agronomy

MDPI

Article

New Fertilisers with Innovative Chelates in Wheat Cultivation

Marzena S. Brodowska [1], Mirosław Wyszkowski [2,*] and Ryszard Grzesik [3]

1 Department of Agricultural and Environmental Chemistry, University of Life Sciences in Lublin, Akademicka 15 Str., 20-950 Lublin, Poland; marzena.brodowska@up.lublin.pl
2 Department of Agricultural and Environmental Chemistry, University of Warmia and Mazury in Olsztyn, Łódzki 4 Sq., 10-727 Olsztyn, Poland
3 Departament Rozwoju, Grupa Azoty Zakłady Azotowe Kędzierzyn S.A., ul. Mostowa 30 A, 47-220 Kędzierzyn-Koźle, Poland; ryszard.grzesik@grupaazoty.com
* Correspondence: miroslaw.wyszkowski@uwm.edu.pl

Abstract: The aim of the study was to determine the effect of three new solid fertilisers (based on Salmag®) with innovative IDHA chelate additives (Cu, Mo and Fe) on the yield, yield (grain, straw), biometric characteristics and chemical composition (total N, Ca, Mg and Cu, Mo, and Fe) of spring wheat and soil properties in the pot experiment. The nitrogen dose in all fertilised plots was 140 mg kg^{-1} of soil (60% before sowing, 40% at tillering). Before sowing, uniform fertilisation with phosphorus (60 mg kg^{-1} of soil) and potassium (60 mg kg^{-1} of soil) were also applied. At the stem elongation stage, nitrogen fertilisers, especially Salmag® with Cu, promoted an increase, and Salmag® with Mo and Fe promoted a decrease in leaf greenness at other growth stages of spring wheat. All nitrogen fertilisers had a positive effect on height (especially Salmag® and Salmag® with Mo) and yield (especially Salmag® with Cu and Mo) of spring wheat grain and straw. The effect on grain yield was stronger, while Salma^{g}® with Fe was slightly weaker than pure Salmag®. All applied nitrogen fertilisers increased total N in grain and straw and Ca and Mg in spring wheat straw. Nitrogen fertilisers enriched with micronutrients generally had a weaker effect than Salmag® on the content of total N in grain (in contrast to straw) and Ca and Mg. The addition of Cu, Mo, and especially Fe chelates increased the content of chelated elements in spring wheat, especially in straw. The pH value of the soil after harvest of spring wheat was slightly higher after the application of Salmag® and lower in the soil fertilised with Salmag® with Mo and Salmag® with Fe than in the control. Salmag® and Salmag® with Cu showed a significant increase in soil Mg and all nitrogen fertilisers (especially Salmag® with Fe) in soil Ca content after spring wheat harvest. Salmag® with Cu caused the greatest increase in soil Cu content. The new fertilisers with Mo chelate and especially with Cu chelate showed a significant effect on yield formation and quality of spring wheat.

Keywords: new ammonium nitrate fertiliser; innovative chelates; spring wheat; SPAD; yield; biometric characteristics; soil properties

Citation: Brodowska, M.S.; Wyszkowski, M.; Grzesik, R. New Fertilisers with Innovative Chelates in Wheat Cultivation. *Agronomy* **2024**, *14*, 1832. https://doi.org/10.3390/agronomy14081832

Academic Editor: Monika Mierzwa-Hersztek

Received: 9 July 2024
Revised: 13 August 2024
Accepted: 18 August 2024
Published: 20 August 2024

1. Introduction

To achieve high yields of good quality, plants need to be supplied with nutrients in sufficient quantities to meet their nutritional requirements. In addition to macronutrients, micronutrients are also an important component of fertilisers for the proper growth and development of plants. However, their levels in soils are not always adequate. More than two-thirds of the countries in the European Union are severely deficient in at least one of the micronutrients. The situation is not much better in Poland, where most micronutrients are highly deficient [1].

The availability of micronutrients depends on soil properties, in particular soil acidity and the presence of organic matter [2–6]. In the case of copper, soil pH is of particular importance due to the formation of soluble and mobile forms at low pH values, as well as the content of organic matter, e.g., humic compounds, with which copper forms chelate connections. Copper is also strongly bound by clay minerals and precipitates as sulphides, sulphates and carbonates to form forms that are not very mobile. The bioavailability of copper is also affected by the presence of amorphous Fe, Mn, and Al hydroxides, so small amounts of copper are present in dissolved and exchangeable forms [3]. Soil pH has a very strong influence on the availability of molybdenum to plants. Molybdenum is much more available to plants in alkaline soils than in neutral or alkaline soils [2,5]. Molybdenum deficiency is most common in light soils, which are usually acidic. In these soils, it occurs in forms that are difficult to access, such as iron molybdate or aluminium molybdate, and is more easily leached from them. Unlike other micronutrients, the availability of molybdenum to plants can be increased by raising the pH of the soil through liming. In soils, iron is a very mobile element that migrates deep into the soil profile and becomes unavailable to plants. The causes of iron unavailability in soils can also be due to inappropriate air conditions, leading to the oxidation of the iron ion Fe^{2+} to Fe^{3+}. Iron deficiency is therefore most common in sandy, organic, and freshly limed soils. Iron content is higher in compacted and excessively wet soils, and its availability to plants (like copper) is higher in acidic soils [2,4]. The bioavailability of iron to plants decreases with increasing soil pH and oxidation-reduction potential. Iron is most available to plants in chelated form [6]. The availability of these nutrients may depend on the presence of other elements in the soil, e.g., zinc and phosphorus may favour iron uptake by plants and excess manganese may limit it. Inadequate availability of iron and zinc can increase the uptake of copper by plants [2,4]. Combining micronutrients with macronutrients such as nitrogen, magnesium or calcium gives good fertilisation results.

In recent years, micronutrients have increasingly been supplied to plants in chelated form, which greatly improves the efficiency of their use by plants. Chelates are compounds formed by combining metals with organic ligands [7]. There are many natural chelating agents (decomposition products of organic matter) in the environment. These include amino acids, organic acids, sugars, acids and derivatives, lignin sulfonates, lignin polycarboxylates, phenols, polyflavonoids, siderophores, and phytosiderophores [8,9].

The structure of a fertiliser chelate includes a microelement and a synthetic ligand with at least two coordination sites. The chelating agent (multi-chelating ligand) forms at least two to eight bonds with a single metal ion [7]. This protects it from adverse changes in the soil and in plant organisms. In practice, synthetic ligands such as EDTA and IDHA are most commonly used [7]. Most of the chelate formulations currently available on the market have been developed on the basis of EDTA [10]. The advantage of EDTA is its low molar mass, which allow the production of fertilisers with higher metal content by weight, and the main disadvantage is its relatively poor biodegradability in soil. The biochemical degradation time of EDTA can be up to 15 years. In contrast, used as chelators of IDHA ligands belong to biodegradable compounds [7].

Microelement fertilisers based on various chelates are characterised by varying plant uptake and utilisation rates, biodegradability and micronutrient concentration. Chelating compounds are a beneficial factor in the introduction of micronutrients into the fertiliser formulation as well as into the soil complex. Chelated fertiliser nutrients in plant production can be applied both foliarly and topically and its efficacy of chelates depends largely on the structure of the molecule. Their application, even in the absence of micronutrient deficiencies, can result in increased yields due to their often biostimulatory effect on plants [11]. The structure of chelates prevents transition metal ions from reacting with components of the soil complex, protecting them from unwanted transformations after application to soil and facilitating nutrient uptake by leaves after foliar application, unlike the use of typical inorganic salts. The structure of chelates facilitates the movement of micronutrient ions in the soil solution (this occurs at the same rate as for ionised particles). This allows the dosage of such a fertiliser additive to be reduced after both the soil and foliar application [12]. Chelates are usually soluble in water but dissociate only slightly. The slower release of micronutrients increases their bioavailability to plants and prevents their excessive accumulation in plants. This type of fertiliser is used for a wide range of crops [11].

The current emphasis on reducing the environmental impact of agricultural production, including fertilisation, is forcing fertiliser manufacturers to search for new compounds which, in addition to their strong metal ion complexing properties, high stability over a wide pH and temperature range and good solubility, would have a short biodegradation period [7].

Most research on chelates has focused mainly on synthetic chelate ligands based on EDTA or on natural chelating agents (e.g., amino acids). There is therefore a need for research on synthetic IDHA ligands, which were used to produce the fertilisers used in our study. The IDHA-based chelate forms of the micronutrients tested in the study have very good plant availability and are much safer for the environment than the commonly used EDTA-based chelate forms, which have very poor biodegradability in the soil environment.

