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ORIGINAL PAPER

Effect of a herbicide and biostimulants on the content and uptake of selected micronutrients by edible potato tubers*

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Abstract

The research material consisted of table potato tubers harvested in a three-year field experiment carried out at the Agricultural Experimental Station in Zawady of University of Siedlce in 2018-2020. It was set up in triplicate on tawny soil. The main factor were two mid-early potato cultivars, Oberon and Malaga, and the sub-plot factor included five options of treatment with a herbicide and biostimulants: 1. control, 2. the herbicide Avatar 293 ZC, 3. the herbicide Avatar 293 ZC and the biostimulant PlonoStart, 4. the herbicide Avatar 293 ZC and the biostimulant Aminiolant, 5. the herbicide Avatar 293 ZC and the biostimulant Agro-Sorb Folium. The objective of the study was to determine the impact of biostimulant and herbicide applications on the content and uptake of selected micronutrients by potato tubers. Manganese (Mn) and copper (Cu) contents were determined in tuber dry matter using an ICP-OES spectrometer (Perkin Elmer, Optima 8300, USA). Higher Cu content was found in cv. Malaga tubers compared with Oberon, while greater uptake of both elements (Mn, Cu) with tuber yield was determined in cv. Oberon due to its higher yield. An application of biostimulants increased the Cu content as well as Mn and Cu uptake compared with control tubers. The most beneficial effect was produced by using the biostimulant Agro-Sorb Folium. Manganese and copper were significantly affected by the weather during the study years. It should be added that the agricultural sector has recently become increasingly aware of the environmental impact of the measures used, and in this context, biostimulants are gaining popularity to improve the quality of crops, minimizing the negative impact on the environment.

Keywords: *Solanum tuberosum* L., biostimulants, cultivars, copper, manganese

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INTRODUCTION

The potato plant (*Solanum tuberosum* L.) is one of the most commonly cultivated crops in the world (Ewais et al. 2020). In developing countries, potato is the second most valuable food crop, following maize, and its cultivation is the most profitable (Gikundi et al. 2021). Potato is highly productive, offered at an affordable price, and can be stored for a long period without substantial quality loss, thus enhancing its importance for food security (Ginter et al. 2022, Xu et al. 2023). Potato tubers contain a wide range of organic and mineral compounds. Their chemical composition is affected by numerous factors such as cultivar, agronomic practices, climatic and soil conditions, and storage conditions (Beals 2019, Ewais et al. 2020). Potato tubers contain 1-1.2% minerals in the form of macro- and micronutrients. Macroelements primarily serve structural and physiological functions. Micronutrients are components of enzymes which activate biochemical processes, participate in organic compound metabolism, and in potatoes, they mainly include iron, manganese, copper, zinc, and boron (Sharma et al. 2017, Wierzbowska et al. 2018, Mystkowska, Rogóż-Matyszczak 2019). Modern agriculture is oriented towards achieving the highest yields of crops possible with high nutritional potential, as food products are the foundation of human health (Beals 2019). The use of natural plant biostimulants is an eco-friendly and promising innovation as they enhance plant growth, crop performance, and yield quality, improve nutrient utilisation efficiency, and alleviate stress (Jardin 2015, Keutgen et al. 2019, Rouphael, Colla 2020). According to the EU Regulation (2019), a plant biostimulant is an EU fertilising product which stimulates plant nutrition processes and is applied to improve one or more plant characteristics, such as nutrient use efficiency, tolerance to abiotic stress, quality traits, or the availability of limited nutrients in the soil or rhizosphere. The stimulating preparations are more and more frequently an addition and a sustainable alternative to synthetic chemicals (fertilisers and pesticides). Moreover, their application brings benefits to human health, the environment, biodiversity, and the economy (Malik et al. 2021). Previous research has confirmed the beneficial effect of biostimulants on potato yield levels, tuber nutritional value, mineral content, and crop profitability (Zarzecka et al. 2019, Ginter et al. 2022). The most popular is an application of biostimulants independently from other plant protection agents (Głosek-Sobieraj et al. 2018, Mystkowska, Rogóż-Matyszczak 2019). There is a paucity of scientific reports on an application of biostimulants in combination with pesticides, particularly herbicides. Matysiak et al. (2018) evaluated a foliar application of Kelpak and Asahi, whether used separately and mixed with herbicides, in spring wheat cultivation. These authors observed that regardless of the biostimulant application method, Kelpak increased spring wheat yield compared to the control crop, while Asahi mixed with herbicides improved grain quality parameters, and tended to increase yield over the study years. Gugała et al. (2017), who made separate applications of the mixtures of the herbicide Harrier 295 ZC + the biostimulant Kelpak SL, and Sencor 70 WG + the biostimulant Asahi SL, achieved a respective yield increase of 21.6 and 33.2% in potatoes, compared to the control crop. They also claimed that an application of growth biostimulants may be a factor that mitigates adverse weather conditions, which affect potato growth and development. However, there is a paucity of studies on the influence of biostimulants and herbicides on the potato tuber content of micronutrients. Therefore, it is of utmost importance to study, analyse, and understand the impact of various practices applied in cultivation and the effect of climatic conditions on the quality parameters of table potato tubers. The aim of the study was to determine the effect of biostimulant and herbicide applications on the content and uptake of selected micronutrients by table potato tubers on the example of selected cultivars due to belonging to the same earliness group.

