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Foliar Application of Copper-Tetramine-Sulphate from Microelectronic Waste to Improve Yield and Quality Parameters of Winter Wheat

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The growth of the world's population is an increasing challenge for agricultural production. Improving soil productivity is the key to ensuring the quantity, quality and safety of food for a growing population. In addition to macroelements, microelements also play an important role in the biochemical processes. A large percentage of soils in Hungary show a deficiency in copper. For three years, we treated the leaves of winter wheat with a copper-tetramine-sulphate complex derived from microelectronic waste. Aim to provide an alkaline pH range of 9.3 for effective foliar treatment. Treatments were applied on 10 m^2 small plots at 0; 0.1; 0.3; 0.5; 1.0; and 2.0 kg×ha^{-1} copper dose in the budding and flowering phenological stages with copper-tetramine-sulphate produced from microelectronic waste. After harvesting the crop from the plots, the yield, raw protein, and gluten content were measured. In the copper-deficient soil, a significant increase in yield and protein and gluten levels was observed after treatment with copper foliar fertiliser. The most significant increase in yield was obtained in the treatment at flowering (0.40 t/ha), with a 0.37 % increase in crude protein content and a 1.95 % increase in wet gluten content.

1. Introduction

The world's population has been growing at an explosive rate since the middle of the last century, with the population expected to reach 9.8 billion by 2050. Providing food - in sufficient quantity, quality and security - for a growing population is a major challenge in itself. Agriculture, including arable farming, has an inescapable role to play in this (Giczi et al., 2020).

For sustainability, more attention needs to be paid to soil nutrient availability, structure and quality (Kalocsai et al., 2022). In order to produce quantitative agricultural products, worldwide priority has been given to replenishing the three macro elements (N, P, K). It is only in the last decades that the deficiency of micronutrients in the soil, which is a result of their removal from the products, has started to be noticed, and its negative impact on the quantity and quality of the crop has been demonstrated (Allen et al., 2006).

Wheat is one of the world's most important cereal crops from a nutritional point of view, which is essential for developing countries (Erenstein et al., 2022). In Hungary, winter wheat is one of the most important crops, grown on nearly 1 Mha. For wheat production, the best-quality soils show a lack of copper, which can be replaced to improve yield and quality (Giczi et al., 2020). In addition, winter wheat is sensitive to copper deficiency.

The aim of the research is to increase the quantitative and qualitative parameters of winter wheat grown on soils with copper deficiencies, which are often found in agricultural production, in order to achieve higher nutrient content and healthy nutrition. Complex compounds produced by recycling copper-containing wastes were used to make up for the copper deficiency in the crops. A novel solution is to recycle copper-containing waste to make up for nutrient deficiencies in crop production (Szakál et al., 2022).

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1.1 Effect of copper on wheat yield and quality

Copper supplementation as foliar fertilizer on copper-deficient soils has been shown to improve winter wheat yield and quality (Flynn et al., 1987). The beneficial effect of copper foliar treatment on the main quality parameters of wheat flour (moisture, protein, wet gluten, dry gluten, specific weight, flour extraction, percentage of copper in grains, starch and ash) was investigated (Rawaa and Enas, 2023). Ratan Kumar and colleagues (2009) observed an improvement in yield and a decrease in leaf iron with increasing soil copper content. Polish researchers increased gluten content by foliar treatment of winter wheat with copper. Yassen and co-workers (2020) treated wheat foliage with EDTA and amino acid complex. The excellent fungicidal activity of copper compounds may improve their role in the healthy nutrition of food (Giczi et al., 2021).
In copper-deficient soils of winter wheat, foliar fertilisation with copper treatments has been reported to improve nitrogen uptake (Schmidt et al., 2004).
Due to the high cost of copper supplementation through soil, foliar fertilisation has been preferred. The composition and structure of the soil and the weather conditions do not allow the soil to meet the constantly changing needs of the plants during the growing season and to supply them with adequate nutrients, and an imbalance in the supply of nutrients can occur. These negative effects can be reduced by understanding the dynamics of foliar fertilisation. Variable nutrient requirements during plant development can be well compensated by applying the right nutrients per foliar fertiliser.