Therefore, a study was carried out with the following research hypotheses (1) new solid fertilisers (based on Salmag®) with chelate additives (Cu, Mo and Fe) will cause an increase in yield (grain, straw) and have a positive effect on the biometric characteristics of spring wheat and (2) fertilisers (based on Salmag®) with chelate additives (Cu, Mo, and Fe) will cause an increase in the content of elements (included in their composition—total N, Ca, Mg and Cu, Mo, and Fe) in plants and soil and a change in other soil properties. The reference point for the new fertilisers was a solid fertiliser (Salmag®) without the chelate coating.

2. Materials and Methods

2.1. Methodological Assumptions

In recent years, research and development work at Grupa Azoty ZAK S.A. (Kędzierzyn-Koźle, Poland) has focused on expanding the product range with modern speciality fertilisers containing biodegradable and micronutrient additives. The project has developed a number of new fertilisers with external funding: PO-IR.01.02.00-00-0023/16 project for the development of an innovative high nitrogen fertiliser in the form of ammonium nitrate enriched with microelements in the form of chelates of biologically important metals based on newly developed chelating ligands. The above project aimed to the develop of new nitrate fertilisers containing organic biodegradable chelating additives. The project developed a range of new innovative chelating additives based on available and biodegradable molecules and IDHA chelates. The fertilisers were produced by coating ready-cooled saltpeter granules (Salmag®, Grupa Azoty Zakłady Azotowe Kędzierzyn S.A., Kędzierzyn-Koźle, Poland) in a fluid bed with solutions of manufactured chelates (Cu, Mo and Fe). Laboratory produced IDHA chelates of iron and molybdenum (a new innovative method of producing IDHA—iminodisuccinic acid—$C_8H_{11}O_8N$) and the copper chelate of the innovative patented ligand N-butyl-D-gluconamide [13] were used. Biodegradability was confirmed for all used chelators.

The research was based on a rigorous pot experiment in the vegetation hall of the University of Warmia and Mazury in Olsztyn (Poland). The soil material for the pot experiment was taken from the arable layer of typical eutrophic brown soil at the Tomaszkowo Teaching and Experimental Centre (Poland), which belongs to the University of Warmia and Mazury in Olsztyn (Poland). According to the soil classification [14] and in accordance with the agronomic categories, the soil was classified in the group sands, subgroup loamy sands. The granulometric composition of the soil was as follows: sand fraction—range 2.0–0.05 mm—77.55%, dust fraction—range 0.05–0.002 mm—19.95%, and clay fraction—range below 0.002 mm—2.5%. It was characterised by the following properties: pH—5.85, total nitrogen—1.120 g N kg^{-1} dry matter (DM), magnesium—2.229 g kg^{-1} DM, calcium—5.481 g kg^{-1} DM, copper—7.829 mg kg^{-1} DM, molybdenum—0.959 mg kg^{-1} DM and iron—10,108 mg kg^{-1} DM.

Pots containing 9 kg of soil were used for the experiments. The test plant was spring wheat (*Triticum aestivum* L.) of the Harenda variety. The effect of the new fertilisers with chelate additives (Cu, Mo and Fe) was compared with a commercial Salmag® (saltpeter—mixture of ammonium nitrate with calcium carbonate and magnesium carbonate) and a control (no nitrogen fertilisation). Salmag® contained 27% N (13.5% nitrate-N and 13.5% ammonium-N), 5.0% Ca as calcium oxide (including 1.4% water-soluble Ca) and 2.4% Mg as magnesium oxide (including 1.2% water-soluble Mg) [15]; 95% of the product was in the form of granules with dimensions of 2.0–5.0 mm and a bulk density of 0.97 kg dm^{-3}. A series of trials with Salmag®-based fertilisers specially produced by Grupa Azoty Zakłady Azotowe Kędzierzyn S.A. (Kędzierzyn-Koźle, Poland). The micronutrient content of the chelated fertilisers was as follows Salmag® with copper chelate—0.25% Cu, Salmag® with molybdenum chelate—0.25% Mo and Salmag® with iron chelate—0.25% Fe. The nitrogen dose in all fertilised plots was 140 mg kg^{-1} of soil (60% before sowing, 40% at tillering). Before sowing, uniform fertilisation with phosphorus (60 mg kg^{-1} of soil) and potassium (60 mg kg^{-1} of soil) and the first dose of nitrogen fertiliser were also applied. Solid fertilisers with chelate additives (Cu, Mo and Fe) were applied to the soil as recommended for pot experiments. Phosphorus was applied in the form of Super Fos Dar 40 (41.2% P_2O_5) and potassium in the form of potassium salt (60% K_2O). Nitrogen, phosphorus, and potassium fertilisers were thoroughly mixed into the soil during the establishment of the experiment. This was followed by sowing spring wheat grain at a target planting rate of 15 plants per pot. The second dose of nitrogen fertiliser was applied at the tillering stage and carefully worked into the soil between the growing plants. The experiment was carried out in 5 replications. Constant soil moisture was maintained in the pots throughout the growing season (60% of field water capacity).

During the study, the characteristic development stages of spring wheat were photographed (Figure 1). A beneficial effect was noted, and both Salmag® and Salmag® with chelates were observed at the beginning of the vegetation of spring wheat. The larger and positive impact of Salmag® with copper chelates on the growth and development of plants was highlighted in the later stages of the vegetation of this plant. The spring wheat was harvested at full maturity. Immediately after harvest, plant height, grain and straw yields, and the weight of 1000 grains were determined. At the same time, samples of plant and soil material were taken for laboratory analysis.

2.2. Laboratory and Statistical Analysis Methods

The SPAD index was measured in three places in the same leaf in all plants during the vegetation. The measurement was performed using a SPAD-502Plus meter (Konica Minolta, Inc., Chiyoda, Japan). The height of each plant from each pot was determined during their harvesting measurement from the vertex of the ears to the roots. The dry matter of wheat grains and straw has been determined by drying method by drying to a constant weight at a temperature below 60 °C [16]. In the plant material, the contents of basic macronutrients (total-N, Ca and Mg) and micronutrients (Cu, Mo and Fe) added together with the new fertilisers were determined. Soil properties (pH; total-N; Mg and Ca; and Cu, Mo, and Fe) were also determined before the start of the experiment and after harvesting of the experimental plants. The granulometric composition of the soil was also determined by laser diffraction before the pot experiment was set up [17].

The macronutrient and micronutrient contents of the plants were determined by the following methods: total nitrogen—by the Kjeldahl method after digestion of the plant material in concentrated H_2SO_4 with H_2O_2 [16]; calcium and magnesium—by the AAS method after digestion of the plant material in concentrated H_2SO_4 with H_2O_2 [16]; and copper, molybdenum and iron—by the AAS method after digestion of the plant material in concentrated nitric acid [16]. Soil analyses were performed using the following methods: pH in 1M KCl—potentiometric method [18]; total nitrogen—modified Kjeldahl method after soil digestion in concentrated H_2SO_4 with H_2O_2 [19]; calcium and magnesium, copper, molybdenum, and iron—AAS method after soil digestion in royal water [16]. The SpectrAA 240FS spectrophotometer (Varian Inc., Mulgrave, VIC, Australia) was used for the AAS method.

The results obtained from the pot experiment were statistically verified using the ANOVA module and a Tukey's HSD post hoc test of the STATISTICA 13.3 programme [20] at a significance level of $p \leq 0.01$ and subjected to PCA analysis to determine the correlations between the studied parameters.

(**a**)
(**b**)
(**c**)
(**d**)
(**e**)
(**f**)

