 mg N kg^{-1} of soil).

In the series with the lower nitrogen dose (130 mg N kg^{-1} of soil), higher doses of potassium fertilizer resulted in an increase in the content of Zn, Co, Ni and Cu in soil, as well as a small but significant decrease in the accumulation of Fe in soil, compared with the soil not fertilized with this element (Tables 1 and 2). Differences in the content of these trace elements in the control versus the soil fertilized with the highest potassium dose (240 mg K_2O kg^{-1} of soil) reached 11% for Zn (r = 0.779), 29% for Co (r = 0.806), 38% for Ni (r = 0.857), 39% for Cu (r = 0.906) and 7% for Fe (r = −0.900). The lowest potassium dose (140 mg K_2O kg^{-1} of soil) caused a small increase in the content of Cd (by 5%, r = −0.743), while the medium dose (190 mg K_2O kg^{-1} of soil) also raised the amount of Cr in soil by 5% (r = −0.060). In the latter case, the increase was not significant statistically. Any further rise in supplied doses of potassium had a negative effect on the soil content of these two elements, especially of Cd. Changes in the soil content of Pb were small and irregular, while those in the amounts of accumulated Mn were insignificant.

Table 1. Trace elements (Cd, Pb, Cr, Co and Ni) content in soil (mg kg^{-1} D.M.).

Nitrogen Dose (mg kg^{-1} of Soil)	**Potassium Dose (mg kg^{-1} of Soil)**				**Average**	**r**
	0	**140**	**190**	**240**		
			Cd			
130	0.292	0.308	0.229	0.104	0.233	−0.743 **
170	0.300	0.325	0.271	0.254	0.288	−0.608 *
Average	0.296	0.317	0.250	0.179	0.260	−0.722 **
LSD for:	N dose—0.039 *, K dose—0.055 **, interaction—n.s.					
			Pb			
130	25.48	25.61	23.64	26.51	25.31	0.034
170	21.41	21.81	21.62	24.62	22.37	0.686 **
Average	23.45	23.71	22.63	25.57	23.84	0.435
LSD for:	N dose—0.69 **, K dose—0.97 **, interaction—1.37 *					
			Cr			
130	40.60	42.21	42.50	39.44	41.19	−0.060
170	43.81	44.53	40.31	45.35	43.50	−0.026
Average	42.21	43.37	41.41	42.40	42.34	−0.089
LSD for:	N dose—1.46 **, K dose—n.s., interaction—2.91 **					
			Co			
130	3.516	3.545	3.929	4.544	3.884	0.806 **
170	3.525	3.910	4.102	3.564	3.775	0.351
Average	3.521	3.728	4.016	4.054	3.829	0.959 **
LSD for:	N dose—n.s., K dose—0.107 **, interaction—n.s.					
			Ni			
130	14.67	15.00	19.04	20.20	17.23	0.857 **
170	17.53	17.99	19.03	19.63	18.55	0.925 **
Average	16.10	16.50	19.04	19.92	17.89	0.877 **
LSD for:	N dose—1.31 *, K dose—1.86 **, interaction—2.63 *					

LSD (least squares deviation). Significant for: ** $p \leq 0.01$, * $p \leq 0.05$, n.s. non-significant; r—correlation coefficient.

Table 2. Trace elements (Zn, Cu, Mn and Fe) content in soil (mg kg^{-1} D.M.).

Nitrogen Dose (mg kg^{-1} of Soil)	**Potassium Dose (mg kg^{-1} of Soil)**				**Average**	**r**
	0	**140**	**190**	**240**		
			Zn			
130	35.11	35.60	36.09	39.14	36.49	0.779 **
170	33.59	36.59	37.69	39.03	36.73	0.999 **
Average	34.35	36.10	36.89	39.09	36.61	0.948 **
LSD for:	N dose—n.s., K dose—1.09 **, interaction—1.54 *					
			Cu			
130	6.611	7.098	8.105	9.186	7.750	0.906 **
170	8.228	8.179	7.565	6.398	7.593	−0.794 **
Average	7.420	7.639	7.835	7.792	7.671	0.953 **
LSD for:	N dose—n.s., K dose—0.271 **, interaction—0.383 **					
			Mn			
130	321.8	332.8	321.2	320.0	324.0	−0.125
170	332.4	338.8	339.1	344.5	338.7	0.965 **
Average	327.1	335.8	330.2	332.3	331.3	0.551
LSD for:	N dose—8.3 *, K dose—n.s., interaction—n.s.					
			Fe			
130	12,224	11,384	11,186	11,384	11,545	−0.900 **
170	11,494	11,287	11,264	11,912	11,489	0.326
Average	11,859	11,336	11,225	11,648	11,517	−0.549
LSD for:	N dose—n.s., K dose—392 *, interaction—554 *					

LSD (least squares deviation). Significant for: ** $p \leq 0.01$, * $p \leq 0.05$, n.s. non-significant; r—correlation coefficient.