MATERIALS AND METHODS

The research material consisted of tubers from two table potato cultivars: Oberon and Malaga. The tubers were obtained from a field trial carried out at the Zawady Experimental Station of the University of Siedlce in 2018-2020. The cultivars used in the trial are ranked among the twenty most popular potato cultivars cultivated in Poland and sold in Polish markets (Dzwonkowski et al. 2021). The field trial was established as a split-plot arrangement of two factors with three replicates. The soil of the experiment was tawny soil with the granulometric composition of sandy loam. Each year, before the experiment, the soil was analysed at the Chemical and Agricultural Station in Wesoła, near Warsaw. The following soil parameters were determined: pH in 1 M KCl 5.25-5.42, soil humus 20.9-22.3 g kg^{-1}, available minerals (mg kg^{-1} soil): P – 35.2-71.0, K – 102.1-141.0, Mg – 36.6-61.0, and the content of total forms (mg kg^{-1} soil) of: Mn – 56.7-328.0, Cu – 1.85-3.10, Zn – 18.45-36.52, and Fe – 5029.2-4200.0. The main experimental factor included two mid-early table potato cultivars, Oberon and Malaga (Table 1).

Table 1

Characteristics of basic parameters of the potato cultivars (Nowacki 2021)

Specification	Oberon	Malaga
Origin	Potato Breeding Zamarte, Poland	Potato Breeding Zamarte, Poland
Yield (t ha^{-1})	53.1	56.7
Starch (g kg^{-1} FM)	200	208
Vitamin C (mg kg^{-1} FM)	235	188
Nitrates (mg NO_3 kg^{-1} FM)	low – below 100	low – below 100
Taste (scale 1-9)	7	7
For organic production	yes	yes

The sub-plot experimental factor consisted of five treatment application options of a herbicide and biostimulants of different chemical composition at different BBCH phases (Tables 2, 3). The BBCH scale is a system for a uniform coding of phenologically similar growth stages of all mono- and dicotyledonous plant species. The abbreviation BBCH derivers from Biologische Bundesanstalt, Bundessortenamt and Chemical industry. The scale is used in the European Union countries to identify the development phases of plants (Badowski et al. 2001).

Table 2

The application of the herbicide and biostimulants

N_0 – symbol	Object	Dose (L ha^{-1})	Time application
1 – C	Control object – mechanical weeding	mechanical weeding only (redlining 3 times, harrowing 1 time)	
2 – A	herbicide Avatar 293 ZC	1.5	about 7 days before emergence (scale BBCH 00-08)
3 – A+P	Avatar 293 ZC + biostimulant PlonoStart	1.5 + 2.0 (1.0+1.0)	herbicide about 7 days before emergence, biostimulant twice – full emergence (BBCH 13-19) and rows covering (BBCH 31-35)
4 – A+Am	Avatar 293 ZC + biostimulant Aminoplant	1.5 + 1.5 (1.0+0.5)	herbicide about 7 days before emergence, biostimulant twice – full emergence (BBCH 13-19) and rows covering (BBCH 31-35)
5 – A+ASF	Avatar 293 ZC + biostimulant Agro-Sorb Folium	1.5 +4.0 (2.0+2.0)	herbicide about 7 days before emergence, biostimulant twice – full emergence (BBCH 13-19) and rows covering (BBCH 31-35)