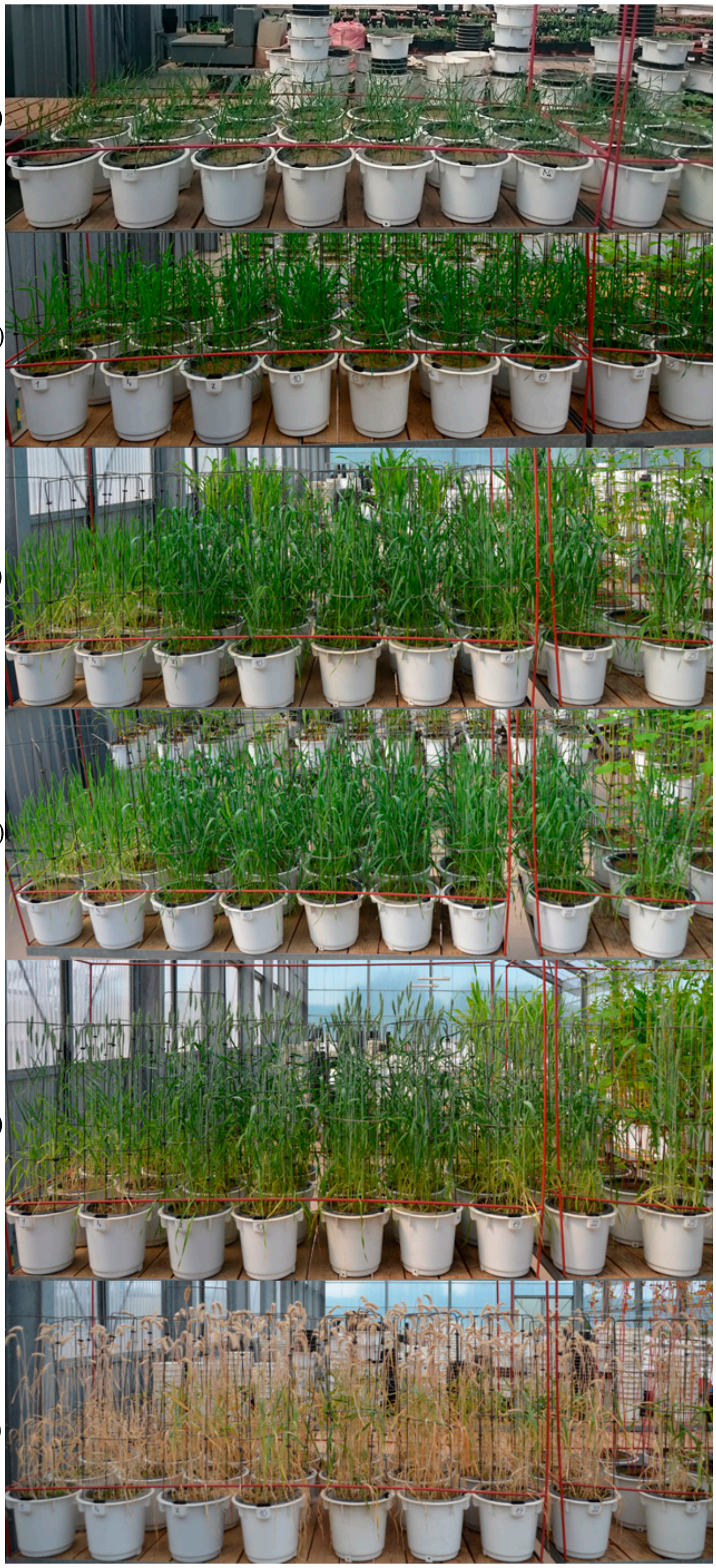

Figure 1. Spring wheat at different phases of vegetation: (**a**) emergence and leaf development, (**b**) tillering, (**c**) stem shooting, (**d**) heading, (**e**) flowering, and (**f**) maturity.

3. Results

3.1. Plants

3.1.1. SPAD Index

In the conducted study, a strong reduction in leaf greenness (SPAD) of spring wheat was observed as the growing season progressed, and grain-maturity-related yellowing of spring wheat leaves and stems also decreased (Figure 2). At the stem emergence stage, nitrogen fertiliser applications increased leaf greenness (as a result of increased leaf chlorophyll content). In contrast, at later growth stages, there was no clear effect of N fertilisers on changes in the greenness index. Of the chelated fertilisers applied at the stem elongation stage, Salmag® with Cu had the strongest effect on the greenness index, while Salmag® with Fe chelate had the weakest effect. It should be noted that only the application of Salmag® with Cu chelate had a greater effect on increasing the greenness index (by 4%) than Salmag® without micronutrient additives. Compared to the control, the application of Salmag® with Cu chelate increased the greenness of the leaves by 51%. Analogous relationships were observed in the flowering phase of the plants, where the effect of Salmag with Cu chelate on leaf greenness was relatively small, 7%, compared to the control.

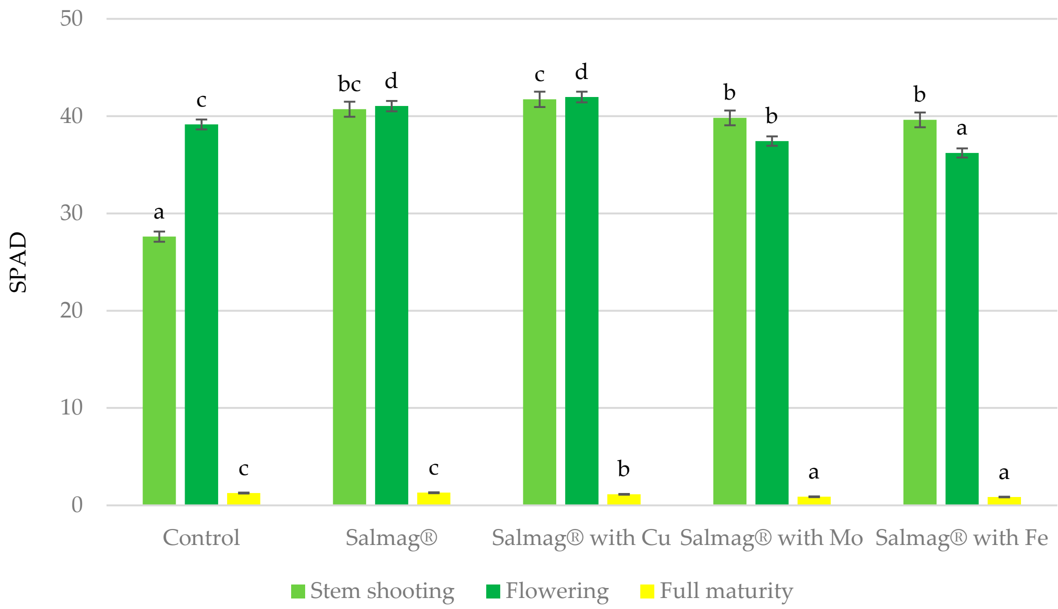

Figure 2. Spring wheat SPAD in phases: stem shooting, flowering and full maturity. Different letters above the bars indicate a significant impact at $p \leq 0.01$.

At the flowering stage of the plants, the application of Salmag® with Mo and Fe chelates reduced the leaf greenness compared to both the Salmag®-only and the control series. An analogous relationship was observed at the full maturity stage of spring wheat, which accelerated the maturity of the experimental plant. At the last stage of spring wheat vegetation (full maturity), an analogous effect was observed for Salmag® with Cu chelate, and only in the Salmag® without micronutrient additives objects the leaf greening was slightly higher than in the control sites. Salmag® with Mo chelate and Salmag® with Fe chelate influenced the greenness by 31 and 33% respectively compared to the control and to the Salmag® without micronutrients.

3.1.2. Plant Height

All applied nitrogen fertilisers had a positive effect on plant growth and development (Figure 3a). Of the fertilisers applied, Salmag® without micronutrients and Salmag® with Mo had the strongest effect on plant height, increasing plant height by 13 and 12% respectively compared to the control. In contrast, Salmag® with Fe had the weakest effect on wheat height.

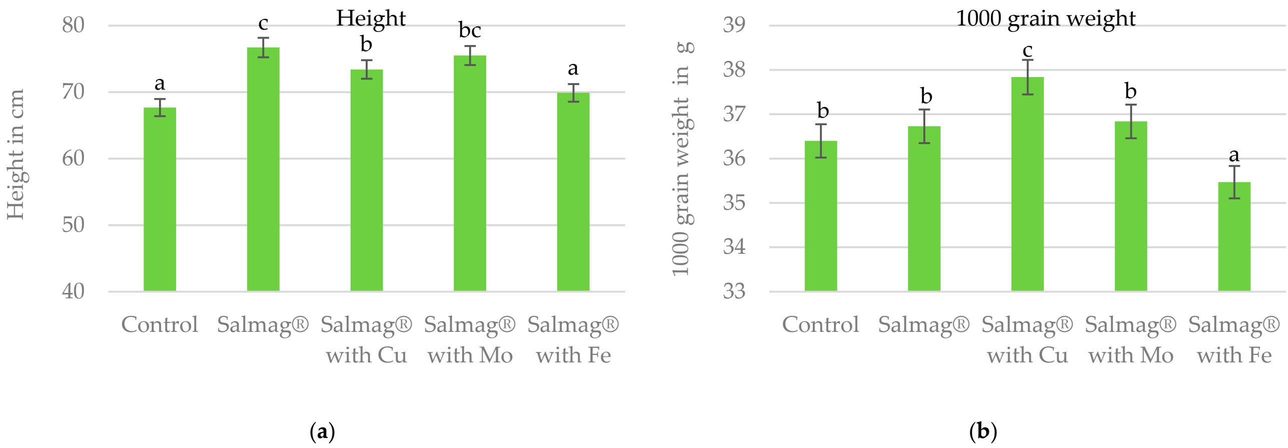

Figure 3. (**a**) Height at full maturity (in cm) and (**b**) 1000 grain weight (in g) of spring wheat. Different letters above the bars indicate a significant impact at $p \leq 0.01$.

3.1.3. 1000-Grain Weight

The weight of 1000 grains of spring wheat at plant harvest ranged from 35.47 to 37.84 g (Figure 3b). The highest 1000-grain weight was recorded in the plants fertilised with Salmag® with Cu, while the lowest was recorded in the series with Salmag® with Fe. The applied nitrogen fertilisers (with the exception of Salmag® with Fe chelate) contributed to a small and generally not significant increase in the 1000 grain weight of the test plant. The exception was Salmag® with Cu addition, which caused a significant increase of 4% in the 1000 grain weight of spring wheat compared to the control and increase of 3% to the Salmag® without micronutrients.