The application of the higher nitrogen dose to soil (170 mg N kg^{-1} of soil) distorted the direction of changes in the content of some trace elements in soil fertilized with potassium (Tables 1 and 2). It was only for Cd, Ni and Zn that the tendencies were the same as in the first experimental series. Under the influence of the increasing potassium doses, the content of Mn rose by 4% (r = 0.965), Ni by 12% (r = 0.925), Pb by15% (r = 0.686) and Zn by 16% (r = 0.999), while the content of Cu in soil declined by 22% (r = −0.794). The first dose of potassium (140 mg K_2O kg^{-1} of soil) contributed to a small increase in Cd, by 8% (r = −0.608), and the second (190 mg K_2O kg^{-1} of soil) to a 16% (r = 0.351) increase in the Co content in soil. Changes in the content of Mn and Cr in soil were insignificant, those in the Fe content were small, not exceeding 4%, and irregular.

Nitrogen fertilization caused the greatest changes in the content of Ni, Cd and Pb, contributing to an average increase by up to 8% (Ni) and 24% (Cd), as well as a decrease by 12% (Pb) in their accumulation in soil fertilized with the higher dose of this element—170 mg N kg^{-1} of soil, in comparison to the lower dose—130 mg N kg^{-1} of soil (Tables 1 and 2). A relatively small increase (5–6%) in the soil content of Mn and Cr in response to nitrogen fertilization was recorded.

Mineral fertilization, especially with nitrogen, decreased the soil pH and thereby enhanced the mobility of many trace elements, such as Cu, Zn, Mn or Fe [42]. In a study by Rutkowska et al. [43], the highest content of Zn, Cu, Mn and Fe was observed in soil fertilized with NPK that had the lowest pH. The analogous influence of the NPK fertilization on the mobility of the aforementioned elements was determined by Li et al. [42]. Singh et al. [44] found that NPK fertilization caused elevated mobility of Cu and Mn in soil.

According to Gudžić et al. [45], long-term (33-year-long) mineral fertilization, apart from increasing the level of soil acidity as well as the soil content of P and K, and decreasing the content of TOC and total-N, raised the mobility of Mn and Fe in the top horizon of soil, but did not have a significant effect on the changes in the chemical composition of a deeper soil horizon (20–40 cm). NK fertilization had a significant effect on the content of Zn, while the fertilization with NP and NPK significantly affected the soil content of Cu and Mn.

Jaskulska et al. [46] maintained that organic fertilization had a stronger effect on soil properties, including the content of macronutrients and trace elements, than mineral fertilization. However, mineral fertilization has been observed to cause positive effects as well. Mazur and Mazur [47] obtained similar results. In their experiment, mineral fertilization led to higher soil concentrations of Cu, Zn and Pb. Organic fertilization had a stronger impact than mineral fertilization, and resulted in an increase in the content of most of the analysed elements.

In a study by Park et al. [14], the long-term (40-years) application of mineral fertilizers increased the content of trace elements in soil. Phosphate fertilizers had the strongest effect. The application of phosphorus fertilizers caused an over 2-fold increase in the Cd content in soil. In the experiment of Zahoor et al. [48], a significantly greater increase in the content of Cu, Zn, Mn and Fe in soil was observed compared with the authors' own research on the effect of NPK fertilization. NPK fertilization had a greater effect than NP fertilization on the content of these trace elements in soil. According to Sungur et al. [49] mineral fertilizers mainly increase the content of Cu and Cd in soil. The trace elements are uptaken by plants and incorporated into the food chain [50].

The content of trace elements in soil under the influence of both nitrogen and potassium fertilization may significantly increase [51]. This was confirmed by our own research. Nitrogen fertilization modifies the soil's sorptive capacity and bioavailability of trace elements for plants, especially Cd. Nitrogen fertilization, regardless of its form, increases the uptake of Cd and other trace elements, and their translocation and accumulation in plants. However, nitrate fertilizers have the strongest effect [52]. The relatively small effect of nitrogen fertilization in the form of UAN on the content of trace elements in soil may also result from the chemical composition of this fertilizer. UAN contains nitrogen in the form of NH_4^+-N and NO_3^--N, which regulates the pH in soil and the availability of trace elements for plants [53]. Similar results were achieved in our own studies. Higher doses of nitrogen caused a relatively small increase in the contents of some trace elements in soil. Of the nine studied elements, only in the case of four elements (Ni, Cd, Cr and Mn) was a small several-percent increase in content in the soil recorded. The increase in the content of trace elements in soil after mineral-fertilizer application to soil was also confirmed in many experiments of other authors [41,42,44–46,51,52]. Potassium sulphate, as a product obtained from severe potassium salts by way of a physical mining process, contains greater amounts of tracing elements than a urea and ammonium nitrate solution (UAN), which is obtained by chemical synthesis [54]. This has been confirmed in our own studies, in which potassium fertilizers caused greater changes in the content of trace elements in soil than nitrogen fertilizers. Bąk et al. [55] found an increase in the content of Zn in maize fertilized with potassium.

