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Micronutrient content in maize grown for green fodder fertilized with suspension fertilizers based on waste phosphorus salts from polyol production

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Abstract: The need to import phosphorus raw materials for fertilization in Europe and the increasing amount of waste have driven the search for alternative phosphorus sources. One such waste material is sodium-potassium phosphate waste generated during polyol production. In addition, ensuring an adequate food supply remains a critical challenge, with fertilizers playing a key role. Due to the increase in meat consumption, the attractiveness of growing feed corn is increasing, given its high yield potential and rich composition. The article examines the effect of suspension fertilizers derived from polyol production waste on the micronutrient content of corn intended for green fodder. In a 3-year field study, the impact of the waste-derived phosphorus source was compared with a commercial granular phosphorus fertilizer, Fosdar 40. Additionally, the composition of suspension fertilizers was assessed, including those containing only basic nutrients (NPK) and those enriched with secondary nutrients (S, Mg) and micronutrients (Zn, Mn, B). The results confirmed the effectiveness of the tested suspension fertilizers. The micronutrient content in the dry matter of maize was comparable to that of the control treatment fertilized with Fosdar 40.two-step method.

Introduction

The global population of both humans and farm animals is steadily increasing, driving a growing demand for food and feed. The United States has the highest per capita meat consumption, which rose by 40% between 1961 and 2020. Israel ranks second, with an average consumption of 90.5 kg per capita, followed by Australia at 89.3 kg per capita. In contrast, many countries in Africa and Asia have significantly lower meat consumption. In the EU, meat consumption is more than twice the global average. In Poland, it remains stable and high (75.5 kg per capita). Given land area limitations, optimizing feed crop quality and efficiency is essential (Kashyap et al., 2023).

Maize (*Zea mays L.*) is a widely used forage plant due to its rapid growth, high dry matter accumulation, and palatability (Bhaumik et al., 2023). Compared to other forage crops, it has high digestibility, and its sugar content facilitates preservation as silage. However, its alternative content is relatively low - about 7-9% in dry matter. (Baljeet et al., 2020; Bhaumik et al., 2023; Kashyap et al., 2023).

Maize is highly demanding in terms of fertilization (Kashyap et al., 2023; Kumar et al., 2017). In addition to essential macronutrient fertilization, micronutrient supplementation enhances both the yield and quality of the crop (Kalashnikov et al., 2020). Micronutrients play a crucial role in nutrient synthesis and transformation, as components of enzymes (Bhaumik et al., 2023; Kalashnikov et al., 2020). They are also essential for key plant processes, including photosynthesis, fruit and seed ripening, productivity, and resistance to stress conditions (Kalashnikov et al., 2020; Services & Division, 2009).

The availability of micronutrients to plants depends on soil pH and decreases as pH increases, primarily due to the high concentrations of calcium and magnesium (Conley, 2011; Farshid Aref, 2012; Services & Division, 2009). A one-unit increase in soil pH within the range of 4-9 results in a thousand-fold reduction in Fe solubility, leading to Fe deficiencies, particularly in limestone soils (Farshid Aref, 2012). Similarly, the bioavailability of Zn, Mn and Cu decreases a hundred-fold with each unit increase in soil pH (Farshid Aref, 2012; Galanti, 2014).

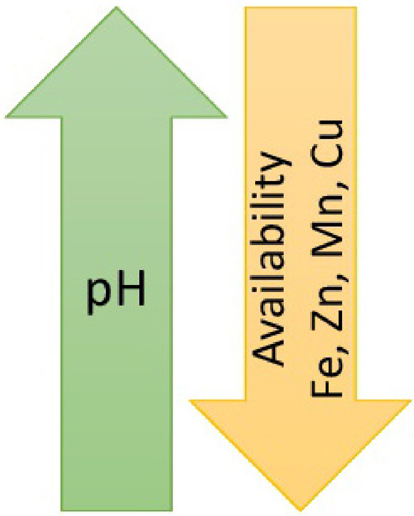

Fig 1. Availability of microelements depending on soil pH

This paper analyzes the content of selected micronutrients (Zn, Mn, Fe, Cu) in whole maize plants grown for feed. The plant samples were collected from a 3-year field experiment testing suspension fertilizers derived from waste sodium-potassium phosphate, a byproduct of polyol production at PCC Rokita in Brzeg Dolny. For comparison, the control group received fertilizers with the same NPK composition, but with phosphorus sourced from a commercially available granular fertilizer - Fosdar 40.

Recovering phosphorus from polyol waste for fertilizer production is a significant challenge. The main source of phosphorus in the fertilizer industry is non-renewable phosphate rock, which is gradually being depleted. Moreover, these deposits are unevenly distributed, with nearly two-thirds located in China, the USA and Morocco. Europe lacks economically significant phosphate resources and is almost entirely dependent on imports. Another concern is phosphate contamination with cadmium. In response, new EU regulations promote phosphorus recovery from waste streams and aim to reduce cadmium content in fertilizers, which is in line with the goals of the circular economy.

Materials and Methods

A field experiment tested the effect of 6 suspension fertilizers, where phosphorus was sourced from sodium-potassium phosphate waste generated during polyol production. A detailed characterization this waste is presented in “The Possibility of Using Waste Phosphates from the Production of Polyols for Fertilizing Purposes” (Bogusz, 2022). The method for producing the suspention fertilizers used in the experiment is described in “Suspension Fertilizers Based on Waste Phosphates from the Production of Polyols” (Bogusz et al., 2022). The field experiment and maize yield results are discussed in "The Impact of Suspension Fertilizers Based on Waste Phosphorus Salts from Polyol Production on the Yield of Maize Intended for Green Fodder"(Bogusz, Brodowska & Rusek, 2024). Additionally, “The Impact of Suspension Fertilizers Based on Waste Phosphorus Salts from Polyol Production on the Content of Macronutrients in Maize Grown for Green Fodder” examines their influence on the macronutrient ontent in maize (Bogusz, Brodowska & Muszyński, 2024).

Figure 1 shows the classification of fertilizers used in the field experiment based on their composition.