3.1.4. Crop Yield

The yield-forming effect of all nitrogen fertilisers applied was recorded in the trials (Table 1). On the sites fertilised with pure Salmag®, the increase in grain fresh matter yield was 64% and grain dry matter yield 65% compared to the control series. The effect of Salmag® with Cu and Mo chelates was stronger, and Salmag® with Fe chelate was comparable to the effect of pure Salmag® on fresh grain weight. Under their influence, the fresh matter yield of spring wheat grain increased by 74, 72, and 63%, and the dry matter yield increased by 75, 74, and 64% compared to the control.

The beneficial effect of all nitrogen fertilisers on wheat straw yield was significantly greater than on grain yield of this crop (Table 1). Fertilisation with Salmag® without chelates contributed to a 149% increase in fresh matter yield and a 117% increase in dry matter yield of spring wheat straw compared to the object without nitrogen fertilisation. Similar to grain yield, the effect of Salmag® with Cu and Mo chelates (as opposed to Salmag® with Fe) was greater than that of pure Salmag®. However, it should be noted that the additional increase in straw yield under their influence did not exceed 4–5% for fresh matter and only 2% for dry matter of spring wheat straw.

3.1.5. Macronutrients

The application of Salmag® resulted in a 51% increase in total nitrogen in the grain and 28% in the straw of the test crop (Table 1). All micronutrient enriched nitrogen fertilisers had a weaker effect on total nitrogen concentration than Salmag®, resulting in a 41% (Salmag® with Cu), 24% (Salmag® with Fe) and 21% (Salmag® with Mo) increase in total nitrogen content in the grain of spring wheat compared to the no nitrogen fertiliser treatment. Of the nitrogen fertilisers applied, only Salmag® enriched with Fe resulted in a significant 7% increase in calcium content in spring wheat grain compared to the control. Only Salmag® and Salmag® enriched with Cu caused a slight increase of 3% in magnesium content in spring wheat grain.

Table 1. Impact of ammonium nitrate fertilisers containing innovative chelate additives on yield and chemical composition of spring wheat.

Fertiliser	Yield FM	Yield DM	Total-N	Ca	Mg	Cu	Mo	Fe
	g pot^{-1}		Content in g kg^{-1} DM			Content in mg kg^{-1} DM		
				Grain				
Control	12.98 ± 0.13 a	11.79 ± 0.12 a	25.46 ± 0.25 a	0.315 ± 0.004 a	1.024 ± 0.002 a	1.883 ± 0.002 b	1.346 ± 0.039 a	35.47 ± 0.46 a
Salmag®	21.23 ± 0.38 b	19.48 ± 0.36 b	38.36 ± 0.46 d	0.315 ± 0.002 a	1.058 ± 0.006 b	1.910 ± 0.007 b	1.354 ± 0.024 ab	39.65 ± 0.68 b
Salmag® with Cu	22.57 ± 0.28 c	20.66 ± 0.23 c	35.84 ± 0.47 c	0.317 ± 0.005 a	1.059 ± 0.010 b	1.911 ± 0.046 b	1.301 ± 0.032 a	36.11 ± 0.59 a
Salmag® with Mo	22.33 ± 0.33 c	20.51 ± 0.28 c	30.80 ± 0.42 b	0.316 ± 0.007 a	1.014 ± 0.004 a	1.813 ± 0.018 a	1.486 ± 0.016 c	37.37 ± 1.09 a
Salmag® with Fe	21.13 ± 0.60 b	19.37 ± 0.54 b	31.64 ± 0.36 b	0.338 ± 0.002 b	1.027 ± 0.005 ab	1.887 ± 0.009 b	1.417 ± 0.010 bc	41.56 ± 0.82 b
$LSD_{0.01}$	0.67	0.60	1.04	0.011	0.031	0.059	0.068	1.97
				Straw				
Control	20.97 ± 0.45 a	15.61 ± 0.40 a	10.92 ± 0.22 a	0.834 ± 0.020 a	0.675 ± 0.017 a	1.897 ± 0.046 a	0.833 ± 0.008 a	66.98 ± 3.45 b
Salmag®	52.23 ± 0.41 b	33.94 ± 0.38 c	14.00 ± 0.12 c	1.491 ± 0.029 c	1.044 ± 0.043 c	2.007 ± 0.001 b	0.858 ± 0.002 ab	63.79 ± 1.94 ab
Salmag® with Cu	53.14 ± 0.43 bc	34.19 ± 0.17 c	14.56 ± 0.06 d	1.309 ± 0.045 b	0.981 ± 0.019 bc	2.008 ± 0.020 b	0.848 ± 0.018 ab	87.14 ± 0.24 c
Salmag® with Mo	53.33 ± 0.50 c	34.21 ± 0.14 c	12.32 ± 0.29 b	1.504 ± 0.031 c	0.953 ± 0.034 b	2.004 ± 0.067 b	0.872 ± 0.014 b	57.78 ± 1.99 a
Salmag® with Fe	50.61 ± 0.71 d	32.95 ± 0.44 b	14.25 ± 0.08 cd	1.291 ± 0.027 b	0.953 ± 0.045 b	1.932 ± 0.025 a	0.861 ± 0.012 ab	87.22 ± 2.96 c
$LSD_{0.01}$	0.91	0.59	0.46	0.092	0.087	0.101	0.031	6.19

Average values ± standard deviation, different letters on the right (after SD) indicate a significant impact at $p \leq 0.01$.

In straw, on the other hand, the increase in total nitrogen content due to the application of Salmag® with Fe was 30%, Salmag® with Cu 33%, and Salmag® with Mo 13% compared to the control. For plants fertilised with Salmag® without micronutrient additives, the increase was 28%. On the other hand, the increase in the calcium content of the straw was lowest after the application of Salmag® with Fe (+55%) and Salmag® with Cu (+57%) and highest after the incorporation of pure Salmag® (+79%) and Salmag® with Mo (+80%) into the soil respectively compared to the control site (without N). All chelated fertilisers had a weaker effect than pure Salmag® on the magnesium content of spring wheat straw. The increases in the content of magnesium in spring wheat straw under the influence of nitrogen fertilisers with micronutrient additives were 41% (Salmag® with Mo and Fe), 45% (Salmag® with Cu), and 55% (Salmag®) in relation to the object without nitrogen fertilisation.

3.1.6. Micronutrients

An analysis of the results obtained shows that the highest copper content, both in the grain and in the straw of spring wheat, was found in plants fertilised with Salmag® with Cu (Table 1). The content of copper in the grain of spring wheat in the nitrogen-fertilised plants was similar to the control, and only after the application of Salmag® with Mo was the content of the analysed micronutrient slightly lower (by 4%) in relation to the series without nitrogen. A favourable effect of nitrogen fertilisation on the molybdenum content in the grain of the test plant was found in the series with Salmag® with Mo and Salmag® with Fe. The increase in molybdenum content in the wheat grain was 10 and 5% respectively compared to the control and to the Salmag® without micronutrients. Nitrogen fertilisers contributed to an increase in the iron content of the wheat grain compared to the control. This ranged from 5% (Salmag® with Mo) to 12% (Salmag®) and 17% (Salmag® with Fe).

Changes in the copper content of spring wheat straw were also small. The copper content in the straw of the test plant after application of pure Salmag®, Salmag® with Cu, and Salmag® with Mo was 6% higher than in the control object. Higher molybdenum contents in the straw (relative to the control) were found in plants from all micronutrient fertiliser series. The increase in molybdenum content in these combinations compared to the series without nitrogen ranged from 5% (Salmag® with Mo) to 2% (Salmag® with Cu). The effect of nitrogen fertilisers on the iron content of spring wheat straw was less clear. There was a 30% increase in iron content in spring wheat straw after application of Salmag® with Cu and Salmag® with Fe. In contrast, pure Salmag® and especially Salmag® with Mo contributed to a decrease in the iron content in the straw of the test crop.

3.2. Soil Properties

3.2.1. pH

Soil pH after spring wheat harvest ranged from 5.81 to 6.03 and showed little dependence on the applied nitrogen fertiliser (Table 2).

Table 2. Impact of ammonium nitrate fertilisers containing innovative chelate additives on soil properties after harvest of spring wheat.