2. Material and method

The statistical software packages agricolae, car and stats of RStudio 2023.9.1 were used for the analysis of variance (ANOVA) for statistical evaluation. Differences between means were evaluated using Tukey's test ($\alpha = 0.05$). Tests of normality and homogeneity of variances were performed before the analysis of the variance of the data. ANOVA was also performed for each year and for the 3 y average.

2.1 Copper-tetramine-sulphate complex compound

The microelectronics industry produces large quantities of copper sulphate solutions of very high purity. The aim is to develop a complex compound from the waste where the ligand is useful to the plant, has good uptake and adequate complex stabilisation. The choice was made to produce copper-tetramine-sulphate from waste. The Cu^{++} ammonia forms a complex with CuX_2 n NH_3 ligands, where n can be 2, 4, 5 or 6. $[Cu(NH_3)_4(H_2O)]SO_4$ is crystallised by adding alcohol to an ammonia solution of copper-sulphate, a complex compound in which the four nitrogen atoms are arranged in a square planar arrangement around copper (II) with water in the fifth position (Morosin and Larson, 1969).
The complex multiplicities in copper tetramine are, in order, β 1 = 4.14, β 2 = 7.66, β 3 = 10.53, β 4 = 12. The copper-tetramine complex solution at pH 9.3 contains the highest amount of $Cu(NH_3)_4^{2+}$ ion (Bjerrum, 1982; Velásquez-Yévenes and Ram, 2022) (Figure 1). A copper complex with a pH of 9.3 produced from waste provides more favourable conditions for plants to uptake nutrients. At lower pH values, a phytotoxic effect is exerted.

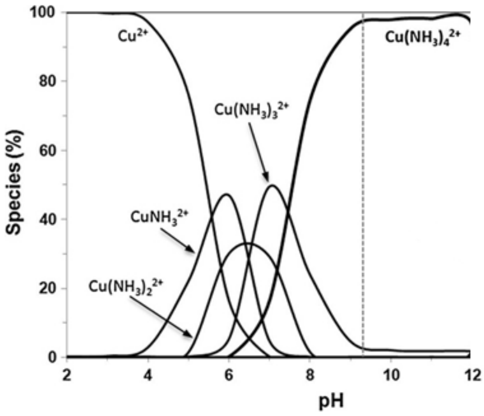

Figure 1: Species distribution of copper-amine complex as a function of pH (Szakál et al., 2021)

2.2 Soil analysis

Copper (Cu) were determined from EDTA extract with KCl (0.05 mol/dm^3 EDTA and 0.1 mol/dm^3 KCl) by ICP-AES.

2.3 Production of copper-tetramine-sulphate

A copper-tetramine-sulphate with a copper content of 12.0 w/w% and a pH of 9.3 was prepared by the reaction of a microelectronic solution containing copper sulphate with concentrated 26.8 w/w% ammonium hydroxide used for the production of agricultural fertilisers under industrial conditions. The species distribution of the copper-amine complexes as a function of pH shows that the tetramine form is predominant at this pH (Figure 1). This pH does not yet cause significant toxic effects on the leaves of winter wheat. The complex compound crystallised from Copper-tetramine-sulphate under cooling was analysed by Q-1500 D MOM derivatography.

2.4 Leaf treatment experiments

Copper foliar fertilisation experiments were set up on copper-deficient soils (Győrszentiván, Hungary) in 2022, 2023 and 2024. Leaf fertilisation experiments were set up in a random block design with four replicates in 10 m^2 plots. Foliar treatments were carried out at budding and flowering phenological stages. The copper doses of the treatments with the copper-tetramine sulphate complex were Cu 0, 0.1, 0.3, 0.5, 1.0, and 2.0 kg^{-1}. After harvesting the plots, the yield, raw protein and gluten were measured. The determination of raw protein was performed with Infratec™ 1241 Grain Analyzer laboratory instrument. The measurement was performed in near-infrared transmission mode at 570 – 1,050 nm.

3. Results and their evaluation

3.1 Derivatographic analysis of copper tetramine sulphate

The derivatogram of copper-tetramine-sulphate is shown in modified Figure 2 (Szakal et al., 2021).