In our experiment, the PCA results (Figures 1 and 2) and Pearson's correlation coefficients (Table 3) revealed significant relationships between the content of some trace elements in the soil. The cumulative impact of fertilization with potassium and nitrogen on the content of trace elements in soil was illustrated in Figure 1, in the form of PCA vector variables. The total correlation of the set of data on Co, Cd, Cu and Zn was 44.32%, and on Pb, Fe, Mn, Cr and Ni it equalled 25.07%. The longest vectors corresponded to Co and Cd, which signifies their greatest importance, while the shortest vector was plotted for Zn, which illustrates its least contribution to variance. Vectors of the other trace elements had an approximately similar length. The distribution of vectors points to quite strong positive correlations between Cr versus Mn, Cu and Zn versus Co and Ni, Ni versus Co, and negative correlations between Cd versus Co, Ni versus Pb, Pb versus Cr and Mn, and the weakest relationship between Ni and Fe.

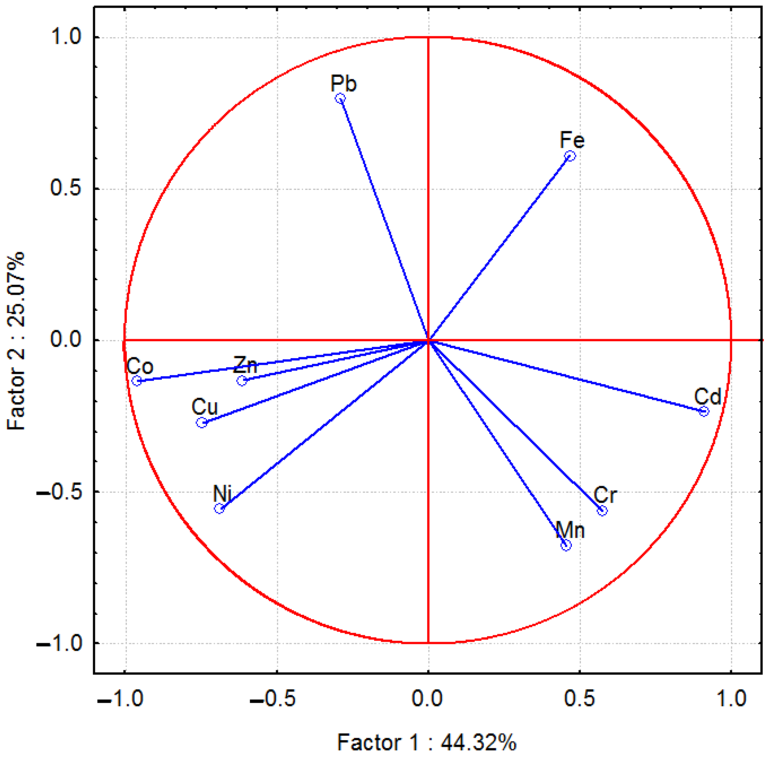

Figure 1. Trace element content in soil calculated with the PCA method. Vectors represent trace elements (content of Cd, Pb, Cr, Co, Ni, Zn, Cu, Mn and Fe).