Fertiliser	pH	Total-N	Ca	Mg	Cu	Mo	Fe
		Content in g kg^{-1} DM			Content in mg kg^{-1} DM		
Control	5.94 ± 0.04 d	1.067 ± 0.067 a	4.882 ± 0.029 a	2.070 ± 0.066 ab	5.472 ± 0.095 a	0.922 ± 0.024 a	9754 ± 206 bc
Salmag®	6.03 ± 0.03 c	1.022 ± 0.051 a	5.694 ± 0.092 b	2.232 ± 0.066 c	5.854 ± 0.181 a	0.940 ± 0.007 a	9957 ± 213 bc
Salmag® with Cu	5.88 ± 0.05 b	1.033 ± 0.088 a	5.987 ± 0.088 c	2.208 ± 0.033 c	7.383 ± 0.117 b	0.929 ± 0.013 a	10256 ± 196 c
Salmag® with Mo	5.83 ± 0.01 ab	1.044 ± 0.019 a	6.695 ± 0.078 d	2.176 ± 0.015 bc	5.472 ± 0.221 a	0.937 ± 0.016 a	9602 ± 210 b
Salmag® with Fe	5.81 ± 0.02 z	1.044 ± 0.051 a	8.428 ± 0.094 e	2.024 ± 0.050 a	5.854 ± 0.268 a	1.018 ± 0.008 a	8513 ± 191 a
$LSD_{0.01}$	0.06	n.s.	0.207	0.130	0.847	n.s.	579

Average values ± standard deviation, n.s.—non-significant, different letters on the right (after SD) indicate a significant impact at $p \leq 0.01$.

Soil pH was slightly higher (6.03) after application of Salmag® and lower (5.81) in soils fertilised with Salmag® with Mo (5.83)—and especially with Salmag® with Fe chelate (5.81)—than in the control (5.94).

3.2.2. Macronutrients

The effect of the application of all nitrogen fertilisers showed a trend towards a decrease in total nitrogen content and an increase in soil calcium content after the harvest of the trial crop, with pure Salmag® having the greatest effect on total nitrogen content and the least on calcium (Table 2). The application of Salmag® contributed to a 4% decrease in total nitrogen concentration and a 17% increase in soil calcium content. However, it should be noted that the effect of Salmag® on the total nitrogen content of the soil was insignificant both without and with chelate additives. The slightly lower total nitrogen content in the soil was associated with a higher crop yield on nitrogen fertilised sites and, at the same time, a higher uptake of this element by the plants. Pure Salmag® also had the greatest effect—an 8% increase in soil magnesium content. Salmag® with Mo and Salmag® with Cu favoured slight increases in soil magnesium content of 5 and 7%, respectively, compared to the control site. However, a significant effect of nitrogen fertiliser on magnesium content was only found after the application of pure Salmag® and Salmag® with Cu chelate. The increase in soil calcium content under the influence of chelated nitrogen fertilisers ranged from 23% (Salmag® with Cu) to 73% (Salmag® with Fe).

3.2.3. Micronutrients

When analysing the effect of the applied nitrogen fertilisers on the content of the studied micronutrients in the soil, it should be noted that they had the least and non-significant effect on the content of molybdenum (Table 2). The application of pure Salmag® and Salmag® with Fe resulted in a 7% and Salmag® with Cu a 35% increase in copper content in the soil after spring wheat harvest. In the case of molybdenum in soils from nitrogen fertilised sites, there was a small and insignificant increase in the content of this element ranging from 2% (Salmag® with Mo and Salmag®) to 4% (Salmag® with Fe). The effect of nitrogen fertilisers on iron content was non-directional and insignificant in most of the sites. The exception was the last plot where Salmag® with Fe chelate was applied, but the iron content was lower than in the control (no nitrogen fertilisation). For Salmag® and Salmag® with Cu, an increase in the soil iron content was found in the micronutrient fertilised objects compared to the control.

The lower content of majority of total contents of macro and microelements of the soil after plant harvest was probably due to the uptake by the plants and the relatively small amount of soil in the pots which influenced the rather large differences compared to the natural field conditions. It is likely that the lower soil pH in the Salmag® facility with iron may have influenced its higher effect (than the other fertilisers) on iron content in plant yield.

3.3. PCA Analysis and the Percentage of Variability Observed

3.3.1. Spring Wheat Grain

The first group of characteristics (1000 grain weight of spring wheat, total nitrogen, magnesium and copper content in grain) determined 40.56% and the second group (fresh and dry matter grain yield of spring wheat, calcium, molybdenum and iron content in grain) determined 34.16% of the total correlation of the data set (Figure 4). The vectors for spring wheat fresh and dry matter grain yield and total grain nitrogen, magnesium and molybdenum content were the most significant and calcium and copper content the least significant in contributing to variability. The strongest positive correlations were found between fresh and dry matter grain yield of spring wheat, between total nitrogen content and grain yield and magnesium content, and between calcium content and iron accumulation in grain. A negative correlation was found between molybdenum content—and, to a much lesser extent, between calcium content—and copper, magnesium, and 1000 grain weight.

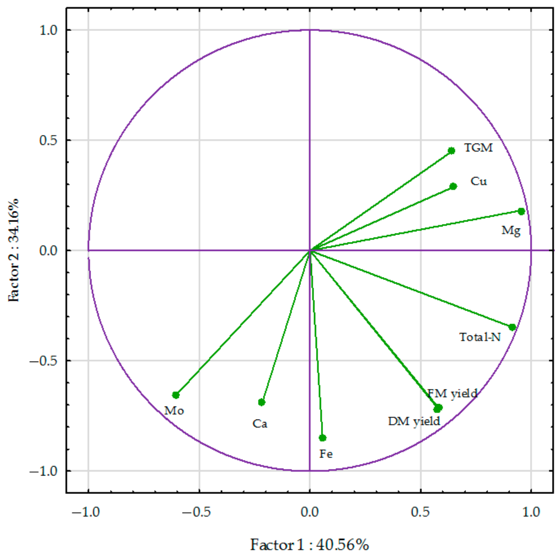

Figure 4. Yield and chemical composition of spring wheat grain plotted using the PCA method. The vectors represent the following parameters (fresh and dry matter yield of spring wheat grain, content in grain: total-N, Ca, Mg, Cu, Mo, and Fe).

3.3.2. Spring Wheat Straw

The first group of properties comprised most of the studied parameters (with the exception of leaf greenness index—SPAD at flowering and full maturity phases) and accounted for 64.32% of the total correlation of the dataset (Figure 5).

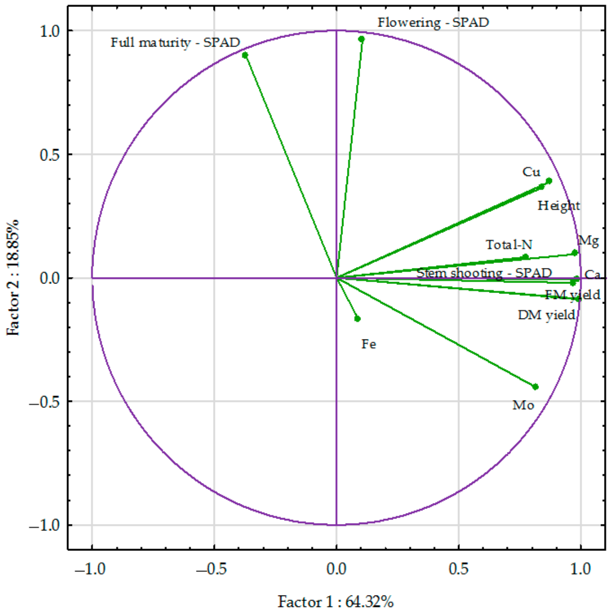

Figure 5. Yield, biometric traits and chemical composition of spring wheat straw presented using the PCA method. The vectors represent the following parameters (SPAD index at stem shooting, flowering and full maturity stages, plant height, fresh and dry matter yield of spring wheat straw, straw content: total-N, Ca, Mg, Cu, Mo, and Fe).

The second group comprising the SPAD index at flowering and full maturity phases of spring wheat accounted for 18.85% of this correlation. The lengths of the vectors of most of the spring wheat parameters, with the exception of iron content, were similar, indicating similar significance in the contribution to variability. There were strong positive correlations between spring wheat straw fresh and dry matter yields and leaf greenness index at the stem shooting stage and between plant height and the content of most of the tested elements in the straw of this plant. The exception was iron.

3.3.3. Soil after Spring Wheat Harvest

The contents of iron, magnesium, molybdenum, and soil pH fell into the first group, accounting for 56.69%, and the contents of total soil nitrogen, calcium, and copper fell into the second group, accounting for 24.72% of the total correlation of the dataset (Figure 6). Most vectors (with the exception of pH and soil copper content) were of similar length, i.e., they were of similar importance in the contributing to variability. The strongest positive correlation was found between calcium content and molybdenum, and a weaker correlation was found between pH and soil iron and magnesium content. There was also a negative correlation between total nitrogen content and soil magnesium and copper contents.