Table 3

Chemical composition of the herbicide and biostimulants

Preparations	Composition
Herbicide Avatar 293 ZC	clomazone 60 g L^{-1} + metribuzin 233 g L^{-1}
Biostimulant PlonoStart	lactic acid bacteria, actinomycetes, N_{total} – 16.4,%, K_2O – 0.75%, CaO – 0.07%, MgO – 0.02%, S – 941 mg kg^{-1}
Biostimulant Aminoplant	free amino acids – 11.57%, N_{total} – 9.48%, $N_{organic}$ – 9.2%, N-NH4 – 0.88%, $C_{organic}$ – 25%, organic substance – 87.7%
Biostimulant Agro-Sorb Folium	free amino acids – 10.66%, total amino acids – 13.11%, N_{total} – 2.2%, B – 0.02%, Mn – 0.05%, Zn – 0.09%

The herbicide Avatar 293 ZC and the biostimulants PlonoStart, Aminoplant, and Agro-Sorb Folium were dissolved in 300 L of water per 1 ha. The biostimulants were applied as recommended by the Institute of Soil Science and Plant Cultivation in Puławy (2023). Each year, in the autumn, the experimental field was fertilised with 25 t ha^{-1} of manure, and phosphorus-potassium fertilisers at the doses of 44 kg P ha and 124.5 kg K ha^{-1}. In the spring, a pre-plant dose of 100 kg N ha^{-1} was applied. The preceding crop was winter triticale. Potatoes were planted in April (23 April 2018, 18 April 2019, and 20 April 2020), with a row spacing of 40 cm and inter-row spacing of 67.5 cm (48 plants per plot). The plot size was 12.96 m^2. During the plant growing period the following insecticides were used: Acatra 25 GW (thiametoxam) – 0.08 kg ha^{-1}, Decis Mega 50 EW (deltamethrin) 0.15 dm^3 ha^{-1}, Karate Zeon 05 CS (lambda-cyhalothrin) 0.25 dm^3 ha^{-1}, Proteus (thiachloprid, deltamethrin) 110 OD – 0.4 dm3 ha^{-1} and fungicides: Ridomil Gold MZ 68 WG (matalaxyl-M, mancozeb) – 2.0 kg ha^{-1} and Dithane Neo Tec 75 WG (mancozeb) – 2.5 kg ha^{-1}.

Potatoes were harvested at full physiological maturity in early and mid-September (4 September 2018, 17 September 2019, and 8 September 2020 – phase BBCH 97-99).

Each year, just prior to harvest, 10 plants were randomly selected from all the plots (30 units), and their tubers were collected to prepare samples for chemical analysis. The total (overall) yield of tubers consisted of the mass of tubers collected from the entire area of a plot and the mass of samples previously taken and converted to t ha^{-1}. Commercial yield included tubers with a diameter of more than 35 mm free of external and internal defects (Regulation 2003). From the samples of the commercial yield, 8-10 tubers were selected, washed, and dried with paper towel. Next, the tuber halves were cut into 0.5-1.0 cm pieces, mixed, and three sub-samples of 200 g each (fresh weight) were taken. The content of manganese and copper was determined in dry matter (mg kg^{-1}).

The dry weight of tubers was determined by a two-stage gravimetric drying method, according to the Polish Standard (Polish Norm PN-EN 12145, 2001). Potato tuber samples were dried in a SLW 115 SIMPLE dryer (Merazet, Poznań) with forced air circulation. The oven was initially set at 70°C and then samples were dried at 105°C to a constant weight. Dry matter content was calculated and expressed on a percentage basis:

$$\text{dry matter (\%)} = \text{(dry weight/fresh weight)} \times 100.$$

Chemical analyses were carried out on the dry weight of tubers in triplicate. Dry samples weighing approximately 0.2-0.3 g were digested with 6 ml of HNO_3 and 2 mL of HCl. The samples and the acid mixture were placed in a rotor and heated in a microwave digestion system. The mineralised samples were diluted to 50 mL with ultrapure water. The resulting solution was tested using an ICP-OES spectrometer (Perkin Elmer, Optima 8300, USA). Manganese and copper contents were determined. Mineral intake was calculated as the product of tuber dry weight yield and the content of each element.