Suspension fertilizers were prepared in two formulations of the main NPK nutrients, which differed in phosphorus content (4% and 6%). Each formulation was tested in three variants: as a basic NPK fertilizer, with the addition of secondary nutrients (Mg and S), and with the addition of micronutrients (Zn, Mn and B). For comparison, two control fertilizers with the same NPK composition as the suspension fertilizers were used, but with phosphorus sourced from the commercial granular fertilizer Fosdar. Each fertilizer was applied to the field in two nitrogen doses: 135 and 180 kg N ha^{-1}.

A 3-year field study (2021-2023) was conducted in Czesławice, eastern Poland, using medium-early Pioneer P8244 feed corn. The experimental site was classified as

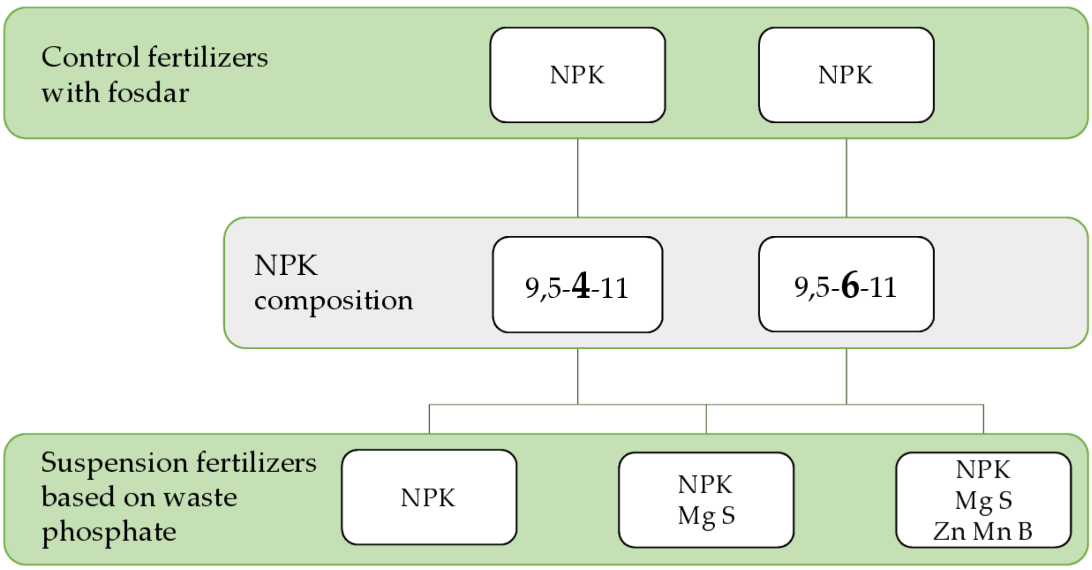

Fig 2. Division of fertilizers used in the field experiment according to their composition

Table 1. Average soil pH value due to the source of phosphorus and its percentage content in the fertilizer.

Year	N dose, kg N/ha (C)	Source of phosphorus in fertilizer (A)						Control without fertilization
		Polyol waste			Fosdar 40 (control)			
		Percentage of P (B)						
		4%	6%	avg.	4%	6%	avg.	
I	180	6.30	6.57	6.43	6.20	5.60	5.90	6.63
	135	6.73	6.60	6.67	6.23	6.57	6.40	
	avg.	6.52	6.58		6.22	6.08		
	avg.	6.55			6.15			
II	180	6.73	6.50	6.62	6.67	6.80	6.73	6.83
	135	6.90	6.73	6.82	6.73	6.93	6.83	
	avg.	6.82	6.62		6.70	6.87		
	avg.	6.72			6.78			
III	180	6.53	6.43	6.48	6.23	6.23	6.23	6.57
	135	6.53	6.47	6.50	6.47	6.70	6.58	
	avg.	6.53	6.45		6.35	6.47		
	avg.	6.49			6.41			

medium soil with a C_{org} content of 0.56%. The soil had very high levels of phosphorus (35 mg · 100 g^{-1} soil P_2O_5), potassium (29.1 mg · 100 g^{-1} soil K_2O), and magnesium (9.2 mg · 100 g^{-1} soil), medium sulfur content (1.04 mg · 100 g^{-1} soil SO_3), and low nitrogen content (N_{min} 57.7 kg· ha^{-1} in the 0-60 cm layer). Essential micronutrients for maize cultivation, such as zinc (10.6 mg · kg^{-1} soil Zn) and manganese (260 mg · kg^{-1} soil Mn), were at moderate levels, while boron content was low (0.99 mg kg^{-1} soil). The soil had a slightly acidic reaction (pH 6.3 in 1 mol KCl · dm^{-3}) and was classified as brown soil.

Fertilizer was applied in two stages: 70% pre-sowing and the remaining portion at the 5-6 leaf stage. Corn was harvested at the milky-waxy maturity stage when moisture content ranged from 30-35%. For analysis, 2m^3 of whole plants were collected from the center of each plot, then cut, mechanically mixed, and sampled (500g) for chemical testing. The samples were dried in an air circulation oven at 70°C until the plant biomass reached a constant weight.

Wet mineralization of plant material from both test and control samples was carried out using a high-temperature

