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Trace Element Content in Soils with Nitrogen Fertilisation and Humic Acids Addition

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Abstract: Application of mineral fertilisers can entail an increase in trace element content in the soil. In consequence, their elevated uptake by plants and transfer to further trophic chain links may occur. The aim of the research reported here was to determine the usefulness of the tested organic materials, such as humic acids, for reduction of the content of trace elements in two soils fertilised with excessive doses of nitrogen fertilisers. Soil type had a considerable effect on soil trace element content. The content of most trace elements (cadmium, lead, chromium, cobalt, nickel, manganese, and iron) was higher in loamy sand than in sand. Among the tested fertilisers, a higher content of most soil trace elements was found after the application of ammonium nitrate. Urea fertilisation led to a decrease in the content of cadmium, chromium, copper, and zinc in both soils; cobalt, manganese, and nickel in sand; and an increase in concentration of cobalt and manganese in loamy sand, relative to the subjects fertilised with ammonium nitrate. Urea ammonium nitrate solution (UAN) decreased the content of chromium, cadmium, copper, nickel, and zinc in both soils; lead in the sand; and cobalt in the loamy sand, while raising the content of lead in the loamy sand, relative to the subjects fertilised with ammonium nitrate. The impact of urea and UAN on the remaining trace element content in the soils was comparable to that effected by ammonium nitrate. The effect of humic acids on trace element content in the soil tended to be beneficial, as they reduced the soil concentrations of these elements compared to the control subject (without their application). However, it should be emphasised that their effect depended on nitrogen fertiliser form and soil type. Humic acids can effectively reduce the uptake of trace elements by some plant species.

Keywords: fertilisation; humic acids; nitrogen; soils; trace elements

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1. Introduction

Fertilisation is a basic factor in ensuring good yields, and the application of mineral fertilisers, especially nitrogen ones, plays a key role in food production [1,2]. In the effort to satisfy the food demand of contemporary civilization, high-yielding cultivars are grown, which are characterized by a large requirement for nutrients [3,4]. As a consequence, considerable quantities of mineral fertilisers are constantly added to soil. The application of fertilisers, however, is a high energy-consuming process, and any excessive and irrational use of fertilisers has a negative impact on the environment, also causing the release of reactive forms of nitrogen into the atmosphere, which add to the greenhouse effect [5]. Mineral fertilisation, including its type, size of a dose applied, and date of application, also considerably affects soil trace elements speciation and regulation of their bioavailability [6,7]. Introducing fertilisers that contain reduced forms of nitrogen, such as ammonium sulphate or urea, to soil resulted in a decrease in soil pH and an increase in available trace element forms content [8]. Application of mineral fertilisers can also lead to the concurrent supply of trace elements to soil [9], as it has been demonstrated that the composition of some fertilisers is characterized by high levels of cadmium, copper, and chromium [10]. The accumulation of the mentioned elements in a fertiliser depends primarily on the technology used to make it and the material from which it is produced [11].

Humic substances (HS) are specific, complex, and heterogeneous mixtures of polydisperse organic compounds which appear naturally in aquatic and terrestrial environments [12]. They form in soils as a result of humification, which is the second most important organic process on Earth (after photosynthesis) [13]. Humification is a complex biochemical process consisting of decomposition and resynthesis of organic compounds as well as polymerisation and condensation of products of the former processes. Humification leads to the production of fractions of humic compounds: humic acids (HA), fulvic acids (HF), and humins (HM), which are very important for the quality of soil organic matter [14,15]. The application of organic matter to soil contributes to an increase in the amount of humic acid [16].

Humic substances play a very important role in various environmental processes. They regulate the global circulation of carbon and nitrogen, stimulate life processes of soil organisms and plants [17], and accelerate decomposition of substances that pollute the natural environment [18,19]. Humic acids (HA) behave similarly to auxin hormones and other growth stimulants [20]. They are also used as biostimulants. They accelerate the germination of seeds and elongation of roots [21–23]; enhance the growth, development, and yielding of plants [24,25], owing to the effect they have on the primary and secondary metabolism in plants [26,27]; and they also improve the availability of nutrients (mainly nitrogen, phosphorus, potassium, magnesium, iron, and zinc) [21,28].

Humic acids are characterised by high water capacity, which enables them to prevent adverse effects of drought [29,30]. HA also demonstrate high reactivity and large sorption capacity (500–1200 cmol kg^{-1}) [31], thereby shaping the buffer capacity of soil, mainly in acid and neutral pH [32], in addition to which they regulate bioavailability and mobility of trace elements in soil [33,34]. The amount and quality of humus in the soil affects the physical and chemical properties of the soil and improves its fertility [35]. Humic substances compose a pool of nutrients for plants and improve the soil's texture and structure. Binding with mineral particles through multivalent cations (Ca^{2+}, Mg^{2+}), humic acids lead to the formation of stable soil aggregates [36], hence they influence water and air relations in soil as well as soil's permeability [37,38]. This is particularly important in sandy soils [39]. The presence of humic acids in soil is a decisive factor for the soil's production and retention functions, also playing a significant role in carbon sequestration, thereby contributing to the reduction of greenhouse effect [40]. Maji et al. [41] maintain that humic substances have a positive influence on the development of soil microorganisms; hence they are beneficial for the interaction of plants and beneficial microorganisms, the so-called PGPBs (plant growth-promoting bacteria), which stimulate the growth and development of many plants [42,43]. The sorption properties and ion-exchange capacity of humic substances mean that they can be applied to decrease the salinity of soil and improve the efficiency of fertilisation [35]. In addition, particular fractions of humus enable the soil to warm up quickly [14] and affect the enzymatic activity of cultivated soils [44].