Selyaninov's hydrothermal coefficient values were determined for each month of the potato growing season (April to September) in the three study years. The coefficient reflects the precipitation and air temperature during a given month. The meteorological conditions during the study years were varied (Table 4).

Table 4

Selyaninov's hydrothermal coefficient (K) in the years of research (Zawady Meteorological Station in Poland)

Months	Years		
	2018	2019	2020
April	0.88	0.20	0.23
May	0.52	1.44	1.74
June	0.57	0.67	2.05
July	1.06	0.51	1.15
August	0.86	0.71	0.29
September	1.69	0.41	0.83
April-September	0.93	0.66	1.05

K = 10 P/ Σt, Skowera et al. (2014) where: P – the sum of the monthly rainfalls in mm, Σt – monthly total air temperature > 0°C Ranges of values of this coefficient were classified as follows: up to 0.4 – extremely dry, 0.41-0.7 – very dry, 0.71-1.0 – dry, 1.01-1.3 – relatively dry, 1.31-1.6 – optimal, 1.61-2.0 – relatively humid, 2.01-2.5 – humid, 2.51-3.0 – very humid, above 3.0 – extremely humid

In 2018, April, May, June, and August were dry and very dry, leading to the categorisation of the growing season as dry. The next growing season was highly dry, primarily marked by very dry months, which were unfavourable for the growth and development of potato crop. The year 2020 was relatively dry, although the distribution of precipitation and thermal conditions was irregular across the individual months of the growing season.

All data were subjected to variance analysis based on the Fisher-Snedecor's *F* test. The Tukey test was used to test differences between mean values at a significance level of $p \leq 0.05$ (Trętowski, Wójcik 1991).

RESULTS AND DISCUSSION

Potatoes hold a significant place in human diet; for example, its consumption in Poland in 2021 was 88 kg per capita, equivalent to 240 g per day (Dzwonkowski et al. 2021). Both mineral deficiencies and excesses can have harmful effects on the human body. Hence, it is crucial to consider the microelement content when evaluating the nutritional value of potato tubers.

Manganese (Mn) is a major component and activator of numerous enzymes involved in fundamental metabolic pathways, such as protein, nucleic acid, and fatty acid synthesis, glucose metabolism, and bone formation. As it is part of antioxidant enzymes (e.g., superoxide dismutase), Mn provides a defensive shield against free radicals in the body. According to the European Food Safety Authority (EFSA), the average daily intake of manganese in adults in the EU is approximately 3 mg/day (EFSA 2013, Wołonciej et al. 2016).

In the study reported here, the tuber content of manganese ranged from 10.47 (control object) to 11.55 (A+Am object) mg kg^{-1} dry matter (Figure 1), and it ranged between 7.07 and 18.63 mg kg^{-1} (Figure 2).

Similar manganese concentrations in potatoes have been observed by other researchers (Gugała et al. 2018, Wierzbowska et al. 2018). Sharma et al. (2017) analysed chemical composition of 48 potato cultivars and found that manganese content ranged from 17.21 to 33.57 mg kg^{-1}. In our experiment, the concentration of manganese was significantly affected only by the weather conditions in the study years, and by the application of herbicide