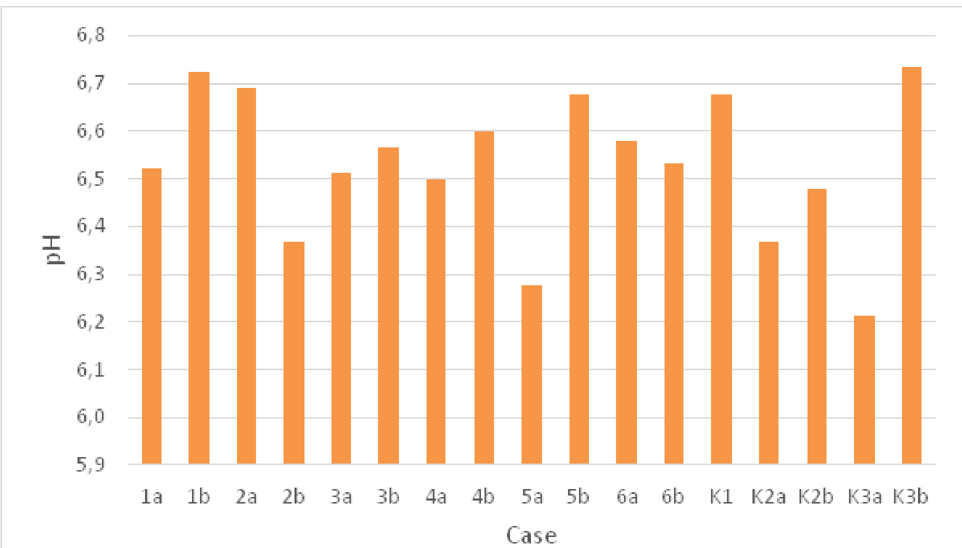

Fig 3. Average soil pH from 3 years of field tests for individual sites

mineralization block. From the dried and ground plant material, 2 g was weighed into glass test tubes, mixed with 15 ml of concentrated sulfuric acid (96%), and left for 24 h. Mineralization was carried out over 5 hours at 350°C in stages: 80/ 120/ 200/ 350°C. The next day, hydrogen peroxide was added to the cooled sample and heated at 350°C until discoloration occurred. The mineralizate was then quantitatively transferred to a volumetric flask and diluted with water to the mark.

The micronutrient content in maize plant material presented in this study was determined using the atomic absorption spectrometry (ASA).

Statistical analysis

The statistical results were prepared using the Statistica 13 program. For this purpose, ANOVA (analysis of variance) for factorial designs was used, and the significance of differences was determined using the post hoc test (Tukey test) at a significance level of α = 0.05, separately for each year of research. Assumptions for the ANOVA test were tested using the Levene test (homogeneity of variances) and the Shapiro–Wilk test (normality of distribution).

For each parameter in individual years, the impact of individual factors (denoted as A, B and, C) and their interaction effects (A × B, A × C, B × C and A × B × C) are presented. The extendt of this influence was assessed using partial eta squared (η^2_p coefficient, which indicates the proportion of variance in the measured parameter explained by each factor.

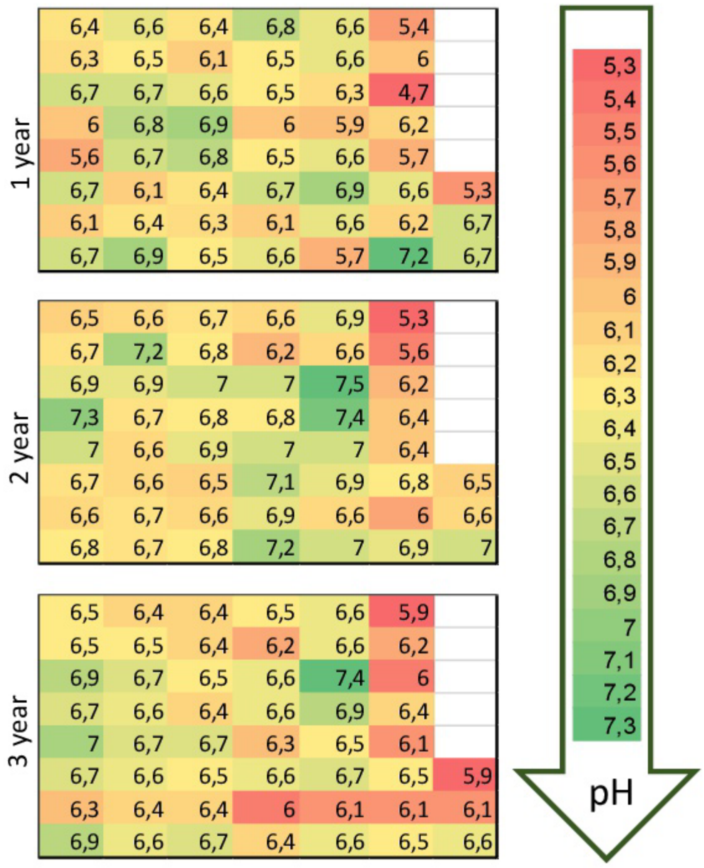

Fig 4. Changes in pH in the plots during the field experiment

Table 2. Average soil pH value due to the type of suspension fertilizer and the percentage of phosphorus.

Year	N dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg micro	avg.	NPK	NPK S Mg	NPK S Mg micro	avg.
I	180	6.30	6.60	6.17	6.36	6.57	6.17	6.30	6.34
	135	6.73	6.23	6.43	6.47	6.60	6.53	6.43	6.52
	avg.	6.52	6.42	6.30		6.58	6.35	6.37	
	avg.	6.41				6.43			
II	180	6.73	6.70	6.80	6.74	6.50	6.30	6.83	6.54
	135	6.90	6.47	6.70	6.69	6.73	7.03	6.67	6.81
	avg.	6.82	6.58	6.75		6.62	6.67	6.75	
	avg.	6.72				6.68			
III	180	6.53	6.77	6.57	6.62	6.43	6.37	6.60	6.47
	135	6.53	6.40	6.57	6.50	6.47	6.47	6.50	6.48
	avg.	6.53	6.58	6.57		6.45	6.42	6.55	
	avg.	6.56				6.47			

The statistical analysis of the results was divided into two parts:

Part I—The effects of fertilizers were compared based on the source of phosphorus (primary factor, 2 levels: polyol waste or phosphorus fertilizer). The secondary factors in this analysis were the phosphorus dose (2 levels: 4% or 6%) and the nitrogen dose (2 levels: 135 or 180 kg N·ha^{-1}). The obtained results were compared againts a control test without fertilization. Using the Tukey test, homogeneous groups were identified for individual results (denoted by lowercase letters: a or b) and for mean values, irrespective of the nitrogen dose (vertical) and phosphorus dose (horizontal), marked with uppercase letters: A, B.

Part II—The effects of the produced suspension fertilizers were analyzed based on the phosphorus dose (4% or 6%), the type of fertilizer (NPK, NKP + Mg + S or NPK + Mg + S + micro), and the nitrogen dose (135 or 180 kg N·ha^{-1}). Using the Tukey test, homogeneous groups were determined for individual results (denoted by lowercase letters: a or b) and for average values, irrespective of the nitrogen dose (vertical) and fertilizer type (horizontal), marked with uppercase letters: A, B.