The ability to interact with ions of trace elements is one of the most important properties of humic substances [12]. Immobilisation of trace elements by humic substances occurs via binding (complexing, ion exchange, and physical adsorption) or oxidation-reduction reactions [30,45,46]. As a result of these processes, the mobility and availability of elements change, or else their partial detoxication occurs [30]. Functional groups of these organic compounds have high affinity to inorganic ions, organic ions, and other molecules found in soil [47], and can form complexes with metal cations, such as cations of zinc, manganese, copper, and iron [25]. Weng et al. [48] demonstrated that humic substances created complexes with lead and copper more effectively than with cadmium, zinc, and nickel in soil solution of pH within the range of 3.7–6.1. The usefulness of humic acids for reduction of Cr(VI) to less toxic Cr(III) was proved by Zhilin et al. [49], and the course and success of the reaction depended on pH (the optimum pH was 5.4). Humic acids can also intensify the microbiological bioreduction of trace elements by playing the role of an acceptor of electrons. Gu and Chen [50] found that the reduction rate of Cr(VI) to U(VI) by *Shewanella putrefaciens* CN32 was enhanced in the presence of humic acids. In these conditions, about 50% of Cr(VI) and 82% U(VI) were reduced in the first 24 h of the reaction compared to about 10% of both elements in the control variant (where no organic matter fraction was added).

In view of the above, it is pertinent to take measures to improve the efficiency of fertilisation [51] while securing ecological and food safety [52]. In this context, the biological activity of humic substances and their use in agriculture are significant for the development of sustainable agriculture, and for lowering the environmental and economic costs associated with intensive farming.

Studies conducted on different soils in separate experiments do not necessarily reflect the true effect of humic acids on soil properties such as trace element content. A novelty of the research reported here is the comparison of the use of humic acids to reduce the trace element content of three nitrogen fertilisers—ammonium nitrate, urea, and urea ammonium nitrate solution (UAN)—simultaneously in one experiment.

The aim of the research was to determine the usefulness of the tested organic materials, such as humic acids, for reduction of trace element content in two soils fertilised with excessive doses of nitrogen fertilisers.

2. Material and Methods

2.1. Methodology of the Experiment

A three-factorial pot experiment was used for this study. Our research hypotheses were that trace element contents would be higher in loamy sand than in sand; that their contents in the soil would vary depending on the form of nitrogen fertiliser used; and that humic acids would reduce the contents of these elements in the soil. The first order experimental factor was the application of humic acids, the second order factor was composed of three forms of nitrogen fertiliser, and the third order factor consisted of two soils from different textural classes. These were sand and loamy sand [53]. Soils for the pot experiment were taken from humus layers. Humic acids in doses 0, 0.05, 0.10, and 0.15 g kg^{-1} were applied to soil three times, in order to alleviate the potentially negative effect of nitrogen fertilisers. The doses of humic acids were established on the basis of earlier research, but also on the basis of fertiliser recommendations. The application of humic acids was carried out before sowing and during the growth of the test plant (maize): at the 5-leaf stage, and at the stage of intensive stem elongation. Three nitrogen fertilisers were compared in the trials: ammonium nitrate (34%), urea (46%), and urea ammonium nitrate solution (UAN) (32%). All subjects received the same dose of nitrogen: 160 mg N per kg of soil. At the same time, each pot was supplied with phosphorus and potassium fertilisers (Super FosDar 40 and KCl 50) in doses of 60 mg P and 170 mg K per kg of soil. Humic acids were added to the soil in the form of an organic-mineral fertiliser called Humik. The chemical composition of Humik was as follows: humic acids 25%, organic carbon 22%, nitrogen (N) 4%, phosphorus (P_2O_5) 0.10%, potassium oxide (K_2O) 5%, magnesium (MgO) 0.5%, amino acids 10%, and betaine 10%. More detailed information on soil properties can be found in Table 1 and another published paper [54].

At the beginning of the experiment, the soil was sieved through a sieve with a mesh size of 1 cm. A weighed batch of 9 kg of soil was mixed carefully by hand with the nitrogen fertiliser, humic acid first dose, as well as the phosphorus and potassium fertilisers. Next, the soil was placed in pots and seeds of the maize cultivar Kadryl were sown. Planting density was 6 plants per pot. Soil moisture was maintained at 60% of maximum capacity while the plants grew and developed. The research was carried out in triplicate. When the maize plants were harvested at tassel emergence stage (BBCH 59), soil samples were taken and analysed in the laboratory.

Table 1. Soil characteristics.