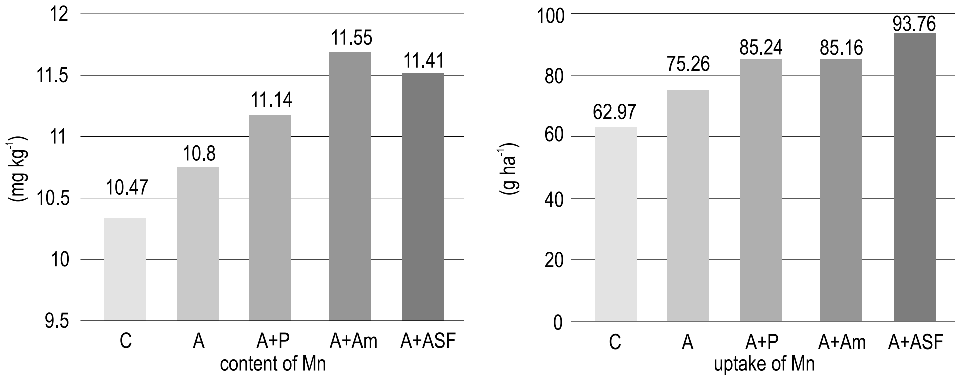

Fig. 1. Content and uptake of Mn by potato tubers in dry matter (C – control object, A – Avatar 293 ZC, A+P – Avatar 293 ZC + PlonoStart, A+Am – Avatar 293 ZC + Aminoplant, A+ASF – Avatar 293 ZC + Agro-Sorb Folium). Significantly different values are marked with different letters above bars (separately *a*-*b*) at $p \leq 0.05$

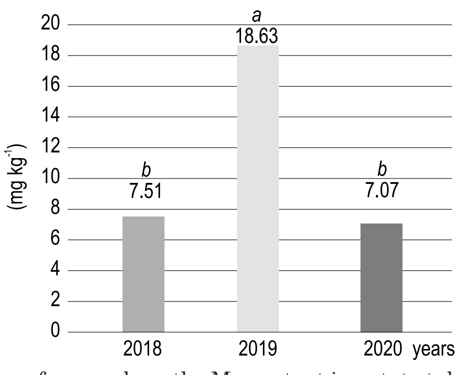

Fig. 2. Effect of years of research on the Mn content in potato tubers (in dry matter). Significantly different values are marked with different letters above bars (separately *a*-*b*) at $p \leq 0.05$

and biostimulants. Treatment with biostimulants was only associated with a tendency for manganese content to increase compared to control (Figure 1). Also Głosek-Sobieraj et al. (2018) observed no significant changes in the manganese content in the flesh and skin of potato tubers following an application of the biostimulants Asahi SL, Bio-Algeen S 90, Kelpak SL, and Trifender WP. The weather conditions prevailing in 2019, which was a very dry year, were the most conducive to the accumulation of manganese, while in the remaining study years, its content was significantly lower (Figure 2). A similar response to moisture and thermal conditions was observed by Głosek-Sobieraj et al. (2018). Kunicki et al. (2010) found that the effect of biostimulants can be dependent upon the species, or even the cultivar, application dose, or environmental factors. Variance analysis confirmed an interaction of the application methods of the herbicide and biostimulants with the cultivars (Figure 3). Cv. Malaga tubers harvested on the object

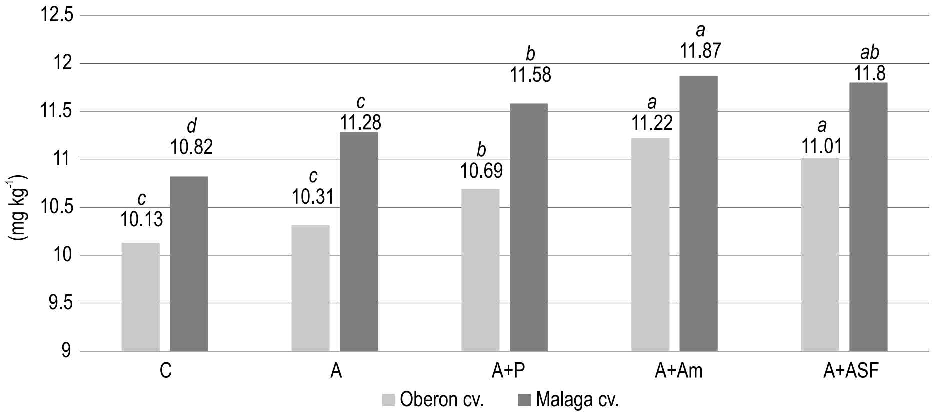

Fig. 3. Manganese content in tubers of potato cultivars depending on the application herbicide and biostimulants (in dry matter). C, A, A+P, A+Am, A+ASF denote the same as in Fig. 1. Significantly different values are marked with different small letters above bars (*a-d*) at $p \leq 0.05$.

sprayed with the herbicide Avatar 293 ZC + the biostimulant Aminoplant had the highest manganese content, and the lowest one was determined in cv. Oberon tubers from the control object. A similar response of cultivars to biostimulant application was reported by Mystkowska (2018).