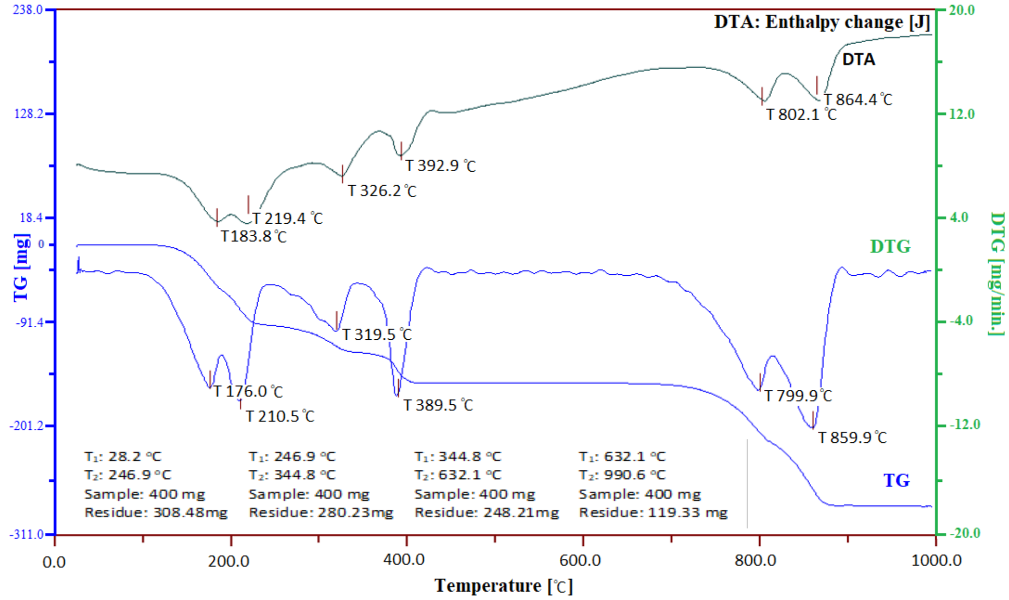

Figure 2: Thermal stability of copper-tetramine-sulphate (Szakal et al., 2021) modified figure

The four peaks at 176.0 °C, 210.5 °C, 319.5 °C and 389.5 °C during heating show mass loss and endothermic processes (DTA). The mass loss associated with the four peaks (TG curve) is assumed to be related to the removal of four ammonium species from the copper-tetramine complex by decomposition of the complex. Up to the measured 632.1 °C, the four ammonia molecules were completely removable during the decomposition of the complex. The calculated ammonia content of the measured 400 mg of copper-tetramine-sulphate is 119.53 mg (29.882 w/w%). The weight loss measured at higher temperatures on TGs (799.9 °C and 859.9 °C) is due to the decomposition of sulphate ($2CuSO_4 \xrightarrow{t°C} 2CuO + 2SO_2 + O_2$).
The studies confirm that by spraying copper-tetramine-sulphate on the surface of the plant under the temperature conditions of the growing season, the compound remains stable, does not undergo any harmful transformation and does not decompose. The copper-ion remains in a complex that can be taken up by plants.

3.2 Soil testing

The composition of the soil samples taken at depths of 0-30 cm, 30-60 cm, and 60-90 cm in the selected copper-deficient experimental area is shown in Table 1.

Table 1: Changes in the copper content of soils in the deeper layers. Győrszentiván (Hungary)

Year	**Depth**		
	0-30 cm	*30-60 cm*	*60-90 cm*
2022	0.68 mg×kg^{-1}	0.41 mg×kg^{-1}	0.29 mg×kg^{-1}
2023	0.81 mg×kg^{-1}	0.41 mg×kg^{-1}	0.31 mg×kg^{-1}
2024	1.21 mg×kg^{-1}	0.71 mg×kg^{-1}	0.29 mg×kg^{-1}

The soil test results show that the experimental field soil has a low value for the uptake copper content. The copper content of the soils in all three experimental sites steadily decreases towards the lower layers, not providing the plant with a sufficient copper supply.