Parameter	Sand	Loamy Sand
	% or Value Per kg^{-1} Soil	
Grain size		
<0.002	0.68%	2.50%
0.002–0.050	7.44%	19.95%
>0.050	91.88%	77.55%
Cation exchange capacity (CEC)	76.11 mM (+)	82.41 mM (+)
pH in KCl	6.47	6.33
Total nitrogen	0.579 g	0.620 g
Available forms:		
P	125.35 mg	105.48 mg
K	65.02 mg	91.07 mg
Mg	62.36 mg	40.99 mg
Total:		
Cd	0.602 mg	0.850 mg
Pb	10.26 mg	11.97 mg
Cr	22.68 mg	22.47 mg
Ni	22.60 mg	26.78 mg
Zn	21.16 mg	21.09 mg
Cu	4.685 mg	4.236 mg
Mn	223.6 mg	284.3 mg
Fe	8754 mg	9998 mg
Co	3.205 mg	3.626 mg

2.2. Methods of Laboratory Analyses

A mixture of concentrated hydrochloric acid (HCl analytical grade—1.18 g cm^{-3}) and nitric acid (HNO_3 analytical grade—1.40 g cm^{-3}) was used to digest soil samples. In line with the US-EPA3051 methodology [55], soil was digested in the microwave digestion system MARS 6 (CEM Corporation, Matthews, NC, the USA), and the content of trace elements was determined using the atomic absorption spectrometry (AAS) method [56] on a SpectrAA 240FS spectrometer (Varian Inc., Mulgrave, VIC, Australia). To ensure high accuracy of the results, the Fluka reference materials (51994 for Cd, 16595 for Pb, 02733 for Cr, 42242 for Ni, 188227 for Zn, 38996 for Cu, 63534 for Mn, 16596 for Fe, 119785.0100 for Co) were used in addition to the Soil S-1 Certified Analytical Reference Material (the AGH University of Science and Technology in Kraków, Poland). Prior to the experiment, a Mastersizer 3000 apparatus (Malvern Instruments Ltd., Worcestershire, United Kingdom) was used to analyse the grain-size composition of the soil by laser. Soil samples were analysed for basic properties: soil reaction (pH) by the potentiometric method in a water solution KCL at 1 m DM^{-3} [56]; content of total nitrogen by the Kjeldahl method; available phosphorus and potassium by the Egner-Riehm method [56]; available magnesium by the Schachtschabel method [56], and trace elements by the AAS method [56].

2.3. Methods of Statistical Analysis

The experimental results were statistically processed using Statistica software [57]. Two-factor analysis of variance ANOVA using the Tukey HSD test ($p \leq 0.01$), as well as principal component analysis (PCA), were performed, in addition to calculating the percentage of observed variance and the simple Pearson correlation coefficients.

3. Results

Trace element content in soils varied according to soil type, nitrogen fertiliser form, and humic acid applied (Table 2).

Table 2. Trace element content of in soil (mg kg^{-1} DM).