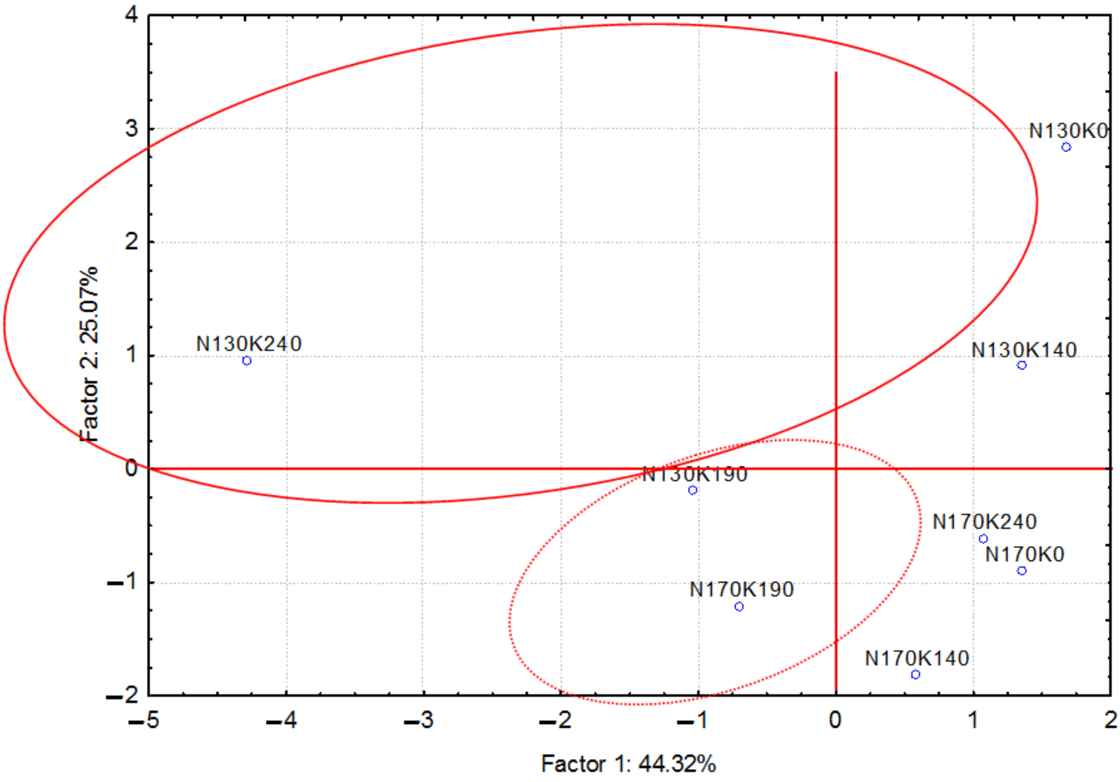

Figure 2. Effect of mineral (N and K) fertilization on trace elements content in soil calculated with the PCA method. Points show all trace elements content in soil (N 130—130 mg N kg^{-1}, N 170—170 mg N kg^{-1}; K 0—0 mg K kg^{-1}, K 140—140 mg K kg^{-1}, K 190—190 mg K kg^{-1}, K 240—240 mg kg^{-1} of soil).

Table 3. Correlation coefficients between content of trace elements in soil.

Element	Cd	Pb	Cr	Co	Ni	Zn	Cu	Mn
Pb	−0.440 *							
Cr	0.392	−0.427 *						
Co	−0.484 *	0.102	−0.366					
Ni	−0.532 **	−0.219	0.157	0.555 **				
Zn	−0.243	0.152	0.110	0.582 **	0.569 **			
Cu	−0.352	−0.116	−0.259	0.706 **	0.422 *	0.184		
Mn	0.474 *	−0.442 *	0.606 **	0.018	0.206	0.380	−0.117	
Fe	0.034	0.314	0.108	−0.040	−0.285	0.078	−0.361	0.099

Significant at ** $p \leq 0.01$ * $p \leq 0.05$; r—correlation coefficient.

The distribution of the research results displayed in Figure 2 justifies the conclusion that the second (190 K_2O kg^{-1} of soil) and especially the highest dose of potassium (240 mg K_2O kg^{-1} of soil) had the strongest effect on the soil content of trace elements. It was much stronger in the series fertilized with the lower nitrogen dose (130 mg N kg^{-1} of soil) than in the one treated with its higher dose (170 mg N kg^{-1} of soil).

The percentage of observed variance, calculated with the help of η2 coefficient from the ANOVA approach, indicates a stronger effect of potassium fertilization on the content of Co, Fe, Zn, Cd and Ni in soil (Figure 3). The percentage contribution of potassium to the variance of these elements was 25.5%, 28.7%, 35.3%, 49.4% and 60.3%, respectively. Quite a high value of this indicator was also achieved for Pb, 30.8%. The highest contribution of nitrogen fertilization was determined for Mn, 40.6%, and Pb, 57.8%, while a moderate one was for Cr, 28.1%.