3.3 Statistical evaluation of results

The primary objective was to develop a reliable treatment that would have a consistent effect over several years under different environmental conditions. A detailed statistical analysis of the experimental data was carried out using the average of the data for the three experimental years (2022, 2023 and 2024). Statistical evaluation was carried out separately to determine the effects of treatments at budding and flowering on yield, raw protein, and gluten content. ANOVA analysis showed that the treatments applied had a significant effect on the traits tested: $F(5,15) = 10.0$, $p < .001$ (at budding) and $F(5,15) = 13.5$, $p < .001$ (at flowering) for yield; $F(5,15) = 38.9$, $p < .001$ and $F(5,15) = 19.6$, $p < .001$ for raw protein content, and $F(5,15) = 5.73$, $p = .004$ and $F(5,15) = 13.8$, $p < .001$ for the gluten content. Since the effect of treatments was significant, differences between means were also evaluated using Tukey's test ($\alpha = 0.05$). The resulting minimum significant difference (MSD) values for yield were 0.32 t/ha for the tillering-time treatment and 0.40 t/ha for the flowering treatment (Figure 3). The same values for raw protein content were 0.37 % and 0.36 % (Figure 4), and for gluten content, 1.95 % and 0.82 % (Figure 5).

In the experiments, the highest yields were obtained in the 3 y average for the treatment at 2 kg×ha^{-1} for the tillering-time treatment and 0.5 kg×ha^{-1} for the flowering treatment, with 6.78±0.30 t×ha^{-1} and 6.93±0.29 t×ha^{-1}, but in the latter case, the difference between the three highest dose treatments was not significant at the 95 % significance level. The yield of the bushing treatment at 2 kg×ha^{-1} was significantly higher than the control (0.52 t×ha^{-1}). For treatment at flowering, starting from a dose of 0.5 kg×ha^{-1} at 0.57-0.74 t×ha^{-1}. Compared to the tillering-time treatment, the flowering-time treatment was more favourable for increasing yield (Figure 3).

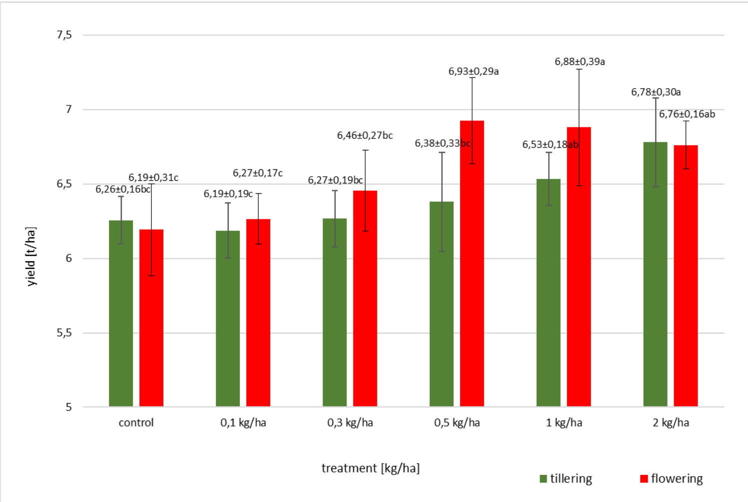

Figure 3: Effect of copper treatments on yield. The error bars represent the 95 % confidence interval. Different letters indicate significantly different effects between treatments (ANOVA, Tukey test, p < 0.05)

The treatments used resulted in higher raw protein content than the control treatment, from 0.3 kg×ha^{-1} for the tillering-time treatment and 0.5 kg×ha^{-1} for the flowering-time treatment. The highest raw protein content, 12.4±0.1 %, was obtained with 2 kg×ha^{-1} treatment at the tillering stage. Maximum raw protein content was 11.9±0.2 % in the flowering treatments at 1 kg×ha^{-1} and 2 kg×ha^{-1}. Compared to the control treatment, the increase in protein content was 1.2 % in the treatment at budding and 0.8 % in the treatment at flowering (Figure 4).