HA Dose g kg^{-1} of Soil	**Sand**				**Loamy Sand**			
	Ammonium Nitrate	**Urea**	**UAN**	**Mean**	**Ammonium Nitrate**	**Urea**	**UAN**	**Mean**
Cadmium								
0	0.661 $^{j–k}$	0.472 ^{ef}	0.304 ^{bc}	0.479 ^{D}	0.914 ^{m}	0.858 ^{m}	0.626 $^{h–j}$	0.799 ^{H}
0.05	0.651 $^{i–k}$	0.444 ^{e}	0.237 ^{b}	0.444 ^{C}	0.721 ^{kl}	0.784 ^{l}	0.533 ^{hg}	0.679 ^{G}
0.10	0.623 $^{h–i}$	0.440 ^{e}	0.153 ^{a}	0.405 ^{B}	0.737 ^{l}	0.647 ^{ij}	0.423 ^{de}	0.602 ^{F}
0.15	0.567 ^{jk}	0.363 ^{cd}	0.128 ^{a}	0.353 ^{A}	0.658 $^{i–k}$	0.588 $^{g–i}$	0.416 ^{de}	0.554 ^{E}
Mean	0.626 ^{D}	0.430 ^{B}	0.206 ^{A}	0.420 ^{A}	0.758 ^{F}	0.719 ^{E}	0.500 ^{C}	0.659 ^{B}
r	−0.949	−0.915	−0.981	−0.995	−0.884	−0.988	−0.956	−0.981
Lead								
0	11.58 ^{fg}	14.21 ^{kl}	8.09 ^{cd}	11.29 ^{B}	12.22 ^{gh}	15.16 ^{m}	12.46 ^{h}	13.28 ^{A}
0.05	12.23 ^{gh}	14.09 $^{j–l}$	7.39 ^{b}	11.24 ^{B}	13.43 ^{ij}	13.67 $^{j–l}$	12.50 ^{h}	13.20 ^{A}
0.10	11.44 ^{f}	8.43 ^{d}	7.62 ^{bc}	9.16 ^{D}	12.91 ^{hi}	13.51 $^{i–k}$	15.49 ^{m}	13.97 ^{E}
0.15	10.20 ^{e}	7.96 $^{b–d}$	5.75 ^{a}	7.97 ^{C}	13.93 $^{j–l}$	11.10 ^{f}	14.27 ^{l}	13.10 ^{A}
Mean	11.36 ^{A}	11.17 ^{A}	7.21 ^{C}	9.92 ^{A}	13.12 ^{B}	13.36 ^{B}	13.68 ^{D}	13.39 ^{B}
r	−0.751	−0.915	−0.861	−0.952	0.813	−0.948	0.738	0.075
Chromium								
0	23.05 ^{ij}	17.05 ^{ef}	6.81 ^{b}	15.64 ^{D}	22.85 ^{ij}	11.53 ^{d}	19.37 ^{gh}	17.92 ^{E}
0.05	23.28 ^{j}	15.45 ^{e}	4.29 ^{b}	14.34 ^{A}	19.58 ^{gh}	10.64 ^{cd}	11.57 ^{d}	13.93 ^{A}
0.10	21.00 ^{hj}	11.11 ^{d}	3.37 ^{a}	11.83 ^{B}	17.05 ^{ef}	10.24 ^{cd}	15.50 ^{e}	14.26 ^{A}
0.15	18.60 ^{fg}	7.78 ^{b}	3.26 ^{a}	9.88 ^{C}	17.92 ^{fg}	8.46 ^{bc}	7.18 ^{b}	11.19 ^{B}
Mean	21.48 ^{E}	12.85 ^{A}	4.43 ^{B}	12.92 ^{A}	19.35 ^{D}	10.22 ^{C}	13.41 ^{A}	14.32 ^{B}
r	−0.927	−0.986	−0.905	−0.993	−0.874	−0.962	−0.806	−0.928
Nickel								
0	25.53 ^{hi}	27.59 ^{k}	20.40 ^{e}	24.51 ^{A}	31.57 ^{m}	26.36 ^{ij}	20.30 ^{e}	26.08 ^{D}
0.05	24.88 ^{h}	27.10 ^{jk}	23.01 ^{g}	25.00 ^{A}	32.31 ^{mn}	30.15 ^{l}	21.68 ^{f}	28.05 ^{F}
0.10	22.88 ^{g}	18.67 ^{cd}	17.70 ^{c}	19.75 ^{C}	32.85 ^{no}	33.93 ^{o}	19.71 ^{de}	28.83 ^{G}
0.15	22.50 ^{fg}	18.38 ^{c}	16.47 ^{a}	19.12 ^{B}	27.80 ^{k}	32.80 ^{no}	20.16 ^{e}	26.92 ^{E}
Mean	23.95 ^{E}	22.94 ^{B}	19.40 ^{D}	22.09 ^{A}	31.13 ^{A}	30.81 ^{A}	20.46 ^{C}	27.47 ^{B}
r	−0.965	−0.913	−0.757	−0.895	−0.609	0.887	−0.363	0.352
Zinc								
0	22.83 ^{ef}	19.81 ^{bc}	21.20 $^{c–e}$	21.28 ^{AB}	22.72 ^{ef}	17.69 ^{a}	23.80 ^{fg}	21.40 ^{A}
0.05	26.06 ^{h}	21.02 $^{c–e}$	21.05 $^{c–e}$	22.71 ^{C}	20.54 ^{cd}	22.17 $^{d–f}$	18.41 ^{ab}	20.37 ^{BD}
0.10	23.53 ^{fg}	19.85 ^{bc}	20.56 ^{cd}	21.31 ^{AB}	25.10 ^{gh}	22.61 ^{ef}	18.45 ^{ab}	22.05 ^{AC}
0.15	23.60 ^{fg}	23.83 ^{fg}	18.02 ^{ab}	21.82 ^{AC}	23.80 ^{fg}	18.45 ^{ab}	17.15 ^{a}	19.80 ^{D}
Mean	24.01 ^{D}	21.13 ^{B}	20.21 ^{A}	21.78 ^{B}	23.04 ^{C}	20.23 ^{A}	19.45 ^{A}	20.91 ^{A}
r	-0.020	0.745	−0.873	0.041	0.522	0.139	−0.868	−0.399
Copper								
0	5.834 ^{j}	5.147 ^{h}	3.688 ^{bc}	4.890 ^{F}	4.841 ^{g}	4.047 $^{d–f}$	4.124 $^{d–f}$	4.337 ^{BC}
0.05	5.674 ^{j}	5.246 ^{h}	4.276 ^{f}	5.065 ^{F}	4.651 ^{g}	3.887 ^{cd}	4.032 $^{d–f}$	4.190 ^{B}
0.10	5.590 ^{ij}	4.101 $^{d–f}$	4.208 ^{ef}	4.633 ^{D}	4.253 ^{f}	3.933 $^{c–e}$	3.917 ^{cd}	4.034 ^{A}
0.15	5.338 ^{hi}	3.291 ^{a}	3.589 ^{b}	4.073 ^{AB}	4.208 ^{ef}	4.238 ^{f}	4.040 $^{d–f}$	4.162 ^{AB}
Mean	5.609 ^{C}	4.446 ^{B}	3.940 ^{A}	4.665 ^{B}	4.488 ^{B}	4.026 ^{A}	4.028 ^{A}	4.181 ^{A}
r	−0.980	−0.934	−0.134	−0.860	−0.962	0.511	−0.557	−0.708
Manganese								
0	244.3 $^{a–c}$	242.2 $^{a–c}$	245.5 ^{bc}	244.0 ^{A}	320.8 ^{de}	338.0 ^{ef}	319.7 ^{de}	326.2 ^{B}
0.05	245.5 ^{bc}	233.0 $^{a–c}$	249.9 ^{c}	242.8 ^{A}	322.5 $^{d–f}$	340.2 ^{f}	320.6 ^{de}	327.8 ^{B}
0.10	247.2 ^{bc}	228.7 ^{ab}	249.4 ^{c}	241.8 ^{A}	316.6 ^{d}	330.3 $^{d–f}$	317.9 ^{d}	321.6 ^{B}
0.15	246.2 ^{bc}	226.6 ^{a}	245.0 $^{a–c}$	239.3 ^{A}	312.7 ^{d}	329.2 $^{d–f}$	317.7 ^{d}	319.9 ^{B}
Mean	245.8 ^{A}	232.6 ^{C}	247.5 ^{A}	242.0 ^{A}	318.2 ^{B}	334.4 ^{D}	319.0 ^{B}	323.9 ^{B}
r	0.784	−0.954	−0.101	−0.977	−0.886	−0.853	−0.798	−0.869