Results

Soil pH in the experimental plots

Tables 1 and 2 present the average soil pH values for the objects in which the analysis of individual micronutrient content was conducted. This inclusion is due to the strong relationship between soil pH and the availability of specific nutrients for plants. The structure of the tables follows the methodology used for analyzing micronutrient content.

Across all studied sites, the average soil pH value ranged from 5.60 to 7.03, with a median value of 6.60, classifying it as neutral (Fig. 3).

Table 3. Average zinc content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the source of phosphorus and its percentage content in the fertilizer (experimental factors: A – Source of phosphorus in fertilizer, B – Percentage of phosphorus, C – Nitrogen dose).

Year	N dose, kg N/ha (C)	Source of phosphorus in fertilizer (A)						Control without fertilization
		Polyol waste			Fosdar 40 (control)			
		Percentage of P (B)						
		4%	6%	avg.	4%	6%	avg.	
I	180	10.47 cd	7.97 a-c	9.22 B	6.35 ab	8.65 b-d	7.50 AB	7.60 ab
	135	11.20 d	6.57 ab	8.88 B	5.75 a	8.05 a-c	6.90 A	AB
	avg.	10.83 C	7.27 AB		6.05 A	8.35 B		AB
	avg.	9.05 B			7.20 A			AB
	A – η^2_p = 53.82% B – s.i.			C - s.i.		AxB – η^2_p = 74.55% AxC – s.i.		BxC – s.i. AxBxC – s.i.
II	180	8.73 c	8.33 c	8.53 B	8.77 c	7.83 bc	8.30 B	7.10 bc
	135	8.10 bc	7.55 bc	7.83 B	6.15 ab	4.87 a	5.51 A	B
	avg.	8.42 B	7.94 B		7.46 AB	6.35 A		AB
	avg.	8.18 B			6.90 A			AB
	A – η^2_p = 53.48% B – η^2_p = 30.71%			C – η^2_p = 68.41%		AxB – s.i. AxC – η^2_p = 43.42%		BxC – s.i. AxBxC – s.i.
III	180	10.37 bc	11.17 c	10.77 B	9.87 a-c	7.85 a	8.86 A	9.80 a-c
	135	10.53 bc	9.17 a-c	9.85 AB	8.73 ab	9.33 a-c	9.03 A	AB
	avg.	10.45 B	10.17 B		9.30 AB	8.59 A		AB
	avg.	10.31 B			8.95 A			AB
	A – η^2_p = 49.39% B – s.i.			C – s.i.		AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – η^2_p = 42.92%

The field experiment plan shows the soil pH values for each years of the study, accompanied by a colour scale (Fig. 4).

Zinc content

Table 3 presents the average zinc content in corn depending on the phosphorus source in the fertilizer and its percentage, categorized by research year and nitrogen dose applied.

In all years of the study, significant differences in zinc content in plant material were observed based on the phosphorus source in the fertilizer. Fertilization with Fosdar, which contains phosphorus in the form of calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$), resulted in lower zinc content compared to fertilization with waste sodium-potassium phosphate. The higher calcium content in Fosdar may have contributed to reduced zinc absorption. Additionally, higher zinc content was observed at lower phosphorus doses, though significant differences were only noted in the first year of the study.

Table 4 presents the average zinc content in corn depending on the type of suspension fertilizer and phosphorus percentage, categorized by research year and the nitrogen dose applied.

In the first and third years of field tests, significantly higher zinc content was observed in plant material when a lower phosphorus dose (4%) was applied. In all years of the study, microelement fertilization, including zinc, contributed to increased zinc content in the corn yield. Converrsely, high calcium and phosphorus levels in the soil negatively affected zinc absorption by the test plants.

Manganese content

Table 5 presents the average manganese content in corn based on the phosphorus source in the fertilizer, categorized by research year and the nitrogen dose applied.

In the first year of the study, significantly higher manganese content was observed in plant material from plots fertilized with

Table 4. Average zinc content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the type of suspension fertilizer and the percentage of phosphorus (experimental factors: A - percentage of phosphorus, B – type of fertilizer, C – Nitrogen dose).

Year	N dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg micro	avg.	NPK	NPK S Mg	NPK S Mg micro	avg.
I	180	10.47 bc	8.80 a-c	11.17 c	10.14 B	7.97 ab	7.05 a	9.51 a-c	8.18 A
	135	11.20 c	8.87 a-c	10.80 bc	10.29 B	6.57 a	8.73 a-c	9.50 a-c	8.27 A
	avg.	10.83 C	8.83 AB	10.98 C		7.27 A	7.89 AB	9.51 BC	
	avg.	10.22 B				8.22 A			
	A – η^2_p = 45.67% B – η^2_p = 58.03%		C – s.i.		AxB – η^2_p = 30.82% AxC – s.i.		BxC – s.i. AxBxC – s.i		
II	180	8.73 bc	8.40 bc	11.13 d	9.42 B	8.33 bc	7.30 ab	9.71 cd	8.45 AB
	135	8.10 a-c	5.90 a	8.87 bc	7.61 A	7.55 a-c	7.95 a-c	9.20 b-d	8.23 A
	avg.	8.42 AB	7.15 A	9.98 C		7.94 A	7.63 A	9.46 BC	
	avg.	8.52 A				8.34 A			
	A – η^2_p = 69.65% B – s.i.		C – 38.70%		AxB – s.i. AxC – s.i.		BxC – η^2_p = 28.19% AxBxC – s.i		
III	180	11.17 bc	10.50 bc	14.70 d	12.12 B	10.37 bc	7.47 a	11.30 bc	9.71 A
	135	9.17 ab	10.53 bc	12.57 cd	10.76 A	10.53 bc	10.19 a-c	10.60 bc	10.44 A
	avg.	10.17 AB	10.52 AB	13.63 C		10.45 AB	8.83 A	10.95 B	
	avg.	11.44 B				10.08 A			
	A – 66.78% B – η^2_p = 42.86%		C – s.i.		AxB – η^2_p = 38.03% AxC – η^2_p = 37.43%		BxC – η^2_p = 30.74% AxBxC – s.i.		

Table 5. Average manganese content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the source of phosphorus and its percentage content in the fertilizer (experimental factors: A – Source of phosphorus in fertilizer, B – Percentage of phosphorus, C – Nitrogen dose).