The manganese uptake with potato tuber yield was affected by the cultivars, application of the herbicide and biostimulants, and the weather conditions (Figures 1, 4).

Cv. Oberon took up significantly more Mn than cv. Malaga. By stimulating the tuber content of manganese, an application of biostimulants resulted in a significant rise in Mn uptake compared with the control. In the study years, the highest Mn uptake was observed in the very dry year 2019, it being significantly lower in the remaining growing seasons. This was likely

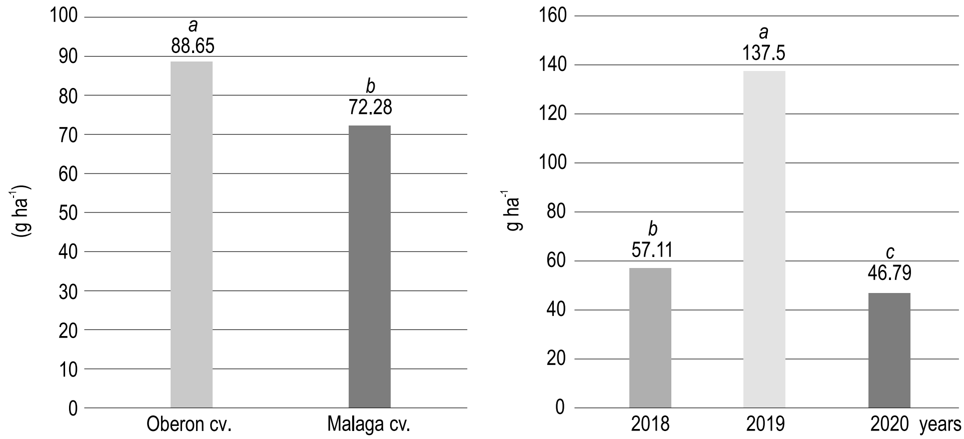

Fig. 4. Effect of the cultivar and years of research on Mn uptake by potato. Significantly different values are marked with different letters above bars (separately *a-c*) at $p \leq 0.05$

due to the highest concentration of this micronutrient in the tubers in 2019. It should be added that this year (2019) the manganese content of the soil was the highest (328,0 mg kg^{-1}). Gugała et al. (2018) reported a significant influence of cultivars, the biostimulants Asahi SL and Kelpak SL, and the weather conditions, whereas Wierzbowska et al. (2015) found that micronutrient (Mn, Cu, Fe, Zn) uptake with potato yield was more affected by the cultivar, particularly its yield, than by the applied biostimulants (Kelpak SL, Asahi SL, Bio-Algeen S 90).

Copper (Cu) primarily serves as a cofactor for enzymes. The element is essential for the proper functioning of many metabolic pathways responsible for energy production within cells, scavenging of free radicals, collagen and elastin synthesis, and melanin production. Cu is also essential for the normal functioning of the nervous system. According to the European Food Safety Authority (EFSA), the average daily intake of copper for adults in the EU is 1.6 mg/day for men and 1.3 mg/day for women (EFSA 2015, Wołonciej et al. 2016).

In our study, tubers accumulated copper in a range between 3.99 (A – Avatar 293 ZC) to 4.29 mg kg^{-1} in dry matter (A+ASF – Avatar 293 ZC + Agro-Sorb Folium), with values from 2.12 to 6.11 mg kg^{-1} in dry matter. Similar copper concentrations in potato have been reported by Šrek et al. (2012) and Głosek-Sobieraj et al. (2018). Copper content and uptake with tuber yield were significantly affected by the cultivars, herbicide and biostimulants, as well as the moisture and thermal conditions during the study years (Figures 5, 6, 7).