Table 2. *Cont.*

HA Dose g kg^{-1} of Soil	Sand				Loamy Sand			
	Ammonium Nitrate	**Urea**	**UAN**	**Mean**	**Ammonium Nitrate**	**Urea**	**UAN**	**Mean**
Iron								
0	9097 $^{\text{b–d}}$	8842 $^{\text{a–d}}$	8858 $^{\text{a–d}}$	8932 $^{\text{A}}$	10,447 $^{\text{ef}}$	10,371 $^{\text{ef}}$	10,113 $^{\text{e}}$	10310 $^{\text{B}}$
0.05	9202 $^{\text{cd}}$	8774 $^{\text{a–c}}$	9090 $^{\text{b–d}}$	9022 $^{\text{A}}$	10,490 $^{\text{ef}}$	10,403 $^{\text{ef}}$	10,264 $^{\text{e}}$	10386 $^{\text{B}}$
0.10	9102 $^{\text{b–d}}$	8615 $^{\text{ab}}$	9335 $^{\text{d}}$	9017 $^{\text{A}}$	10,538 $^{\text{ef}}$	10,917 $^{\text{f}}$	10,160 $^{\text{e}}$	10538 $^{\text{B}}$
0.15	9067 $^{\text{b–d}}$	8472 $^{\text{a}}$	8945 $^{\text{a–d}}$	8828 $^{\text{A}}$	10,416 $^{\text{ef}}$	10,928 $^{\text{f}}$	10,001 $^{\text{e}}$	10448 $^{\text{B}}$
Mean	9117 $^{\text{A}}$	8676 $^{\text{C}}$	9057 $^{\text{A}}$	8950 $^{\text{A}}$	10,473 $^{\text{B}}$	10,655 $^{\text{B}}$	10,135 $^{\text{D}}$	10421 $^{\text{B}}$
r	−0.418	−0.988	0.313	−0.450	−0.110	0.911	−0.521	0.757
Cobalt								
0	3.345 $^{\text{a–d}}$	2.776 $^{\text{a–c}}$	3.263 $^{\text{a–d}}$	3.128 $^{\text{BC}}$	3.895 $^{\text{a–d}}$	4.422 $^{\text{b–d}}$	3.768 $^{\text{b–d}}$	4.028 $^{\text{A}}$
0.05	3.428 $^{\text{a–d}}$	3.018 $^{\text{a–d}}$	3.766 $^{\text{a–d}}$	3.404 $^{\text{AB}}$	4.113 $^{\text{cd}}$	4.647 $^{\text{d}}$	3.428 $^{\text{a–d}}$	4.063 $^{\text{A}}$
0.10	4.647 $^{\text{d}}$	3.180 $^{\text{a–d}}$	4.290 $^{\text{cd}}$	4.039 $^{\text{A}}$	3.596 $^{\text{a–d}}$	4.156 $^{\text{a–d}}$	3.263 $^{\text{a–d}}$	3.672 $^{\text{AB}}$
0.15	3.098 $^{\text{a–d}}$	3.428 $^{\text{a–d}}$	3.263 $^{\text{a–d}}$	3.263 $^{\text{A–C}}$	3.387 $^{\text{a–d}}$	3.262 $^{\text{a}}$	2.697 $^{\text{ab}}$	3.115 $^{\text{C}}$
Mean	3.630 $^{\text{A}}$	3.101 $^{\text{A}}$	3.646 $^{\text{A}}$	3.459 $^{\text{A}}$	3.748 $^{\text{A}}$	4.122 $^{\text{A}}$	3.289 $^{\text{A}}$	3.720 $^{\text{A}}$
r	0.089	0.997	0.138	0.333	−0.822	−0.844	−0.975	−0.919

ANOVA with Tukey's HSD test; $^{\text{A–H}}$, $^{\text{a–o}}$: different letters significant at $p \leq 0.01$; *r*: correlation coefficient.

3.1. Content of Trace Elements in Soil Depending on Type of Soil and Form of Nitrogen Fertilisers

The type of soil had a considerable impact on the soil content of trace elements (Table 2). The content of most trace elements was higher in loamy sand than in sand. The mean differences in content were as follows: 8% for cobalt, 11% for chromium, 16% for iron, 24% for nickel, 34% for manganese, 35% for lead, and 57% for cadmium. The content of zinc was on mean 4% and that of copper 10%, lower in loamy sand than in sand.

Among the tested fertilisers, the highest content of most of the trace elements in soil was observed after the application of ammonium nitrate (Table 2). Fertilisation with urea resulted in a lower content of cadmium (means: 31% in sand and 5% in loamy sand), chromium (by 40% in sand and 47% in loamy sand), copper (by 21% in sand and 10% in loamy sand), zinc (by 12% in sand and in loamy sand), cobalt (by 15% in sand), manganese (by 5% in sand) and nickel (by 4% in sand), while raising the concentration of cobalt (by 10% in loamy sand) and manganese (by 5% in loamy sand) compared to the subjects fertilised with ammonium nitrate. The influence of urea and UAN on the content of the other trace elements in soil was comparable to that produced by ammonium nitrate.

3.2. Effect of Humus Acids on Content of Trace Elements in Soils

The influence of humic acids on trace element content in soils was generally positive, as they resulted in reduced concentrations thereof compared to the control series (where no humic acids were applied) (Table 2). However, it should be highlighted that their exact effects depended on the form of nitrogen fertiliser and soil type.