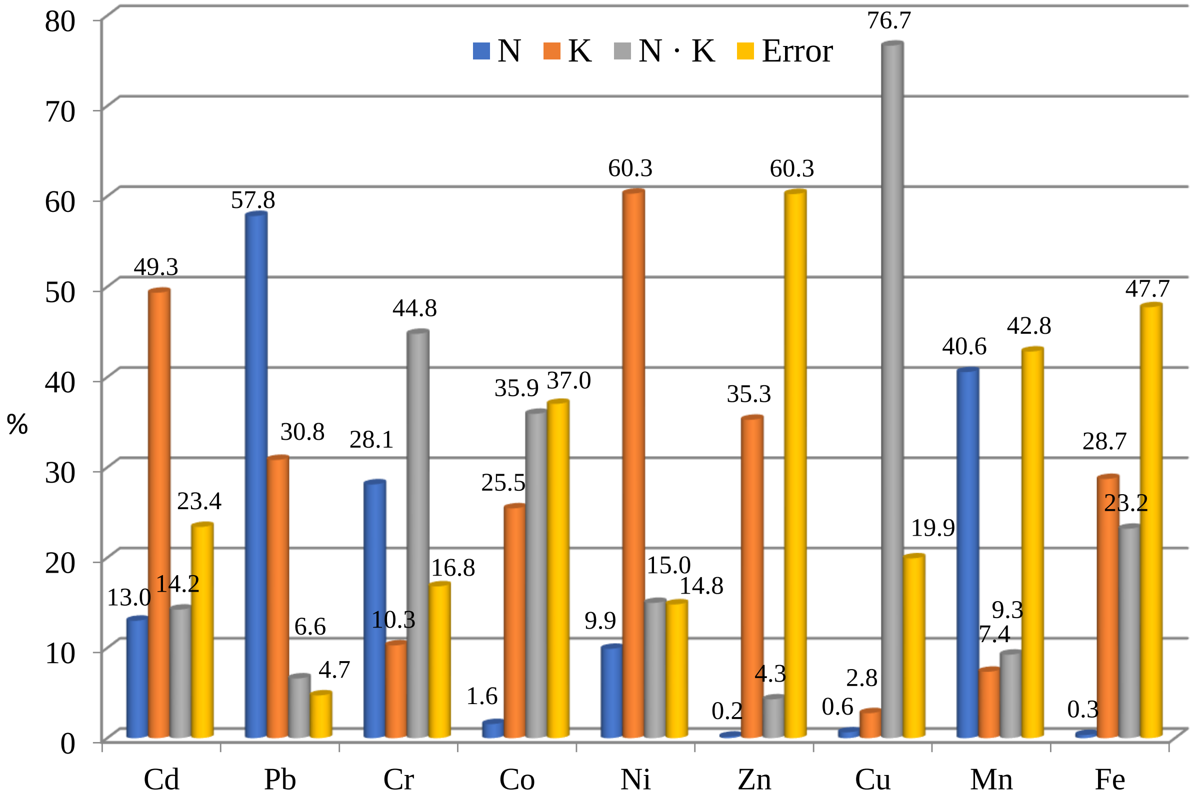

Figure 3. Percent contribution of mineral fertilization according to the content of trace elements in soil: N—nitrogen dose, K—potassium dose, interaction (N · K).

Concentrations of micronutrients in soil tend to be sufficient to satisfy the nutritional requirements of crops during their growth and development [39]. The content of trace elements determined in this study was sufficient to nourish the maize grown in this soil; this fact was confirmed by the amounts of these trace elements determined after the maize harvest and reported in this paper.

Strong relationships emerged in this experiment between concentrations of some trace elements in soil, confirmed statistically (PCA, Pearson's correlation coefficients). Mazur and Mazur [47] implicate strong relationships between Mn and Cd or Ni, between Cd and Ni in lighter soil, between Mn and Cd, and between Cd and Zn versus Pb in heavier soil.

In this experiment, fertilization with potassium and nitrogen caused an increase in soil content of some trace elements, but never above the thresholds set for agriculturally used soil, stipulated by law [9].

Mineral fertilizers usually cause a small increase in the contents of trace elements in soil. Of course, the uptake of trace elements by plants has an effect on the contents of trace elements in soil. This may result in reducing the effect of fertilizers on the content of trace elements in soil after harvesting plants. Therefore, there is a correlation between the content of trace elements in soil and the yield of plants. It is also an explanation of a small increase in the content of trace elements in soil, resulting from the influence of mineral fertilizers [52]. Reducing the content of trace elements in soil under the influence of higher doses of mineral fertilizers results from their favorable effect on the yield of plants. The plants uptake larger quantities of trace elements and decrease their contents in soil.

4. Conclusions

The soil content of trace elements depended on the fertilization with potassium and nitrogen. Potassium fertilization had a stronger effect on the content of trace elements in plots fertilized with the lower nitrogen dose (130 mg N kg^{-1} of soil).

The increasing doses of potassium led to a higher soil content of Ni and Zn. The biggest changes were observed for Ni. The impact of potassium fertilization on the content of the remaining trace elements in soil was less unambiguous, and depended on the dose of potassium and nitrogen fertilization. Nitrogen fertilization resulted in a higher soil content of Mn, Cr, Ni and Cd, as well as a decreased soil content of Pb. It needs to be underlined that changes in the soil content of Ni, Cd and Pb, effected by nitrogen fertilization, were bigger than in the case of the other trace elements.

The presence of significant relationships was noticed between the content of some trace elements in soil, which was confirmed statistically after performing the PCA and calculating Pearson's simple correlation coefficients.

The influence of potassium and nitrogen fertilization did not lead to exceeding the current threshold amounts of trace elements set for agriculturally used soil.

Application potassium and nitrogen fertilizers increased the contents of some trace elements in the soil. This is beneficial from an agricultural point of view, as some of these elements are necessary for the correct growth and development of arable plants.