Cv. Malaga accumulated more copper in its tubers than Oberon did, while the uptake of this micronutrient was higher in cv. Oberon, which produced a greater yield. The test biostimulants significantly increased both the

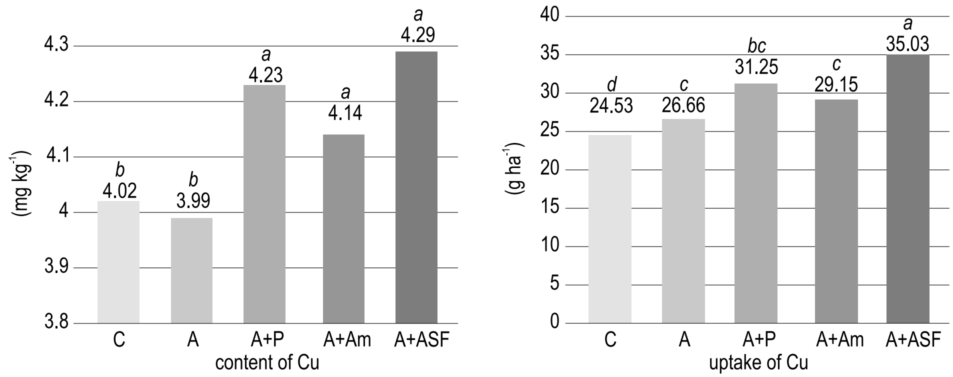

Fig. 5. Content and uptake Cu by potato tubers (in dry matter). C, A, A+P, A+Am, A+ASF denote the same as in Fig. 1. Significantly different values are marked with different letters above bars (separately *a-d*) at $p \leq 0.05$

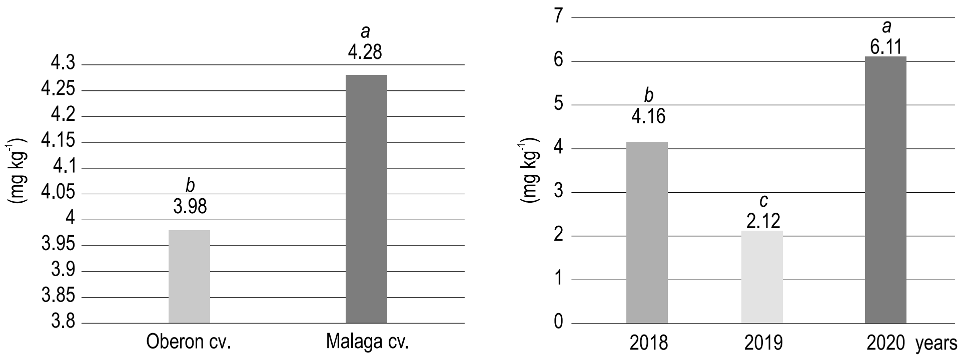

Fig. 6. Effect of the cultivars and years of research on Cu content in potato tubers (in dry matter). Significantly different values are marked with different letters above bars (separately *a-c*) at $p \leq 0.05$

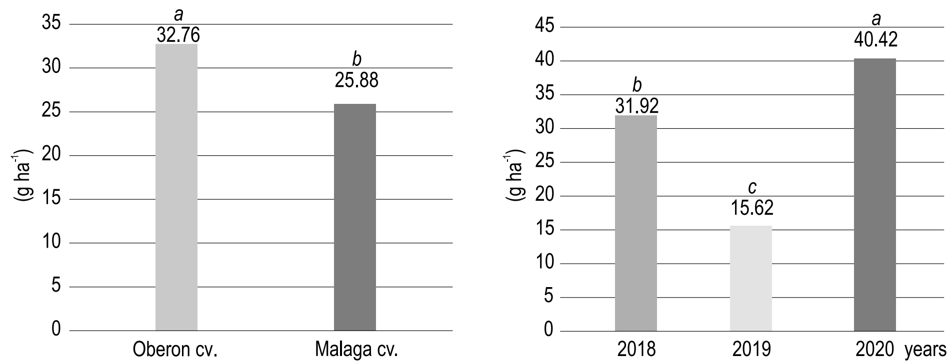

Fig. 7. Effect of the cultivars and years of research on Cu uptake by potato. Significantly different values are marked with different letters above bars (separately *a-c*) at $p \leq 0.05$