Year	N dose, kg N/ha (C)	Source of phosphorus in fertilizer (A)						Control without fertilization
		Polyol waste			Fosdar 40(control)			
		Percentage of P (B)						
		4%	6%	avg.	4%	6%	avg.	
I	180	7.67 a	10.67 ab	9.17 A	13.67 b	13.33 b	13.50 B	10.00 ab
	135	7.67 a	13.33 b	10.50 AB	11.00 ab	10.33 ab	10.67 AB	AB
	avg.	7.67 A	12.00 B		12.33 B	11.38 B		AB
	avg.	9.83 A			12.08 B			AB
		A – η^2_p = 31.96% B – η^2_p = 25.42%		C - s.i.	AxB – η^2_p = 35.14% AxC – η^2_p = 28.71%			BxC – s.i. AxBxC – s.i.
II	180	11.00 a	9.33 a	10.17 A	9.33 a	8.67 a	9.00 A	9.67 a
	135	6.33 a	8.00 a	7.17 A	11.67 a	9.33 a	10.50 A	A
	avg.	8.67 A	8.67 A		10.50 A	9.00 A		A
	avg.	8.67 A			9.75 A			A
		A – s.i. B – s.i.		C – s.i.	AxB – s.i. AxC – η^2_p = 23.18%			BxC – s.i. AxBxC – s.i.
III	180	2.33 ab	21.00 ab	20.67 AB	24.00 b	20.33 ab	22.17 B	17.67 ab
	135	16.67 a	17.00 a	16.83 A	18.00 ab	20.00 ab	19.00 AB	AB
	avg.	18.50 A	19.00 A		21.00 A	20.17 A		A
	avg.	18.75 A			20.58 A			A
		A – s.i. B – s.i.		C – η^2_p = 41.25%	AxB – s.i. AxC – s.i.			BxC – s.i. AxBxC – s.i.

Table 6. Average monthly air temperatures (°C) during the field experiment

Year	Month						Avg.
	IV	V	VI	VII	VIII	IX	
I	6.4	12.6	19.7	22.3	17.3	12.8	15.2
II	5.9	12.8	19.4	19.4	20.5	10.8	13.1
III	8.2	12.9	17.4	20.0	21.0	17.6	16.1
Avg.	6.8	12.8	18.8	20.6	19.6	13.7	
Avg. 2011–2020	9.5	14.4	18.5	20.1	19.7	14.7	

Table 7. Average monthly rainfall totals (mm) during the field experiment

Year	Month						Avg.
	IV	V	VI	VII	VIII	IX	
I	49.1	55.7	43.2	43.0	231.7	62.1	80.7
II	53.2	36.3	38.7	111.8	52.3	112.3	67.4
III	57.9	66.0	60.0	84.7	46.4	28.5	57.3
Avg.	53.4	52.7	47.3	79.8	110.1	67.6	
Avg. 2011–2020	40.8	80.3	64.3	91.3	54.9	60.2	

Table 8. Average manganese content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the type of suspension fertilizer and the percentage of phosphorus (experimental factors: A – percentage of phosphorus, B – type of fertilizer, C – Nitrogen dose).

Year	N dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg micro	avg.	NPK	NPK S Mg	NPK S Mg micro	avg.
I	180	7.67 ab	8.67 ab	9.67 ab	8.67 A	10.67 a-c	10.67 a-c	9.33 ab	10.22 AB
	135	7.67 ab	16.67 c	10.67 a-c	11.67 B	13.33 bc	11.33 bc	7.00 a	10.56 AB
	avg.	7.67 A	12.67 B	10.17 AB		12.00 B	11.00 B	8.17 A	
	avg.	10.17 A				10.39 A			
	A – η^2_p = 30.50% B – s.i.		C – η^2_p = 19.18%		AxB – η^2_p = 41.98% AxC – η^2_p = 26.51%		BxC – s.i. AxBxC – η^2_p = 26.51%		
II	180	11.00 ab	8.67 ab	7.33 ab	9.00 AB	9.33 ab	12.33 b	10.00 ab	10.56 B
	135	6.33 a	9.67 ab	9.33 ab	8.44 AB	8.00 ab	7.33 ab	8.33 ab	7.89 A
	avg.	8.67 A	9.17 A	8.33 A		8.67 A	9.83 A	9.17 A	
	avg.	7.72 A				9.22 A			
	A – s.i. B – s.i.		C – η^2_p = 19.91%		AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – η^2_p = 27.35%		
III	180	20.33 a-c	27.67 c	21.00 a-c	23.00 B	21.00 a-c	20.67 a-c	24.67 bc	22.11 AB
	135	16.67 a	23.00 a-c	20.33 a-c	20.00 AB	17.00 ab	20.33 a-c	20.33 a-c	19.22 A
	avg.	18.50 A	25.33 B	20.67 AB		19.00 A	20.50 A	22.50 AB	
	avg.	21.50 A				20.67 A			
	A – η^2_p = 39.37% B – s.i.		C – η^2_p = 31.80%		AxB – η^2_p = 30.85% AxC – s.i.		BxC – s.i. AxBxC – s.i.		

Table 9. Average copper content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the source of phosphorus and its percentage content in the fertilizer (experimental factors: A – Source of phosphorus in fertilizer, B – Percentage of phosphorus, C – Nitrogen dose).

Year	N dose, kg N/ha (C)	Source of phosphorus in fertilizer (A)						Control without fertilization
		Polyol waste			Fosdar 40 (control)			
		Percentage of P (B)						
		4%	6%	avg.	4%	6%	avg.	
I	180	2.97	3.53	3.25	4.57	2.27	3.47	3.67
	135	2.13	3.30	2.72	2.47	4.00	3.23	
	avg.	2.55	3.42		3.52	3.13		
	avg.	2.98			3.33			
II	180	5.33	4.73	5.03	6.27	5.57	5.92	6.03
	135	10.80	5.53	8.17	3.93	5.33	4.63	
	avg.	8.07	5.13		5.10	5.45		
	avg.	6.60			5.28			
III	180	3.00	3.13	3.07	2.70	2.00	2.35	3.10
	135	2.43	2.10	2.27	3.47	3.47	3.47	
	avg.	2.72	2.62		3.08	2.73		
	avg.	2.67			2.91			

phosphorus. However, this relationship was not confirmed in the next two years of the study. The results from the third year of the study were significantly higher than those from the previous years, which may have been influenced by weather conditions, including higher temperatures and lower rainfall ompared to earlier years (Tables 6 and 7). The overall manganese content is classified as low due to the high pH of the soil.