Author Contributions: Conceptualization, M.S.B. and M.W.; methodology, M.S.B. and M.W.; software, M.W.; analysis, M.S.B. and M.W.; references collect, M.W. and B.B.-H.; writing—review and editing, M.S.B. and M.W.; supervision, M.W. and M.S.B.; M.S.B., corresponding author. All authors contributed significantly to the discussion of the results and the preparation of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: The results presented in this paper were obtained as part of a comprehensive study financed by the University of Life Sciences in Lublin, Faculty of Agrobioengineering, Department of Agricultural and Environmental Chemistry (grant No. RKC/S/59/2021) and by the University of Warmia and Mazury in Olsztyn, Faculty of Agriculture and Forestry, Department of Agricultural and Environmental Chemistry (grant No. 30.610.006-110).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are available by contacting the authors.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Lemaire, G.; Tang, L.; Bélanger, G.; Zhu, Y.; Jeuffroy, M.-H. Forward new paradigms for crop mineral nutrition and fertilization towards sustainable agriculture. *Eur. J. Agron.* **2021**, *125*, 126248. [CrossRef]
2. Buchner, B.; Fischler, C.; Gustafson, E.; Reilly, J.; Riccardi, G.; Ricordi, C.; Veronesi, U. Eating in 2030: Trends and Perspectives. Barilla Center for Food and Nutrition, 2012; p. 52. Available online: https://www.barillacfn.com/m/publications/eating-in-2030-trends-and-perspectives.pdf (accessed on 10 September 2021).
3. Nagajyoti, P.C.; Lee, K.D.; Sreekanth, T.V. Heavy metals, occurrence and toxicity for plants: A review. *Environ. Chem. Lett.* **2010**, *8*, 199–216. [CrossRef]
4. Kabata-Pendias, A. *Trace Elements in Soils and Plants*, 4th ed.; CRC Press: Boca Raton, FL, USA, 2011; p. 403. Available online: http://base.dnsgb.com.ua/files/book/Agriculture/Soil/Trace-Elements-in-Soils-and-Plants.pdf (accessed on 10 September 2021).
5. Latifi, Z.; Jalali, M. Trace element contaminants in mineral fertilizers used in Iran. *Environ. Sci. Pollut. Res.* **2018**, *25*, 31917–31928. [CrossRef] [PubMed]
6. Chibuike, G.U.; Obiora, S.C. Heavy metal polluted soils: Effect on plants and bioremediation methods. *Appl. Environ. Soil Sci.* **2014**, *2014*, 1–12. [CrossRef]
7. Belon, E.; Boisson, M.; Deportes, I.Z.; Eglin, T.K.; Feix, I.; Bispo, A.O.; Galsomies, L.; Leblond, S.; Guellier, C.R. An inventory of trace elements inputs to French agricultural soils. *Sci. Total Environ.* **2012**, *439*, 87–95. [CrossRef] [PubMed]
8. Alloway, B.J. Sources of heavy metals and metalloids in soils. In *Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability*; Alloway, B.J., Ed.; Environmental Pollution, 22; Springer: Dordrecht, The Netherlands, 2013; pp. 11–50. [CrossRef]
9. Regulation of Minister of the Environment of 1 September 2016 on the Procedures for the Assessment of Land Surface Contamination. In *Journal of Laws*; 2016; Poz. 1395. Available online: http://prawo.sejm.gov.pl/isap.nsf/download.xsp/WDU20160001395/O/D20161395.pdf (accessed on 10 September 2021).
10. Wuana, R.A.; Okieimen, F.E. Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. *Int. Sch. Res. Not. Ecol.* **2011**, *2011*, 402647. [CrossRef]
11. Ali, H.; Khan, E.; Ilahi, I. Environmental chemistry and ecotoxicology of hazardous heavy metals: Environmental persistence, toxicity, and bioaccumulation. *J. Chem.* **2019**, *2019*, 6730305. [CrossRef]
12. Jiao, W.; Chen, W.; Chang, A.C.; Page, A.L. Environmental risks of trace elements associated with long-term phosphate fertilizers applications: A review. *Environ. Pollut.* **2012**, *168*, 44–53. [CrossRef]
13. Gorlach, E.; Gambuś, F. Phosphorus and compound fertilizers as a source of soil contamination with heavy metals. *Probl. J. Adv. Agric. Sci.* **1997**, *448a*, 139–146.
14. Park, H.J.; Kim, S.U.; Jung, K.Y.; Lee, S.; Choi, Y.D.; Owens, V.N.; Kumar, S.; Yun, S.W.; Hong, C.O. Cadmium phytoavailability from 1976 through 2016: Changes in soil amended with phosphate fertilizer and compost. *Sci. Total Environ.* **2021**, *762*, 143132. [CrossRef] [PubMed]
15. Bracher, C.; Frossard, E.; Bigalke, M.; Imseng, M.; Mayer, J.; Wiggenhauser, M. Tracing the fate of phosphorus fertilizer derived cadmium in soil-fertilizer-wheat systems using enriched stable isotope labeling. *Environ. Pollut.* **2021**, *287*, 117314. [CrossRef] [PubMed]
16. Gray, C.W.; McLaren, R.G.; Roberts, A.H.C. An assessment of the effect of contact time on cadmium phytoavailability in a pasture soil. *Environ. Sci. Pollut. Res.* **2016**, *23*, 22212–22217. [CrossRef] [PubMed]
17. Wyszkowski, M.; Brodowska, M.S. Potassium and nitrogen fertilization vs. trace element content of maize (*Zea mays* L.). *Agriculture* **2021**, *11*, 96. [CrossRef]
18. Czarnecki, S.; Düring, R.-A. Influence of long-term mineral fertilization on metal contents and properties of soil samples taken from different locations in Hesse, Germany. *Soil* **2015**, *1*, 23–33. [CrossRef]
19. Zhao, S.; Qiu, S.; He, P. Changes of heavy metals in soil and wheat grain under long-term environmental impact and fertilization practices in North China. *J. Plant Nutr.* **2018**, *41*, 1970–1979. [CrossRef]
20. Rolka, E.; Wyszkowski, M. Availability of trace elements in soil with simulated cadmium, lead and zinc pollution. *Minerals* **2021**, *11*, 879. [CrossRef]
21. Nunes, J.R.; Ramos-Miras, J.; Lopez-Piñeiro, A.; Loures, L.; Gil, C.; Coelho, J.; Loures, A. Concentrations of available heavy metals in Mediterranean agricultural soils and their relation with some soil selected properties: A case study in typical Mediterranean soils. *Sustainability* **2014**, *6*, 9124–9138. [CrossRef]
22. Ok, Y.S.; Usman, A.R.A.; Lee, S.S.; El-Azeem, S.A.M.A.; Choi, B.; Hashimoto, Y.; Yang, J.E. Effects of rapeseed residue on lead and cadmium availability and uptake by rice plants in heavy metal contaminated paddy soil. *Chemosphere* **2011**, *85*, 677–682. [CrossRef]
23. Kumpiene, J.; Lagerkvist, A.; Maurice, C. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—A review. *Waste Manag.* **2008**, *28*, 215–225. [CrossRef] [PubMed]
24. Różański, S. Fractionation of selected heavy metals in agricultural soils. *Ecol. Chem. Eng. S* **2013**, *20*, 117–125.