In the first series of the experiment (with ammonium nitrate), the highest dose of humic acids (0.15 g kg^{-1}) caused the following reductions in the content of: cobalt 7%, copper 9%, lead and nickel 12%, cadmium 14%, and chromium 19% in sand; and the concentrations of nickel by 12%, copper and cobalt by 13%, chromium by 22%, and cadmium by 28% in loamy sand, in comparison with the subject where no humic acids were added to soil (Table 2). The highest dose of humic acids also caused an increase in the soil content of lead by 14% in loamy sand. However, it should be mentioned that even the lowest dose of humic acids (0.05 g kg^{-1}) contributed to a rise in lead and zinc content in sand, and cobalt in loamy sand, while the subsequently higher dose (0.10 g kg^{-1}) also raised cobalt concentration in sand as well as nickel and zinc in loamy sand. When higher doses of humic acids were applied, the content of these trace elements in the soils was reduced.

The effect of humic acids in the series with urea or UAN on the content of trace elements in soils tended to be even stronger than in the subjects fertilised with ammonium nitrate, although this was not unidirectional (Table 2). Humic acids in the subjects treated with urea caused a decrease in the content of iron by 4% at most, manganese by 6%, cadmium by 23%, nickel by 33%, copper by 36%, lead by 44%, and chromium by 54% in sand; and the concentration of cobalt by 26%, lead and chromium by 27%, and cadmium by 31% in loamy sand; as well as an increase in the concentration of zinc by 20%, cobalt by 23% in sand, and copper and iron by 5% in loamy sand, relative to the control. The second dose of humic acids (0.10 g kg^{-1}) caused an increase in the content of nickel and zinc in loamy sand, while their highest dose (0.15 g kg^{-1}) had a reducing effect.

The application of humic acids to soils fertilised with UAN caused a decrease in the content of zinc by 15%, nickel by 19%, lead by 29%, chromium by 52%, and cadmium by 58% in sand; and zinc and cobalt by 28%, cadmium by 34%, and chromium by 63% in loamy sand (Table 2). The smallest dose of humic acids (0.05 g kg^{-1}) raised the content of copper in sand, and nickel in sand and loamy sand, while the second dose (0.10 g kg^{-1}) resulted in an increase in the content of cobalt in sand and lead in loamy sand, relative to the control. The content of these elements in the soils were reduced by the higher doses of humic acids.

The PCA performed (Figure 1) shows that the total value of the parameters describing trace element content in soils was 43.60% in the first group, and 26.30% of the correlation of the set in the second group. Only the vector of the cobalt content was very short, implicating a very weak relationship of this element with the analysed factors. Vectors of most of the other trace elements in soil were of a similar length, and the vectors of the concentrations of lead, nickel, and zinc were somewhat shorter than the lengths of the other vectors. Manganese content in soil demonstrated the highest positive correlation with the concentration of iron, and lead with nickel and cadmium. Copper and chromium and zinc were also positively correlated. There was also a weak but negative correlation between the concentrations of iron and manganese versus the concentration of copper in soil. The distribution of the data resulting from the experiment, shown in Figure 2, justifies the conclusion that the cumulative effects of humic acids (especially those applied at the medium and highest doses) on the total soil trace element concentrations were stronger in the pots fertilised with urea or UAN than in those treated with ammonium nitrate.

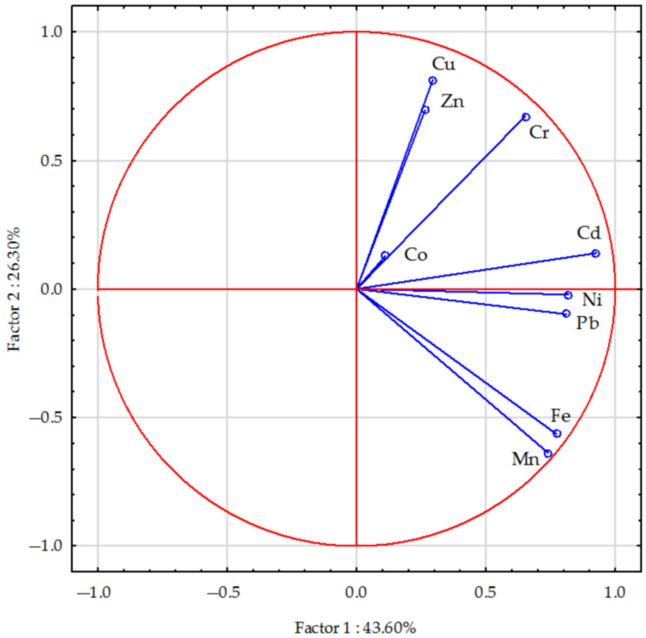

Figure 1. PCA method for soil trace element content. Key: the vectors depict the variables (trace element content in soil).