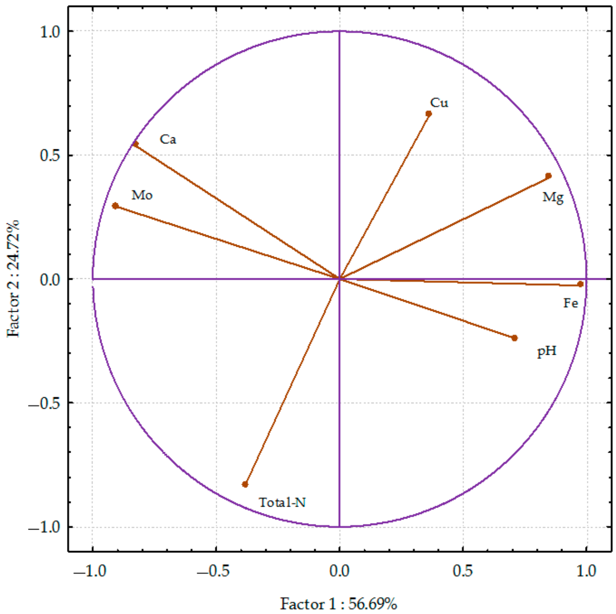

Figure 6. Selected post-harvest soil properties of spring wheat presented using the PCA method. The vectors represent the following parameters (pH, soil contents: total-N, Ca, Mg, Cu, Mo, and Fe).

4. Discussion

Mineral fertilisation is an important factor influencing the quantity and quality of crop yields. Achieving a high yield per hectare is an effective way of combating global food shortages. The content of micronutrients in fertilisers can increase yields through the complementary action of several nutrients. No less important is the use of additives that are biodegradable in the soil. In addition to basic macronutrients such as nitrogen, potassium, phosphorus, calcium, and magnesium, micronutrients such as copper, molybdenum, and iron are among the most important elements on which normal plant growth and development depend [21].

Copper deficiency is responsible for a slowdown in plant growth and development and a significant reduction in yield (up to 20%) and seed quality. Copper is involved in photosynthesis and reproduction and has a beneficial effect in shaping plant resistance to disease [22,23]. It is a component of many enzymes responsible for respiration and oxidation processes as well as the synthesis of cell-strengthening lignin substances that determine stem stiffness. In the plant, it influences the increase of protein, sugar, carotene, vitamin C, and nitrogen metabolism (reduces nitrate content) [24].

Inadequate amounts of molybdenum disrupt plant growth and development, limiting crop yields by affecting N fixation and the synthesis of enzymes [25,26] involved in phosphorus uptake, among other things [26]. It also reduces nitrate nitrogen from fertilisers, allowing protein synthesis to take place, and affects photosynthesis, including chlorophyll content and vitamin C synthesis [24].

Iron is an essential nutrient for plants, animals, and humans. In plants, iron is essential for photosynthesis, nitrogen metabolism, and enzyme synthesis, regulating enzymatic reactions [22]. The total iron content of soils is generally sufficient to meet plant nutritional requirements, but variations in soil properties determine its availability to plants [27]. However, breeding to maximise the yield of plant varieties and improve resistance to pathogens and pests can increase iron requirements, and the use of pesticides can interfere with root growth and the movement of this element to the above-ground parts and seeds of plants, which can contribute to iron deficiency [22].

The yield results for the chelated fertilisers compared to the market saltpetre fertiliser (Salmag®) show the added value for spring wheat vegetation. The addition of copper and molybdenum chelates increased spring wheat yields. Additionally, in the studies by Abbasi et al. [28], Szulc et al. [29], and Wierzbowska and Żuk-Gołaszewska [30], nitrogen fertilisation had a positive effect on yield and its parameters, while plant height and 1000 seed weight varied [30]. In our study, all nitrogen fertilisers increased nitrogen in grain and straw of spring wheat, with Salmag® having the strongest effect in grain and Salmag® with Cu in straw. The applied fertilisers also increased the calcium and magnesium content of the spring wheat straw. According to other authors, nitrogen fertilisers can increase the content of nitrogen [30,31], calcium [31], and magnesium [30,31] in plants.

The results of our own experiment partly confirm other studies. The application of mineral fertilisers can significantly influence the content of some micronutrients in the soil [32]. The application of nitrogen fertilisers to the soil can increase the copper and iron contents of the soil [33–35]. Mineral fertilisers also affect the bioavailability of elements to plants by affecting pH and acidity and sometimes other soil properties, such as sorption capacity and organic matter content [36]. Nitrogen fertiliser application can therefore contribute to an increase [37] or decrease [38] in iron and other trace elements [37,38] in plants. According to Miner et al. [39], nitrogen fertilisation has very little effect on the total content and available form of micronutrients in the soil due to the poor sorption of this element. However, in a study by Miner et al. [39], nitrogen fertilisation increased copper and iron content in maize. Ali et al. [40] also found an increase in its content in maize after their application. This was confirmed in their own research, where the application of fertiliser with copper only caused an increase in copper content in the soil, fertiliser with molybdenum caused an increase in molybdenum content in grain and straw of spring wheat, and fertiliser with iron an increase in iron content in grain and straw of spring wheat.

The levels of micronutrients in plants are strongly correlated with the levels of their bioavailable forms in the soil [41]. Low (deficient) availability of copper in soil occurs at neutral or alkaline pH, in better soils with high organic matter content, and can also be the result of upwelling [42,43]. In good soils, copper is bound by organic matter, clay fractions, carbonates, or (oxy)hydroxides, limiting its availability to plants. Most soluble forms of molybdenum occur at pH 7.5–9, whereas in acidic soils, it is bound to organic matter and iron hydroxides [44,45]. Molybdenum deficiencies are therefore quite common in acidic soils with high leaching. Adding molybdenum to the soil with other fertilisers has a beneficial effect on plants, which is confirmed by Adhikari and Missaoui [44], Shcherbakova et al. [46], and Wen et al. [47] in addition to our own research. However, it may not give good results on acidic soils. Therefore, their acidity should be reduced beforehand, e.g., through the liming or application of organic matter [48]. Most plant-available forms of iron are found in acidic soils, which is not good from a plant perspective, as most plant species grow best in soils with a pH close to neutral [23]. In good soils, however, organic matter subject to microbial mineralisation is a source of iron [49], and organic acids can lower soil pH and thus increase iron availability for plants [50]. At the same time, however, they form permanent complexes with iron that limit its uptake by plants. Therefore, not only iron supplementation in combination with mineral fertilisers but also the use of biofertilisers or organic fertilisers or the application of organic matter in another form for crops that require it [51,52] can provide good results in crop production.

Chelated forms of micronutrients have very good solubility in water and a low dissociation constant. As a result, they protect the chelated elements from volatilisation in the root environment. Therefore, the beneficial effect of chelated forms of micronutrients in fertilisers on plant growth and development and on their content in plants is due to the fact that their use counteracts the formation of insoluble combinations in the soil, thereby increasing their availability to plants. The stability and persistence of a chelate depends on its structure, the pH of the environment, and access to light. In addition, chelated forms of micronutrients are characterised by good long-term availability to plants, which can take up micronutrients either as a released ion or as a whole chelate molecule [7]. Another important feature of chelate-based fertilisers is their high stability over a wide range of pH values. Therefore, when applied topically, micronutrients in chelated form are not bound by soil colloids and are not lost through leaching into deeper soil layers, partly due to their gradual release into ionic form. This gives an advantage to chelated forms of micronutrients, which can be taken up by plants over a longer period than salts. The uptake of chelated micronutrients and their effective use by plants is highly dependent on air temperature, which should be between 15–25 °C. Therefore, the application of micronutrients in chelated form is not recommended when temperatures are lower, such as in autumn or early spring [7,53,54].

Conventional fertilisers in the form of inorganic salts of micronutrients (e.g., nitrates, sulphates and chlorides), despite their good water solubility, are characterised by slower and also weaker uptake by plants compared to chelated forms. In addition, the application of micronutrient salts requires a higher dose of the micronutrient compared to the dose applied in chelated form [2,6,53]. When micronutrients are applied to soil in the form of inorganic salts, they are subject to a higher degree of volatilisation compared to the chelated forms, making them less available to plants or potentially leaching into the soil profile. Inorganic salts of micronutrients, unlike chelated forms, can be applied at lower air temperatures because their uptake by plants does not involve energetic processes. This makes it possible to apply micronutrients in the form of inorganic salts in early spring and late autumn [54,55].

The effect of chelated fertilisers on crop yield and quality is usually more favourable than that of salt-based fertilisers, as confirmed by many authors' studies [53–59]. According to Ghasemi et al. [53], the effect of chelated micronutrient fertilisers on yield and quality parameters of soft wheat can be up to twice as great as after application of micronutrients in salt form.

On soils deficient in micronutrients, the application of micronutrients is therefore essential for high crop yields, as confirmed by our study. The application of new fertilisers with molybdenum chelate and especially with copper chelate proved to be effective in shaping the yield and chemical composition of spring wheat. It seems necessary to extend the research to other crops, especially those of high importance for food and feed production. The next step will be to test the effects of these fertilisers on soil and plants on a larger scale under natural field conditions.