25. Wyszkowska, J.; Borowik, A.; Kucharski, M.; Kucharski, J. Effect of cadmium, copper and zinc on plants, soil microorganisms and soil enzymes. *J. Elem.* **2013**, *18*, 769–796. [CrossRef]
26. Wang, L.; Chen, H.; Wu, J.; Huang, L.; Brookes, P.C.; Rodrigues, M.J.L.; Xu, J.; Liu, X. Effects of magnetic biochar-microbe composite on Cd remediation and microbial responses in paddy soil. *J. Hazard. Mater.* **2021**, *414*, 125494. [CrossRef] [PubMed]
27. IUSS Working Group WRB. World Reference base for soil resources. In *International Soil Classification System for Naming Soils and Creating Legends for Soil Maps*; WRB: London, UK, 2014; Volume 106, p. 182.
28. *US-EPA Method 3051A*; Microwave Assisted Acid Digestion of Sediment, Sludges, Soils and Oils. Office of Solid Waste and Emergency Response, United States Government Printing Office: Washington, DC, USA, 2007; 1–30. Available online: https://www.epa.gov/sites/production/files/2015-12/documents/3051a.pdf(accessed on 23 June 2021).
29. Ostrowska, A.; Gawliński, S.; Szczubiałka, Z. *Methods for Analysis and Evaluation of Soil and Plant Properties*; IOŚ: Warszawa, Poland, 1991; pp. 1–334. (In Polish)
30. *PN-R-04032*; Soil and Mineral Materials—Sampling and Determination of Particle Size Distribution. Polish Committee for Standardization: Warszawa, Poland, 1998.
31. *ISO 10390*; Soil Quality—Determination of Ph. International Organization for Standardization: Geneva, Switzerland, 2005.
32. Shimadzu, Co. *Analytical and Measuring Instruments*; Shimadzu Corporation: Kyoto, Japan, 2019. Available online: https://solutions.shimadzu.co.jp/an/n/en/etc/jpz19014.pdf?_ga=2.50821161.1231336941.1597769507-1298426863.1597769507 (accessed on 11 September 2021).
33. *ISO 11261*; Soil Quality—Determination of Total Nitrogen—Modified Kjeldahl Method. International Organization for Standardization: Geneva, Switzerland, 1995.
34. *PN-R-04023*; Chemical and Agricultural Analysis—Determination of the Content of Available Phosphorus in Mineral Soils. Polish Standards Committee: Warszawa, Poland, 1996.
35. *PN-R-04022*; Chemical and Agricultural Analysis—Determination of the Content Available Potassium in Mineral Soils. Polish Standards Committee: Warszawa, Poland, 1996.
36. *PN-R-04020*; Chemical and Agricultural Analysis—Determination of the Content Available Magnesium. Polish Standards Committee: Warszawa, Poland, 1994.
37. Boratyński, K.; Grom, A.; Ziętecka, M. Research on the content of sulfur in soil. Part I. *Rocz. Gleboz.* **1975**, *3*, 121–139.
38. Dell Inc. Dell Statistica (Data Analysis Software System), Version 13. 2016. Available online: http://software.dell.com (accessed on 29 July 2021).
39. Alloway, B.J. Micronutrients and crop production: An introduction. In *Micronutrient Deficiencies in Global Crop Production*; Alloway, B.J., Ed.; Springer Science + Business Media, B.V.: Dordrecht, The Netherlands, 2008; p. 370.
40. Symanowicz, B.; Kalembasa, S.; Becher, M.; Toczko, M.; Skwarek, K. Effect of varied levels of fertilization with potassium on field pea yield and content and uptake of nitrogen. *Acta Sci. Pol. Agric.* **2017**, *16*, 163–173. [CrossRef]