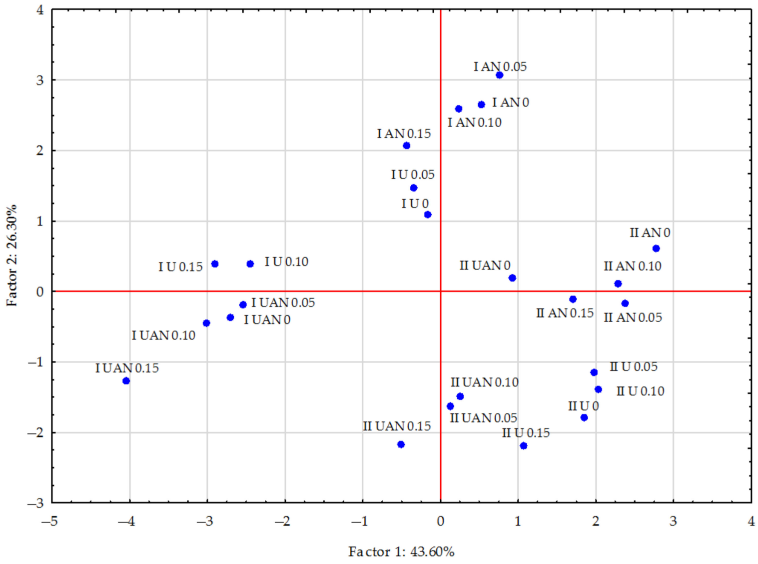

Figure 2. Humic acid application and trace element content in soil (PCA method). Key: the dots represent samples with elements (I—sand, II—loamy sand; AN—ammonium nitrate, U—urea, and UAN—urea and ammonium nitrate solution; and HA doses: 0, 0.05, 0.10, and 0.15 g kg^{-1} of soil).

The percentage of observed variance was calculated (Figure 3) in order to summarise the effects of the experimental factors on soil trace element content. The results substantiate the claim that soil type had the greatest effect on the content of lead (41.3%), iron (86.9%), and manganese (95.4%), and, rather considerably, on the concentration of cadmium (34.1%) in the soils. Nitrogen fertilisation form had the greatest effect on the content of zinc (40.3%), nickel (42.0%), copper (43.4%), cadmium (47.5%), and chromium (60.9%) in the soils. Humic acids produced a slightly weaker influence on soil trace element contents, but their positive effect was especially evident for cobalt (20.6%), as well as chromium (12.6%) and cadmium (11.5%). It is worth mentioning that humic acids were effective in reducing the soil content of trace elements when applied together with nitrogen fertilisers (zinc and lead) and in the interaction with fertilisers and type of soil (zinc, cobalt, and copper).

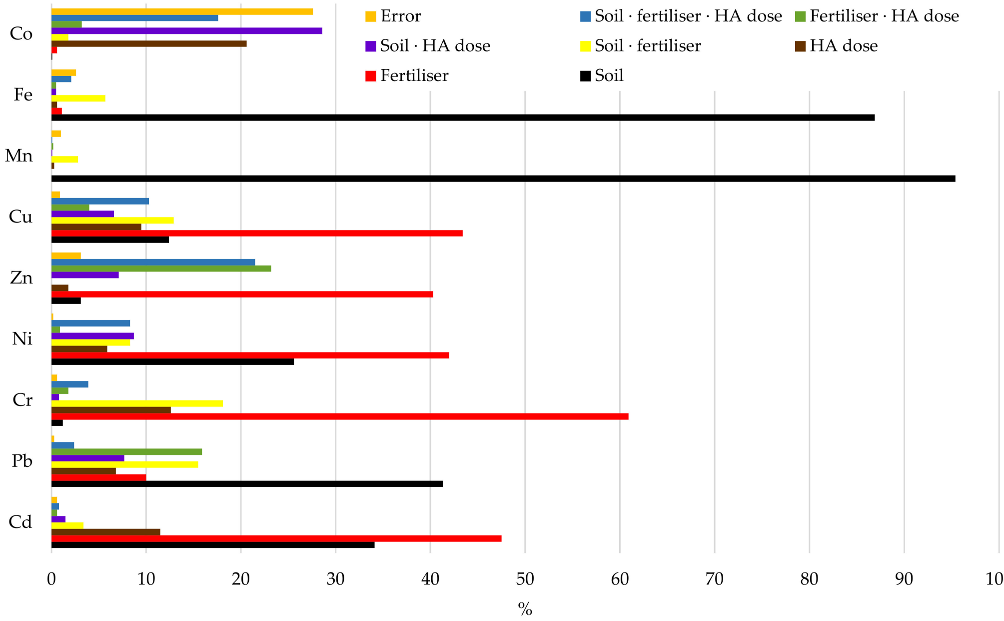

Figure 3. Relative impact of soil type, nitrogen fertiliser form, and HA dose on trace element content in soil (in percent).

4. Discussion

4.1. Content of Trace Elements in Soil Depending on Type of Soil and Form of Nitrogen Fertilisers

The content of trace elements in soil depends on its type [58,59]. The content of most trace elements (cobalt, chromium, iron, nickel, manganese, lead, and cadmium) in soil was higher in loamy sand than in sand. An inverse relationship was found for zinc and copper. Trace element levels generally increase with increasing soil organic matter, including humic acids [58].

As regards the tested fertilisers, in the experiment discussed in this article, the highest content of most trace elements (especially nickel, copper, cobalt, chromium, and cadmium) in soil was noted after the application of ammonium nitrate; this content was lower in soil fertilised with urea or UAN. Analogous results were reported by Brodowska et al. [60], who in their study found an increase in cadmium, chromium, nickel, and manganese content and a decrease in lead content in soil under the fertilisation with nitrogen (UAN, in doses of 130 and 170 mg N kg^{-1} of soil). The same effect of nitrogen fertilisation on the content of nickel, manganese, and chromium content in soil has been demonstrated by Kuppusamy et al. [61]. Rutkowska et al. [62] studied the influence of mineral fertilisation on changes in the concentrations of trace elements in light soil. They found that nitrogen fertilisation significantly raised the content of zinc, copper, manganese, and iron, while depressing the content of boron and molybdenum in the soil solution. A positive correlation between ammonium sulphate application (at a dose of 1.66 g m^{-2}) and soil cadmium and lead content has been demonstrated by Symanowicz et al. [63]. Meanwhile, under the same conditions, ammonium sulphate fertilisation resulted in decreased concentrations of chromium, copper and zinc in soil. Atafar et al. [64] also showed that higher nitrogen doses stimulated soil cadmium and lead accumulation.