5. Conclusions

At the stem elongation stage, nitrogen fertilisers, especially Salmag® with Cu, promoted an increase, and Salmag® with Mo and Fe promoted a decrease in leaf greenness (SPAD) at other growth stages of spring wheat. All nitrogen fertilisers had positive effects on height (especially Salmag® and Salmag® with Mo) and the yield (especially Salmag® with Cu and Mo) of spring wheat grain and straw. The effect on grain yield was stronger, while Salmag® with Fe was slightly weaker than pure Salmag®. All applied nitrogen fertilisers increased total N in grain and straw and Ca and Mg in spring wheat straw. Nitrogen fertilisers enriched with micronutrients generally had a weaker effect than Salmag® on the content of total N in grain (in contrast to straw) and Ca and Mg. The addition of Cu, Mo, and especially Fe chelates increased the content of chelated elements in spring wheat, especially in straw. The pH value of the soil after harvest of spring wheat was slightly higher after the application of Salmag® and lower in the soil fertilised with Salmag® with Mo and Salmag® with Fe than in the control. Salmag® and Salmag® with Cu showed a significant increase in soil Mg and all nitrogen fertilisers (especially Salmag® with Fe) in soil Ca content after spring wheat harvest. Salmag® with Cu caused the greatest increase in soil Cu content.

The study shows that the application of the new fertilisers with Mo chelate and especially with Cu chelate has a significant effect on the yield and quality of spring wheat.

Author Contributions: Conceptualization, R.G., M.S.B., and M.W.; methodology, M.S.B. and M.W.; investigation, M.S.B. and M.W.; analysis, M.S.B. and M.W.; visualization, M.W.; writing—review and editing, M.W., M.S.B. and R.G.; supervision, M.W., M.S.B. and R.G.; M.W., corresponding author. All authors have read and agreed to the published version of the manuscript.

Funding: The study was funded as a part of The National Centre for Research and Development project No. POIR.01.02.00-00-0023/16 in projects realized by the University of Life Sciences in Lublin, Faculty of Agrobioengineering, Department of Agricultural and Environmental Chemistry (grant No. 01/RG/ID/NI/GA ZAK/UPLublin/2021) and by the University of Warmia and Mazury in Olsztyn, Faculty of Agriculture and Forestry, Department of Agricultural and Environmental Chemistry (grant No. 30.690.078-500 and grant No. 30.610.004-110).

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: Author Ryszard Grzesik was employed by the company Grupa Azoty Zakłady Azotowe Kędzierzyn S.A. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Stanisławska-Glubiak, E.; Korzeniowska, J. Analysis of the micronutrient fertiliser market against the needs for micronutrient fertilisation in Poland. *Stud. Rep. Inst. Soil Sci. Plant Cultiv. (IUNG-PIB)* **2016**, *63*, 145–161. [CrossRef]
2. Kabata-Pendias, A.; Szteke, B. *Trace Elements in Abiotic and Biotic Environments*, 1st ed.; CRC Press, Taylor and Francis Group: Boca Raton, FL, USA, 2015; p. 468. [CrossRef]
3. Shiwakoti, S.; Zheljazkov, V.D.; Gollany, H.T.; Kleber, M.; Xing, B.; Astatkie, T. Micronutrients in the soil and wheat: Impact of 84 years of organic or synthetic fertilization and crop residue management. *Agronomy* **2019**, *9*, 464. [CrossRef]
4. Thapa, S.; Bhandari, A.; Ghimire, R.; Xue, Q.; Kidwaro, F.; Ghatrehsamani, S.; Maharjan, B.; Goodwin, M. Managing micronutrients for improving soil fertility, health, and soybean yield. *Sustainability* **2021**, *13*, 11766. [CrossRef]
5. Denton-Thompson, S.M.; Sayer, E.J. Micronutrients in food production: What can we learn from natural ecosystems? *Soil Syst.* **2022**, *6*, 8. [CrossRef]
6. Aciksoz, S.B.; Yazici, A.; Ozturk, L.; Cakmak, I. Biofortification of wheat with iron through soil and foliar application of nitrogen and iron fertilizers. *Plant Soil* **2011**, *349*, 215–225. [CrossRef]
7. Barczyk, K.; Jasiak-Małota, K.; Brodowska, M. Efficiency of using aminochelate fertilizers in plant nutrition. *Przem. Chem.* **2024**, *103*, 271–276. [CrossRef]
8. Sekhon, B.S. Chelates for micronutrient nutrition among crops. *Resonance* **2003**, *8*, 46–53. [CrossRef]
9. Yudaev, P.; Chistyakov, E. Chelating extractants for metals. *Metals* **2022**, *12*, 1275. [CrossRef]
10. Klem-Marciniak, E.; Huculak-Mączka, M.; Marecka, K.; Hoffmann, K.; Hoffmann, J. Chemical stability of the fertilizer chelates Fe-EDDHA and Fe-EDDHSA over time. *Molecules* **2021**, *26*, 1933. [CrossRef]
11. Grzesik, R.; Pankalla, E.; Kuźnik, N. Coating of calcium ammonium nitrate fertilizers with model chelates. *Przem. Chem.* **2022**, *101*, 810–814. [CrossRef]
12. Saridis, G.; Chorianopoulou, S.N.; Ventouris, Y.E.; Sigalas, P.P.; Bouranis, D.L. An exploration of the roles of ferric iron chelation-strategy components in the leaves and roots of maize plants. *Plants* **2019**, *8*, 133. [CrossRef]
13. Patent No. 242478. Process for Obtaining Biodegradable Micronutrient Fertiliser Components and Biodegradable Micronutrient Fertiliser Components. 2022. Available online: https://ewyszukiwarka.pue.uprp.gov.pl/search/pwp-details/P.435383 (accessed on 8 July 2024).
14. IUSS Working Group WRB. World Reference Base for Soil Resources 2014. In *International Soil Classification System for Naming Soils and Creating Legends for Soil Maps*; Update 2015; World Soil Resources Reports No. 106; FAO: Rome, Italy, 2015; p. 182. Available online: https://www.fao.org/3/i3794en/I3794en.pdf (accessed on 28 May 2024).
15. Salmag® Specification. Available online: https://grupaazoty.com/upload/1/files/2024/nawozy/Specification%20Salmag%205.02.2024_EN.pdf (accessed on 5 June 2024).
16. 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.
17. *PN-R-04032*; Soil and Mineral Materials—Sampling and Determination of Particle Size Distribution. Polish Committee for Standardization: Warszawa, Poland, 1998.
18. *ISO 10390*; Soil Quality—Determination of pH. International Organization for Standardization: Geneva, Switzerland, 2005.
19. *ISO 11261*; Soil Quality—Determination of Total Nitrogen—Modified Kjeldahl Method. International Organization for Standardization: Geneva, Switzerland, 1995.
20. TIBCO Software Inc. Statistica (Data Analysis Software System), Version 13.3. 2017. Available online: http://statistica.io (accessed on 28 December 2023).
21. He, Z.L.; Yang, X.E.; Stoffella, P.J. Trace elements in agroecosystems and impacts on the environment. *J. Trace Elem. Med. Biol.* **2005**, *19*, 125–140. [CrossRef]
22. Alloway, B.J. Micronutrient Deficiencies in Global Crop Production. Springer Science & Business Media B.V.: Berlin, Germany, 2008.
23. Kabata-Pendias, A.; Pendias, H. *Trace Elements in Soils and Plants*, 3rd ed.; CRC Press, Taylor and Francis Group: Boca Raton, FL, USA, 2001; p. 403.