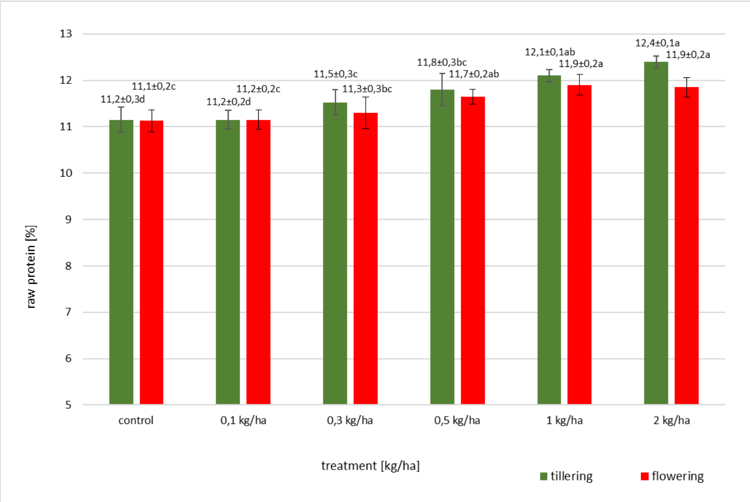

Figure 4: Effect of copper treatments on raw protein content. The error bars represent the 95 % confidence interval. Different letters indicate significantly different effects between treatments (ANOVA, Tukey test, $p < 0.05$).

The highest value (29.3±1.3 %) of gluten content in the treatment at the time of tillering was obtained with the treatment at the dose of 1 kg×ha^{-1}. For both the 1 kg×ha^{-1} and 2 kg×ha^{-1} treatment at flowering, the yield was 28.4±.7 %. Compared to the control treatment, the highest value was obtained in the tillering-time treatment (2.6 %) and the highest in the flowering-time treatment (1.7 %) (Figure 5).

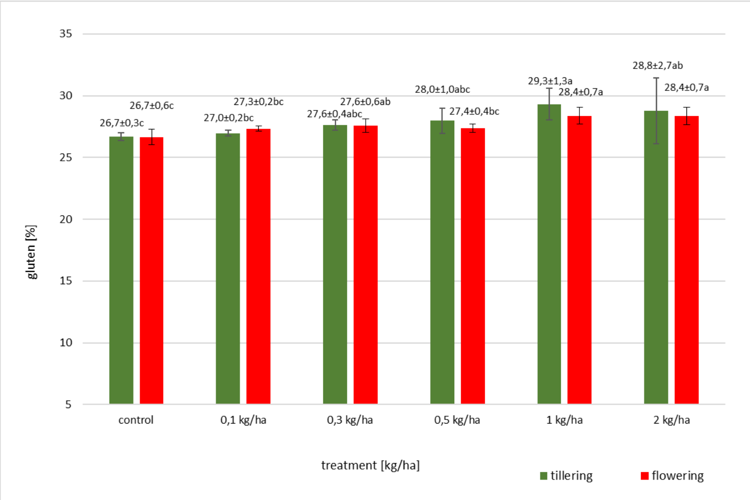

Figure 5: Effect of copper treatments on gluten content. The error bars represent the 95 % confidence interval. Different letters indicate significantly different effects between treatments (ANOVA, Tukey test, $p < 0.05$).

4. Conclusions

The aim of the research is to produce copper tetramine sulphate with alkaline pH from high-purity acidic pH microelectronic waste, which is generated in large quantities and is suitable for increasing the copper content of winter wheat grown on copper-deficient soils.

Experiments with foliar fertilisation over 3 y: They were set in Hungary in 2022, 2023 and 2024 on copper-deficient brown forest soils. The copper-complex compound was applied as foliar fertilizer at the tillering and flowering phenological stages. The copper treatments resulted in a significant increase in yield, protein and gluten content. The yield increases in the phenological phase at flowering, and raw protein and gluten content increase most with the copper complex applied in the phenological phase at budding. The toxic effect of the compound was already observed with the higher dose of 2 kg×ha^{-1} copper applied at flowering.

The treatments showed the most significant yield increase in the flowering treatment (0.40 t/ha), with a 0.37 % increase in crude protein and 1.95 % increase in wet gluten compared to the control.

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