41. Symanowicz, B. Antagonistic changes in the content of molybdenum and boron in field pea and in soil under of the influence potassium fertilisation. *J. Elem.* **2020**, *25*, 193–203. [CrossRef]
42. Li, B.Y.; Zhou, D.M.; Cang, L.; Zhang, H.L.; Fan, X.H.; Qin, S.W. Soil micronutrient availability to crops as affected by long-term inorganic and organic fertilizer applications. *Soil Tillage Res.* **2007**, *96*, 166–173. [CrossRef]
43. Rutkowska, B.; Szulc, W.; Sosulski, T.; Stępień, W. Soil micronutrient availability to crops affected by long-term inorganic and organic fertilizer applications. *Plant Soil Environ.* **2014**, *60*, 198–203. [CrossRef]
44. Singh, A.; Agrawal, M.; Marshall, F.M. The role of organic vs. inorganic fertilizers in reducing phytoavailability of heavy metals in a wastewater-irrigated area. *Ecol. Eng.* **2010**, *36*, 1733–1740. [CrossRef]
45. Gudžić, N.; Šekularac, G.; Djikić, A.; Djekić, V.; Aksić, M.; Gudžić, S. The impact of the long-term fertilisation with mineral fertilizers on the chemical properties of Vertisol (central Serbia). *Appl. Ecol. Environ. Res.* **2019**, *17*, 12385–12396. [CrossRef]
46. Jaskulska, I.; Lemanowicz, J.; Breza-Boruta, B.; Siwik-Ziomek, A.; Radziemska, M.; Dariusz, J.; Białek, M. Chemical and biological properties of sandy loam soil in response to long-term organic–mineral fertilisation in a warm-summer humid continental climate. *Agronomy* **2020**, *10*, 1610. [CrossRef]
47. Mazur, Z.; Mazur, T. The influence of long-term fertilization with slurry, manure and NPK on the soil content of trace elements. *J. Elem.* **2016**, *21*, 131–139. [CrossRef]
48. Zahoor, M.; Afzal, M.; Ali, M.; Mohammad, W.; Khan, N.; Adnan, M.; Ali, A.; Saeed, M. Effect of organic waste and NPK fertilizer on potato yield and soil fertility. *Pure Appl. Biol.* **2016**, *5*, 439–445. [CrossRef]
49. Sungur, A.; Kavdir, Y.; Özcan, H.; İlay, R.; Soylak, M. Geochemical fractions of trace metals in surface and core sections of aggregates in agricultural soils. *Catena* **2021**, *197*, 104995. [CrossRef]
50. McLaughlin, M.J.; Smolders, E.; Zhao, F.J.; Grant, C.; Montalvo, D. Managing cadmium in agricultural systems. *Adv. Agron.* **2020**, *166*, 1–129. [CrossRef]
51. Wyszkowski, M.; Brodowska, M.S. Content of trace elements in soil fertilized with potassium and nitrogen. *Agriculture* **2020**, *10*, 398. [CrossRef]
52. Yang, Y.; Xiong, J.; Tao, L.; Cao, Z.; Tang, W.; Zhang, J.; Yu, X.; Fu, G.; Zhang, X.; Lu, Y. Regulatory mechanisms of nitrogen (N) on cadmium (Cd) uptake and accumulation in plants: A review. *Sci. Total Environ.* **2020**, *708*, 135186. [CrossRef]
53. Hawkesford, M.; Horst, W.; Kichry, T.; Lambers, H.; Schjoerring, J.; Møller, I.S.; White, P. Functions of macronutrient. In *Mineral Nutrition of Higher Plants*; Marschner, P., Ed.; Academic Press: London, UK, 2011; pp. 135–189. [CrossRef]

54. Parkinson, R.; Willson, R. Soils and plant nutrition. In *The Agricultural Notebook*, 21st ed.; Soffe, R.J., Lobley, M., Eds.; John Wiley & Sons Ltd., Wiley-Blackwell: Hoboken, NJ, USA, 2021; pp. 1–50.
55. Bąk, K.; Gaj, R.; Budka, A. Distribution of zinc in maize fertilized with different doses of phosphorus and potassium. *J. Elem.* **2016**, *21*, 989–999. [CrossRef]