copper content and its uptake with the potato yield compared to the control (Figure 5). Also Wierzbowska et al. (2015) and Mystkowska and Rogóż--Matyszczak (2019) confirmed the impact of a cultivar on the copper content and uptake. In addition, Mystkowska and Rogóż-Matyszczak (2019) observed an increase in the copper content and uptake with yield following the application of the biostimulants Tytanit, Green OK, and BrunatneBio Złoto. Wierzbowska et al. (2015) reported an increase in the copper content after treatment with Asahi SL and Kelpak SL, although copper uptake was unaffected by these products. By contrast, Głosek-Sobieraj et al. (2018) found no significant changes in the copper content due to the application of biostimulants. In our experiment, the weather conditions during the study years were found to determine copper accumulation and uptake with tuber yield (Figures 6, 7). The relatively dry year 2020 was the most favourable period for these characteristics. Głosek-Sobieraj et al. (2018) reported that under similar moisture conditions and temperature, which are conducive to potato growth and development (precipitation 303.7 mm, temp. 14.7°C), tubers contained the highest amount of copper. Similarly, Mystkowska and Rogóż--Matyszczak (2019) found that in an optimum year (precipitation 335.4 mm, temp. 14.6°C), copper content and uptake with potato yield were the highest.

According to Stein (2010), at least twenty minerals and trace elements are essential for the proper functioning of the human body. Regular consumption of potatoes contributes to the replenishment of mineral deficiencies, particularly since they are a common dietary component in many countries around the world (Wierzbicka 2012, Xu et al. 2023).

In the study reported here, the average Mn content in potato tubers was 0.21 mg 100 g^{-1} fresh weight, and the average copper content was 0.08 mg 100 g^{-1} of fresh weight (Table 5).

Table 5

Mean daily intake manganese and copper with the diet

Component	Mean in dry matter (mg kg^{-1})	Mean in fresh matter (mg $100g^{-1}$)	Dietary reference intake/day* (mg)	Dietary reference intake/day**	Percent of realisation
Manganese	11.07	0.21	3	1.8-2.3	7 (9.1)
Copper	4.13	0.08	1.3-1.6	0.9	5-6 (8.9)

* by EFSA (2013, 2015)
** by Jarosz et al. (2020)

The daily human requirement for manganese and copper is, respectively, 3.0 and 1.3-1.6 mg, according to the European Food Safety Authority (EFSA 2013, 2015). Therefore, consumption of 100 g of potato tubers meets approximately 7 and 5-6% of the daily requirement for these micronutrients. According to Polish standards (Jarosz et al. 2020), consumption of 100 g of potato tubers covers 9.1 and 8.9% of the respective recommended daily intake for these elements (Table 5). If higher (240 g day^{-1}), the ingestion provides about 20-21% of the required intake for these micronutrients. Similar findings were reported by Wierzbicka (2012) who claimed that potatoes satisfy human requirements for these elements at, respectively, about 6-8% and 11%. Also Gugała et al. (2018) found that a portion of 100 g of potato tubers supplies the human body with 21% of the required Mn, while Rubio et al. (2009) showed that Mn and Cu requirements were covered in about 6 and 18% respectively, and that 48% of dietary manganese originated from cereal plants.

CONCLUSIONS

The copper content and uptake with tuber yield, as well as the manganese uptake with tuber yield were significantly affected by the cultivars, treatment with the herbicide and biostimulants, and the weather conditions during the growing season of potatoes. Higher Cu concentrations were found in cv. Malaga tubers compared with Oberon, whereas higher uptake of the analysed elements (Mn, Cu) with tuber yield was determined for cv. Oberon, which was due to its higher yield. The test biostimulants increased the Cu content along with the Mn and Cu uptake compared with control tubers. The biostimulant Agro-Sorb Folium produced the best effects. Manganese and copper content were significantly affected by the weather conditions during the study years, and the application of biostimulants was only followed by a tendency for manganese increase. An important argument for incorporating biostimulants into potato cultivation is the fact that they enhance the tuber content of minerals, thereby increasing the coverage of the human body's daily requirements for micronutrients.

Author contributions

K.Z., I.M. – conceptualization, K.Z. M.G. – methodology, K.Z., A.G. – formal analysis, writing-original draft preparation, visualization, editing. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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