Table 8 presents the average manganese content in corn based on the type of suspension fertilizer and phosphorus percentage, categorized by research year and the nitrogen dose applied.

Despite fertilization with manganese on the plots treated with micronutrient fertilizer, no significantly increase in manganese content was noted in the plant material during any of the three years of the field experiment. This may be attributed to the antagonistic effect of boron and zinc - components of the microelement fertilizers - on mangase absorption. The study also found no significant effect of the phosphorus dose. High soil pH and weather conditions had a significant effect on manganese absorption by the test plants.

Copper content

Table 9 presents the average copper content in corn based on the phosphorus source and its percentage in the fertilizer, categorized by research year and the nitrogen dose applied.

The copper content in maize plant material did not differ significantly over the 3-year field study, regardless of the phosphorus source used in the fertilizer.

Table 10 presents the average copper content in corn based on the type of suspension fertilizer and phosphorus percentage, categorized by research year and the nitrogen dose applied.

The type of fertilizer used did not significantly affect copper content in plant material throughout the three-year field study. The experiment also did not confirm any influence of different fertilization methods or weather conditions on copper content in the tested plant material.

Iron content

Table 11 presents the average iron content in corn based on the phosphorus source and its percentage in the fertilizer, categorized by research year and the nitrogen dose applied.

Table 10. Average copper content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the type of suspension fertilizer and the percentage of phosphorus (experimental factors: A – percentage of phosphorus, B – type of fertilizer, C – Nitrogen dose).

Year	N dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg micro	avg.	NPK	NPK S Mg	NPK S Mg micro	avg.
I	180	2.97	8.53	1.87	4.46	3.53	3.43	1.90	2.96
	135	2.13	5.93	2.33	3.47	3.30	4.00	5.17	4.16
	avg.	2.55	7.23	2.10		3.42	3.72	3.53	
	avg.	3.96				3.56			
II	180	5.33	4.27	4.73	4.78	4.73	4.53	6.97	5.41
	135	10.80	4.97	2.57	6.11	5.53	6.77	5.80	6.03
	avg.	8.07	4.62	3.65		5.13	5.65	6.38	
	avg.	5.44				5.72			
III	180	3.00	3.60	3.47	3.36	3.13	3.13	3.27	3.18
	135	2.43	2.43	3.83	2.90	2.10	2.20	1.63	1.98
	avg.	2.72	3.02	3.65		2.62	2.67	2.45	
	avg.	3.13				2.58			

In the first two years of the field experiment, significant differences in iron content were observed in plant material depending on the phosphorus source used in the fertilizer. In the first year, fertilization with waste phosphate increased iron content by 24.6% and in the second year by 11.3%, compared to conventional phosphorus fertilization. In the third year, phosphorus fertilization resulted in significant differences based on the applied phosphate dose, with higher iron content recorded at a lower phosphorus dose (4%). Moreover, in the third year of the study, iron content in plant material was noticeably higher than in previous years, likely due to the highest average temperatures recorded during that year.

Table 12 presents the average iron content in corn based on the type of suspension fertilizer and phosphorus percentage, categorized by research year and the nitrogen dose applied.

The variation in fertilization based on applied additives did not have a clear effect on the iron content in corn plant material. Overall, the experiment indicated that the iron content in corn was at an appropriate level.

Additionally, fertilization with waste phosphate resulted in higher iron content in plant material. Increased temperature positively influenced the availability of this element.

Discussion

The nutrient uptake by maize presented in the literature data varies significantly depending on the cultivation conditions and harvest method (Farshid Aref, 2012).

Among micronutrients, corn has the highest demand for zinc (Bhaumik et al., 2023; Kalashnikov et al., 2020). Zink is essential for proper growth as it is a component of many enzymes, plays a role in vitamins synthesis, and contributes to chlorophyll formation (Bhaumik et al., 2023; Courbet et al., 2019; Kalashnikov et al., 2020). It is also crucial in oxidation-reduction processes (Bhaumik et al., 2023; Courbet et al., 2019; Kalashnikov et al., 2020). Additionally, zink is necessary for the synthesis of tryptophan, a precursor to the growth hormone auxin (Baljeet et al., 2020; Services & Division, 2009; Shukla & Mukhi, 1985). It serves as both a structural and functional component of numerous plant enzymes (Burkhead et al., 2009; McCall et al., 2000). Zinc deficiency disrupts photosynthesis, reduces protein synthesis, and leads to RNA degradation (Bhaumik et al., 2023; Services & Division, 2009; Zekri & Obreza, 1969).

Low zinc (Zn) availability in calcareous soils is a major factor contributing to biotic stresses in agriculture,

Table 11. Average iron content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the source of phosphorus and its percentage content in the fertilizer (experimental factors: A - Source of phosphorus in fertilizer, B -Percentage of phosphorus, C – Nitrogen dose).

Year	N dose, kg N/ha (C)	Source of phosphorus in fertilizer (A)						Control without fertilization
		Polyol waste			Fosdar 40 (control)			
		Percentage of P (B)						
		4%	6%	avg.	4%	6%	avg.	
I	180	94.00 c	71.00 ab	82.50 C	66.33 ab	58.00 ab	62.17 A	64.33 ab
	135	73.33 bc	79.00 bc	76.17 BC	79.00 bc	51.33 a	65.17 AB	AB
	avg.	83.67 C	75.00 BC		72.67 BC	54.67 A		AB
	avg.	79.33 B			63.67 A			A
	A – s.i. B – s.i.		C - η^2_p = 23.53%		AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – s.i.	
II	180	99.67 ab	111.33 b	105.50 B	87.00 a	91.67 ab	89.33 A	84.67 a
	135	90.33 ab	96.00 ab	93.17 AB	84.00 a	94.33 ab	89.17 A	A
	avg.	95.00 AB	103.67 B		85.50 A	93.00 AB		A
	avg.	99.33 B			89.25 A			A
	A – η^2_p = 38.37% B – η^2_p = 28.57%		C – s.i.		AxB – s.i. AxC – s.i.		BxC – s.i. AxBxC – s.i.	
III	180	139.00 c-e	140.33 de	139.67 B	155.33 e	108.33 a	131.83 AB	129.33 a-d
	135	123.33 a-d	114.33 ab	118.83 A	131.33 b-d	117.67 a-c	124.50 A	AB
	avg.	131.17 BC	127.33 B		143.33 C	113.00 A		BC
	avg.	129.25 A			128.17 A			A
	A – s.i. B – η^2_p = 61.17%		C – η^2_p = 51.71%		AxB – η^2_p = 48.66% AxC – η^2_p = 19.74%		BxC – s.i. AxBxC – η^2_p = 39.15%	