24. Grześkowiak, A. Vademecum on Fertilisation or Basic and Practical Information on Sustainable Fertilisation; Grupa Azoty Zakłady Chemiczne „Police" S.A., Police, 2016, 1–112. Available online: https://polifoska.pl/images/pliki/vademecum-nawozenia.pdf (accessed on 5 July 2024).
25. Rana, M.S.; Hu, C.X.; Shaaban, M.; Imran, M.; Afzal, J.; Moussa, M.G.; Elyamine, A.M.; Bhantana, P.; Saleem, M.H.; Syaifudin, M.; et al. Soil phosphorus transformation characteristics in response to molybdenum supply in leguminous crops. *J. Environ. Manag.* **2020**, *268*, 110610. [CrossRef]
26. Rana, M.S.; Sun, X.C.; Imran, M.; Ali, S.; Shaaban, M.; Moussa, M.G.; Khan, Z.; Afzal, J.; Binyamin, R.; Bhantana, P.; et al. Molybdenum-induced effects on leaf ultra-structure rhizosphere phosphorus transformation in *Triticum aestivum*, L. *Plant Physiol. Biochem.* **2020**, *153*, 20–29. [CrossRef] [PubMed]
27. Meena, V.S.; Meena, S.K.; Verma, J.P.; Kumar, A.; Aeron, A.; Mishra, P.K.; Bisht, J.K.; Pattanayak, A.; Naveed, M.; Dotaniya, M.L. Plant beneficial rhizospheric microorganism (PBRM) strategies to improve nutrients use efficiency: A review. *Ecol. Eng.* **2017**, *107*, 8–32. [CrossRef]
28. Abbasi, M.K.; Tahir, M.M.; Rahim, N. Effect of N fertilizer source and timing on yield and N use efficiency of rainfed maize (*Zea mays* L.) in Kashmir—Pakistan. *Geoderma* **2013**, *195*, 87–93. [CrossRef]
29. Szulc, P.; Bocianowski, J.; Kruczek, A.; Szymanska, G.; Roszkiewicz, R. Response of two cultivar types of maize (*Zea mays* L.) expressed in protein content and its yield to varied soil resources of N and Mg and a form of nitrogen fertilizer. *Polish J. Environ. Stud.* **2013**, *22*, 1845–1853. Available online: http://www.pjoes.com/pdf-89154-23013?filename=Response%20of%20Two%20Cultivar.pdf (accessed on 8 July 2024).
30. Wierzbowska, J.; Żuk-Gołaszewska, K. The impact of nitrogen fertilization and *Rhizobium* inoculation on the yield and quality of *Trigonella foenum-graecum* L. *J. Elem.* **2014**, *19*, 1109–1118. [CrossRef]
31. 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]
32. 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]
33. 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]
34. Zhou, H.; Meng, H.; Zhao, L.; Shen, Y.; Hou, Y.; Cheng, H.; Song, L. Effect of biochar and humic acid on the copper, lead, and cadmium passivation during composting. *Bioresour. Technol.* **2018**, *258*, 279–286. [CrossRef] [PubMed]
35. Wyszkowski, M.; Brodowska, M.S. Content of trace elements in soil fertilized with potassium and nitrogen. *Agriculture* **2020**, *10*, 398. [CrossRef]
36. 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]
37. Wyszkowski, M.; Brodowska, M.S. Potassium and nitrogen fertilization vs. trace element content of maize (*Zea mays* L.). *Agriculture* **2021**, *11*, 96. [CrossRef]
38. 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]
39. Miner, G.L.; Delgado, J.A.; Ippolito, J.A.; Barbarick, K.A.; Stewart, C.E.; Manter, D.K.; Del Grosso, S.J.; Halvorson, A.D.; Floyd, B.A.; D'Adamo, R. Influence of long-term nitrogen fertilization on crop and soil micronutrients in a no-till maize cropping system. *Field Crops Res.* **2018**, *228*, 170–182. [CrossRef]
40. Ali, N.S.; Hassan, W.F.; Janno, F.O. Soil iron and nitrogen availability and their uptake by maize plants as related to mineral and bio nitrogen fertilizers application. *Agric. Biol. J. North Am.* **2015**, *6*, 118–122. [CrossRef]
41. Aladesanmi, O.T.; Oroboade, J.G.; Osisiogu, C.P.; Osewole, A.O. Bioaccumulation factor of selected heavy metals in *Zea mays*. *J. Health Pollut.* **2019**, *9*, 191207. Available online: https://www.journalhealthpollution.org/doi/pdf/10.5696/2156-9614-9.24.191207 (accessed on 8 July 2024). [CrossRef]
42. Schoffer, J.T.; Sauve, S.; Neaman, A.; Ginocchio, R. Role of leaf litter on the incorporation of copper-containing pesticides into soils under fruit production: A review. *J. Soil Sci. Plant Nutr.* **2020**, *10*, 990–1000. [CrossRef]
43. Jenkins, S.N.; Murphy, D.V.; Waite, I.S.; Rushton, S.P.; O'Donnell, A.G. Ancient landscapes and the relationship with microbial nitrification. *Sci. Rep.* **2016**, *6*, 30733. [CrossRef]
44. Adhikari, L.; Missaoui, A.M. Nodulation response to molybdenum supplementation in alfalfa and its correlation with root and shoot growth in low pH soil. *J. Plant Nutr.* **2017**, *40*, 2290–2302. [CrossRef]
45. Ge, X.X.; Vaccaro, B.J.; Thorgersen, M.P.; Poole, F.L.; Majumder, E.L.; Zane, G.M.; De Leon, K.B.; Lancaster, W.A.; Moon, J.W.; Paradis, C.J.; et al. Iron- and aluminium-induced depletion of molybdenum in acidic environments impedes the nitrogen cycle. *Environ. Microbiol.* **2019**, *21*, 152–163. [CrossRef]
46. Shcherbakova, E.N.; Shcherbakov, A.V.; Andronov, E.E.; Gonchar, L.N.; Kalenskaya, S.M.; Chebotar, V.K. Combined pre-seed treatment with microbial inoculants and Mo nanoparticles changes composition of root exudates and rhizosphere microbiome structure of chickpea (*Cicer arietinum* L.) plants. *Symbiosis* **2017**, *73*, 57–59. [CrossRef]
47. Wen, X.; Hu, C.X.; Sun, X.C.; Zhao, X.H.; Tan, Q.L.; Liu, P.J.; Xin, J.; Qin, S.Y.; Wang, P.C. Characterisation of vegetable nitrogen uptake and soil nitrogen transformation in response to continuous molybdenum application. *J. Plant Nutr. Soil Sci.* **2018**, *181*, 516–527. [CrossRef]

48. Kwiatkowski, C.A.; Harasim, E. Chemical properties of soil in four-field crop rotations under organic and conventional farming systems. *Agronomy* **2020**, *10*, 1045. [CrossRef]
49. Abbasi, M.K.; Zafar, M.; Sultan, T. Changes in soil properties and microbial indices across various management sites in the mountain environments of Azad Jammu and Kashmir. *Commun. Soil Sci. Plant Anal.* **2010**, *41*, 768–782. [CrossRef]
50. Mimmo, T.; Del Buono, D.; Terzano, R.; Tomasi, N.; Vigani, G.; Crecchio, C.; Pinton, R.; Zocchi, G.; Cesco, S. Rhizospheric organic compounds in the soil-microorganism-plant system: Their role in iron availability. *Eur. J. Soil Sci.* **2014**, *65*, 629–642. [CrossRef]
51. Sharma, S.; Dhaliwal, S.S. Effects of sewage sludge and rice straw compost on yield, micronutrient availability and soil quality under rice-wheat system. *Commun. Soil Sci. Plant Anal.* **2019**, *50*, 1943–1954. [CrossRef]
52. Wyszkowski, M.; Wyszkowska, J.; Borowik, A.; Kordala, N. Sewage sludge as a tool in limiting the content of trace elements in *Avena sativa* L. on the soil polluted with diesel oil. *Materials* **2021**, *14*, 4003. [CrossRef]
53. Ghasemi, S.; Khoshgoftarmanesh, A.H.; Afyuni, M.; Hadadzadeh, H. The effectiveness of foliar applications of synthesized zinc-amino acid chelates in comparison with zinc sulfate to increase yield and grain nutritional quality of wheat. *Eur. J. Agron.* **2013**, *45*, 68–74. [CrossRef]
54. Ghasemi, S.; Khoshgoftarmanesh, A.H.; Afyuni, M.; Hadadzadeh, H. Iron(II)-amino acid chelates alleviate salt-stress induced oxidative damages on tomato grown in nutrient solution culture. *Sci. Horticult.* **2014**, *165*, 91–98. [CrossRef]
55. Popko, M.; Michalak, I.; Wilk, R.; Gramza, M.; Chojnacka, K.; Górecki, H. Effect of the new plant growth biostimulants based on amino acids on yield and grain quality of winter wheat. *Molecules* **2018**, *23*, 470. [CrossRef] [PubMed]
56. Jacob, R.H.; Afify, A.S.; Shanab, S.M.; Shalaby, E.A.; Hafez, R.M. Biotechnological studies on *Arthrospira platensis* biomass cultivated in enriched culture with chelated leather waste and chelated glycinate. *Biomass Conv. Bioref.* **2022**, *2022*, 1–23. [CrossRef]
57. Najizadeh, A.; Khoshgoftarmanesh, A.H. Effects of foliar applied zinc in the form of $ZnSO_4$ and Zn-amino acid complexes on pistachio nut yield and quality. *J. Plant Nutr.* **2019**, *42*, 2299–2309. [CrossRef]
58. Yeboah, S.; Asibuo, J.; Oteng-Darko, P.; Adjei, E.A.; Lamptey, M.; Danquah, E.O.; Waswa, B.; Butare, L. Impact of foliar application of zinc and magnesium aminochelate on bean physiology and productivity in Ghana. *Int. J. Agron.* **2021**, *2021*, 9766709. [CrossRef]
59. Soltani, S.M.; Chaleshtori, M.H.; Talab, K.T.; Vahed, H.S.; Katigari, M.S. Rice growth improvement, bio-fortification, and mitigation of macronutrient requirements through foliar application of zinc and iron- glycine chelate and zinc sulfate. *J. Plant Nutr.* **2023**, *46*, 1777–1786. [CrossRef]