Persistent mineral fertilisation leads to a rise in soil trace element content. In an experiment completed by Wierzbowska et al. [65], mineral fertilisation (NPK) over several years (11 years) resulted in an increase in the bioavailable forms of copper, nickel, lead, and zinc in the soil, compared to the control (no fertilisation). Mineral fertilisation carried out for many years can also considerably modify soil properties, including pH, organic matter content, or the content of available forms of macronutrients. Such changes, in turn, affect the content of phytoavailable fractions of trace elements in soil, and thereby their levels of accumulation in plants [66,67]. This is evidenced by the study results achieved by Fan et al. [68], showing that long-term application of nitrogen fertilisers (30 years; urea at a dose of 75 kg N ha^{-1}) lowered the soil pH (6.47 versus 5.73) and elevated the content of copper, iron, manganese, and zinc in the soil solution. Trace elements, introduced together with nitrogen (and other fertilisers) into the soil, are then taken up by plants [69].

4.2. Effect of Humus Acids on Content of Trace Elements in Soils

The buffer properties of soil mean that some of the trace elements are bound to the sorption complex, i.e., the colloidal substance and humic substance, and then become immobilised and unavailable to plant roots [70,71]. Thus, agricultural technologies used to increase soil organic matter content in contribute to immobilising trace elements and reducing the amounts of their bioavailable forms [72]. An example of such treatment is the application of humic substances to soil.

In this experiment, the application of humic substances led to a decrease in the content of many trace elements in soil, most often chromium, cadmium, lead, and nickel, and less often copper or cobalt. A similar tendency was noted by Sönmez and Alp [73], who studied the effect of humic acid amendment (0, 10, 20, 40 kg da^{-1}) on soil properties, including trace element content. After a five-month-long field experiment, these authors concluded that the highest dose of humic acid increased organic matter content by 53.6% and contributed to a reduction in zinc (by 28%), cadmium (by 6%), and lead (by 10%) in soil, relative to the control. No impact on manganese and copper was recorded, while the content of iron and nickel in soil was significantly raised. In another experiment, completed by Rendana et al. [74], the soil application of an organic amendment containing humic acid (HT Organic Compound; at a dose of 250 kg or 500 kg) to the soil of a plot (40×40 m^2)

cultivated with rice resulted in a reduction in the content of cadmium, copper, chromium, and lead, in comparison to a series with mineral fertilisers (NPK). Wu et al. [75] also proved the reducing effect of humic acid on the mobility and content of available fractions of copper, cadmium and lead in soil.

The data from our study suggest that the decrease of trace element content in soil was probably associated with the properties of humic substances. Owing to their chemical structure and the presence of carboxyl and hydroxyl functional groups [76], they can form chelates with metal cations, which are stabilised by internal hydrogen bonds in humus. The formation of these metal-organic complexes results in the immobilisation of trace elements and their depressed migration in the soil environment [77]. Humic acids also indirectly increase the CEC of the soil [78], which depends on the organic matter content. The higher the CEC, the greater the ability of the soil to retain trace elements in its matrix [79].

Organic matter derived from natural and organic fertilisers and from plants (harvest residues, ploughed-in plants) does not persist very long in soil. The humification index for organic carbon introduced to soil with these fertilisers is usually no more than 10% [80,81]. The effect of humic substances [82] and compound fertilisers containing humic substances is much more durable. Therefore, it is justified to conduct further studies on the use of humic substances for fertilisation purposes and development of sustainable agriculture, and for the alleviation of the impact of trace elements originating from different sources on crops.

5. Conclusions

Trace element content in soils varied according to soil type, nitrogen fertiliser form, and humic acid applied. The type of soil had a considerable effect on soil trace element content. The content of most trace elements (cadmium, lead, chromium, cobalt, nickel, manganese, and iron) was higher in loamy sand than in sand. Among the tested fertilisers, the higher content of most of the soil trace elements was found after the application of ammonium nitrate. Urea fertilisation led to a decrease in the content of cadmium, chromium, copper, and zinc in both soils; cobalt, manganese, and nickel in the sand; and an increase in concentration of cobalt and manganese in the loamy sand, relative to the subjects fertilised with ammonium nitrate. UAN decreased the content of chromium, cadmium, nickel, copper, and zinc in both soils; lead in the sand; and cobalt in the loamy sand, while raising the content of lead in the loamy sand relative to the subjects fertilised with ammonium nitrate. The impact of urea and UAN on remaining trace element content in the soils was comparable to that effected by ammonium nitrate. The effect of humic acids on trace element content in the soil tended to be beneficial, as they reduced the soil concentrations of these elements compared to the control subject (without their application). However, it should be emphasised that their effect depended on nitrogen fertiliser form and soil type. Humic acids were effective in reducing soil trace element contents when applied together with nitrogen fertilisers (zinc and lead) and in the interaction with fertilisers and soil type (zinc, cobalt, and copper). Humic acids can be effective in reducing the uptake of some trace elements by their plant species.

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