particularly in cereals (Farshid Aref, 2012). In addition to soil Zn concentration, soil pH and phosphorus (P) content are the main factors influencing Zn availability to plants (Burkhead et al., 2009; Farshid Aref, 2012; Murdock & Howe, 2001). High soil pH and P levels are strongly associated with reduced Zn uptake by plants, with this effect being most pronounced in soils with a pH above 7 and low organic matter content (Burkhead et al., 2009; Farshid Aref, 2012; Murdock & Howe, 2001). Zn deficiency in such soils can be mitigated by supplementing fertilization with water-soluble zinc, such as organic Zn complexes or chelates) (Cakmak, 2008; Farshid Aref, 2012; Kashyap et al., 2023). However, Zn availability decreases over time due to its transformation into stable forms with soil components. If zinc is not applied at the beginning of the plant growth or if additional supplementation is needed, foliar application is recommended during the 6-10 leaf phase of corn. For later growth stages, a fast-acting chelated form of ZN is preferable to ensure efficient absorption (Farshid Aref, 2012).

Motesharezadeh et al. (2011) observed an increase in chlorophyll content and dry plant mass following zinc application (Motesharezadeh et al., 2011). Similarly, El-Azab (2015) reported improved maize yields when using fertilizer containing zinc (1.5%) (El-Azab, 2015). Adesh et al. (2021) found that zinc application enhances yield parameters and forage plant properties. Their study demonstrated higher green corn yield (519.20 q ha^{-1}), dry fodder yield (137.90 q ha^{-1}), protein content (10.27%), and crude fiber (58.33%) when 20 kg $ZnSO_4$ ha^{-1} was applied to the soil along with a 0.5% $ZnSO_4$ foliar spray (Singh et al., 2021). Similarly, Ramakrishna et al. (2022) achieved the highest dry matter production (104 q ha^{-1}), green forage yield (419 q ha^{-1}), and crude protein content (9.3%) with a 1% $ZnSO_4$ foliar application compared to the control. (Ramakrishna et al., 2022). Sulthana et al. (2015) demonstrtaed improved green forage parameters and higher yields (424 q ha^{-1}) along with increased dry matter content (6695 K g ha^{-1}) when applying 50 kg $ZnSO_4$ · ha^{-1} to the soil and 0.2% $ZnSO_4$ foliarly (Sulthana et al., 2015). Sewhag et al. (2022) reached similar conclusions, reporting improved maize yield quality and quantity. Their study, which used a base dose of 25 kg $ZnSO_4$ · ha^{-1} combined with a 1% $ZnSO_4$ foliar spray, resulted in a green forage yield of 463.08 q ha^{-1}, dry feed yield of 118.75 q ha^{-1}, and crude protein content of 9.90 % (Sewhag et al., 2022).

Iron is an essential nutrient for all organisms. It plays a crucial role in respiration, photosynthesis, chlorophyll biosynthesis, and the synthesis of DNA and plant hormones (Burkhead et al., 2009; Farshid Aref, 2012; Kobayashi & Nishizawa, 2012; Services & Division, 2009; Zekri & Obreza, 1969). Although Fe is abundant in the Earth's crust, it is one of the most limiting nutrients for plant growth. This is due to the low solubility of its oxidized form, Fe (III), in alkaline soils. Fe deficiency is also associated with excessive irrigation, prolonged moisture, poor soil drainage, and low temperatures (Farshid Aref, 2012; Zekri

Table 12. Average iron content (mg · kg $^{-1}$) and division into homogeneous groups using the Tukey test (HSD) for α = 0.05 due to the type of suspension fertilizer and the percentage of phosphorus (experimental factors: A - percentage of phosphorus, B – type of fertilizer, C – Nitrogen dose).

Year	N dose, kg N/ha (C)	Percentage of P (A)							
		4%				6%			
		Type of fertilizer (B)							
		NPK	NPK S Mg	NPK S Mg micro	avg.	NPK	NPK S Mg	NPK S Mg micro	avg.
I	180	94.00 b-e	95.00 c-e	86.33 a-e	91.78 BC	71.00 a	83.33 a-d	68.67 a	74.33 A
	135	73.33 ab	103.67 de	70.33 a	82.44 AB	79.00 a-c	107.67 e	93.00 b-e	93.22 C
	avg.	80.67 AB	99.33 C	78.33 A		75.00 A	95.50 BC	80.83 A	
	avg.	87.11 A				83.78 A			
	A – η^2_p = 66.59% B – s.i.		C – s.i.		AxB – s.i. AxC – η^2_p = 37.71%		BxC – η^2_p = 58.06% AxBxC – s.i.		
II	180	99.67 bc	92.33 a-c	85.00 a-c	92.33	111.33 c	73.33 ab	106.67 c	97.11 A
	135	90.33 a-c	98.33 a-c	71.00 a	86.56 A	96.00 a-c	86.33 a-c	72.33 ab	84.89 A
	avg.	95.00 BC	95.33 BC	78.00 A		103.67 C	79.83 AB	89.50 A-C	
	avg.	89.44 A				91.00 A			
	A – η^2_p = 42.31% B – s.i.		C – η^2_p = 25.25%		AxB – η^2_p = 37.97% AxC – η^2_p = 44.78%		BxC – s.i. AxBxC – s.i.		
III	180	139.00 bc	120.00 a-c	108.33 a	122.44 A	140.33 bc	131.00 a-c	113.00 ab	128.11 A
	135	123.33 a-c	178.33 e	171.67 de	157.78 B	114.33 ab	112.00 ab	146.33 cd	124.22 A
	avg.	131.17 AB	149.17 C	140.00 BC		127.33 AB	121.50 A	129.67 AB	
	avg.	140.11 B				126.17 A			
	A – s.i. B – η^2_p = 43.18%		C – η^2_p = 49.14%		AxB – η^2_p = 28.34% AxC – η^2_p = 75.89%		BxC – η^2_p = 60.05% AxBxC – η^2_p = 43.59%		

& Obreza, 1969). More than one-third of the world's soils are considered iron-deficient (Farshid Aref, 2012).

Fe deficiency in most plant species is indicated by Fe content falling below 10-80 mg kg^{-1} in leaves (Galanti, 2014). In maize leaves during the silking period, an adequate Fe content ranges from 21 to 250 mg kg^{-1} (Farshid Aref, 2012).

The presence of boron in the soil positively affects iron uptake by plants (Farshid Aref, 2012). According to Farshid (2012), the application of 6 kg ha^{-1} B increased Fe content in leaves by more than 12% (Farshid Aref, 2012). However, foliar application of B did not affect Fe content in the plant (Farshid Aref, 2012). Similar findings were reported by Patel and Golakiya (1986), who applied 2 mg B kg^{-1} to the soil and observed increased concentrations of N, P, K, Fe, and Cu in plants (Farshid Aref, 2012).

Manganese affects corn yield by participating in the synthesis of respiratory and photosynthetic enzymes. It also prevents the accumulation of nitrates in plant tissues (Services & Division, 2009; Zekri & Obreza, 1969).

Plants absorb manganese in the form of Mn^{2+} ions, and its optimal concentration in plant tissues varies widely, ranging from 30 to over 1000 mg · kg^{-1} in dry matter (Farshid Aref, 2012). According to Reuter and Robinson (1997), Mn concentration in maize leaves at the silk stage is classified as follows: below 15 mg · kg^{-1} as deficiency, 16 to 19 mg · kg^{-1} as minimum range, 20 to 150 mg · kg^{-1} as optimum range, 151 to 200 mg · kg^{-1} as high range, while Mn content above 200 mg · kg^{-1} was considered toxic (Farshid Aref, 2012).

Manganese deficiency is common in plants across a wide range of soils and climatic conditions [7]. This occurs due to the oxidation of Mn into forms unavailable to plants in soils with high pH and elevated oxygen concentrations in the soil solution (Conley, 2011; Farshid Aref, 2012). However, in soils with a pH below 5.5, high concentrations of mobile Mn^{2+} ions can become toxic (Farshid Aref, 2012). In general, as soil pH increases, manganese forms fewer organic compounds and more amorphous and crystalline structures (Farshid Aref, 2012).

Aref (2012) observed a negative effect of boron fertilization on manganese content in maize leaves. At the highest boron application rate (6 kg · ha^{-1} B), the Mn concentration in maize leaves was 124 mg · kg^{-1}, compared to 153.1 mg · kg^{-1} in the control without boron fertilization. The study also demonstrated an antagonistic effect of zinc on manganese uptake. Applying 16 kg ha^{-1} Zn increased Mn content in leaves from 133 to 182 mg · kg^{-1} (Farshid Aref, 2012).

Copper is an essential trace nutrient and a crucial cofactor in molecules involved in basic metabolic processes, including photosynthesis, respiration, and cell wall lignification. However, in excessive amounts, it becomes toxic, resulting in the inhibition of plant growth (Abdel Latef et al., 2020; Farshid Aref, 2012).

Copper in soil is relatively immobile due to its strongl binding with organic matter. Soil pH significantly influences its bioavailability – higher pH levels rapidly decrease the concentration of Cu2+ ions in the soil solution (Burkhead et al., 2009; Farshid Aref, 2012). Therefore, copper uptake can be regulated through liming the soil and manure fertilizing. Corn shows moderate sensitivity to copper deficiency (Farshid Aref, 2012).

The use of suspension fertilizers derived from waste phosphates produced during polyol manufacturing may offer a cost-effective alternative to imported phosphate raw materials. This waste does not contain harmful substances and is therefore environmentally safe. Such an approach aligns with circular economy principles and reduces reliance on mineral raw materials.

Conclusions

In most cases, no significant increase in micronutrient contents was noted in maize plants when using suspension fertilizers with micronutrients. This could mainly be attributed to high soil pH and low rainfall. In such conditions, foliar application of fertilizers in the form of spraying would likely be more effective.

Liquid fertilizers offer more uniform distribution of micronutrients, leading to better utilization. Additionally, their liquid form ensures improved absorption, especially in years with lower rainfall.

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Zawartość mikroelementów w kukurydzy uprawianej na zielonkę nawożonej nawozami zawiesinowymi na bazie odpadowych fosforanów z produkcji polioli

Streszczenie. Konieczność importu surowców fosforowych do celów nawozowych w Europie oraz konieczność zagospodarowania rosnącej ilości odpadów przyczyniły się do poszukiwania alternatywnych źródeł fosforu. Jednym z takich odpadów jest odpad fosforanu sodowo-potasowego powstający podczas produkcji polioli. Ponadto aktualnym problemem jest zapewnienie odpowiedniej ilości żywności, gdzie główną rolę odgrywają nawozy. Ze względu na wzrost spożycia mięsa atrakcyjność uprawy kukurydzy paszowej wzrasta ze względu na jej wysoki potencjał plonowania i bogaty skład. W artykule przedstawiono wpływ nawozów zawiesinowych na bazie odpadów z produkcji polioli na zawartość mikroelementów w kukurydzy przeznaczonej na zielonkę. W 3-letnim badaniu terenowym porównano wpływ odpadowego źródła fosforu z komercyjnym granulowanym nawozem fosforowym – Fosdar 40. Dodatkowo oceniono skład nawozów zawiesinowych, badając nawozy zawierające wyłącznie podstawowe składniki odżywcze (NPK) oraz nawozy wzbogacone o składniki drugorzędne (S, Mg) i mikroelementy (Zn, Mn, B). Testy potwierdziły skuteczność testowanych nawozów zawiesinowych. Zawartość mikroelementów w suchej masie kukurydzy była na podobnym poziomie jak w przypadku kontroli, gdzie do nawożenia użyto Fosdaru 40