ACTA Acta Sci. Pol., Hortorum Cultus 10(2) 2011, 137-151

THE EFFECT OF SULPHUR KIND AND DOSE ON CONTENT AND UPTAKE OF MICRO-NUTRIENTS BY POTATO TUBERS (*Solanum tubersosum* L.)

Hanna Klikocka
University of Live Sciences in Lublin

Abstract. In case of sulphur shortage in the soil that element has a significant impact on yields of plants and their quality. The objective was to assess the impact of the work and the kind of sulphur content of Cu, Zn, Mn and Fe in the dry mass and uptake these elements by yield of dry mass of potato tuber. Experience in the field of potato head was in the years 2004–2006 by applying different kinds of sulphur (elemental and K_2SO_4) and dose (0, 25 and 50 kg·ha^{-1}). Sulphur indeed affected the application to increase the yield of tubers. However, there has been an independent impact dose and kind of sulphur of tested characteristics. Only in the case of interaction of dose and kind of sulphur fertilization it was found that the highest yield was found when using 25 kg·ha^{-1} in the sulphate kind and 50 kg·ha^{-1} S in sulphate and elemental kind. The yield of dry mass was greatest when applied 25 kg·ha^{-1} in the sulphate kind. The content of Cu, Zn, Mn (except Fe) in the dry mass and uptake these elements by yield of dry mass of potato tuber was significantly determined by S fertilization. The highest content of Cu and Zn in the dry mass and uptake these elements by yield of dry mass of tuber was after applying 50 kg S·ha^{-1} in elemental kind and on the control plots (without sulphur). Content and uptake of Mn by tuber was reduced by sulphur fertilization, and the contents and uptake of the Fe by tuber increased as a result of increasing doses of sulphur (although not confirmed that statistically). Elemental sulphur in dose 50 kg·ha^{-1} substantially reduced the pH value of the soil. It was a significant correlation between the pH value of the soil and the contents of Cu (negative), Zn (positive) and Mn (different values depending on years of research) in the dry mass and uptake these elements by yield of dry mass of potato tuber.

Key words: potato tubers, sulphate and elemental sulphur, copper, zinc, manganese, iron

INTRODUCTION

Potatoes (*Solanum tuberosum* L.) are the fourth most important food crop in the world, providing more edible food than the combined world output of fish and meat.

Corresponding author – Adres do korespondencji: Hanna Klikocka, Departament of Plant Production and Agrobusiness, University of Live Sciences in Lublin, ul. Szczebrzeska 102, 22-400 Zamość, e-mail: hanna.klikocka@up.lublin.pl

Statistical Pole consumes annually 116 kg of potato products [Dzwonkowski et al. 2010]. Because of that high consumption the health value of potato varieties i.e. content of macro and micro-nutrients compounds is of great importance. Humans require at least 22 mineral elements for their wellbeing [White and Broadley 2005, 2009, Graham et al. 2007]. These can be supplied by an appropriate diet. However, it is estimated that over 60% of the world's 6 billion people are iron (Fe) deficient, over 30% are zinc (Zn) deficient. In addition copper (Cu) and another element and vitamins deficiencies are common in many developed and developing countries [Graham et al. 2001, White and Broadley 2005, 2009, Welch and Graham 2005, Wang et al. 2008]. Mineral malnutrition is considered to be among the most serious global challenges to humankind and is avoidable [Copenhagen Consensus 2004]. Mineral malnutrition can be addressed through dietary diversification, mineral supplementation, food fortification and/or increasing mineral concentrations in edible crops (biofortification) [Graham et al. 2007; White and Broadley 2009].

Iron (Fe) deficiency proved to nutritional anemia, particular women, lower resistance to infection, reduced learning abilities, stunted growth, fatigue and reduced productivity [Welch and Graham 2002, Nube and Voortman 2006]. Iron is required in numerous essential proteins, such as the hem-containing proteins, electron transport chain and microsomal electron transport proteins, and iron-sulfur proteins and enzymes such as ribonucleotide reductase, prolyl hydroxyls phenylalanine hydroxylase, tyrosine hydroxylase and aconitase [Arredondo and Nunez 2005, Vicente et al. 2009]. The daily iron requirement of an adult person ranges 10 to 15 mg [Gugała and Zarzecka 2008]. However, the eating 200–350 g potatoes containing an average of 150 mg $Fe \cdot kg^{-1}$ tuber d.m. can also very good satisfy the daily iron requirement [Gugała and Zarzecka 2008].

Manganese (Mn) is a key component of enzyme systems, including oxygen-handling enzymes. It supports brain function and reproduction and is required for blood sugar regulation. In addition, it is part of bone structure [Vicente et al. 2009]. The daily manganese requirement of an adult person ranges 2,5 to 6 mg [Leszczyński 2000]. The eating of 200 g potatoes can good satisfy the daily Mn requirement [Zarzecka 2004].

Copper (Cu) is a redox active metal, plays an important role in the oxidative defense system. In fact, oxidative stress is a characteristic of copper deficiency [Uriu-Adams and Keen 2005, Vicente et al 2009]. Copper is necessary for the kindation of hemoglobin and is required for the function of over 30 proteins [Starck 2002]. Deficits of this nutrient during pregnancy can result in gross structural malkindations in the fetus, and persistent neurological and immunological abnormalities in the offspring [Uriu-Adams and Keen 2005]. Zarzecka and Gugała [2005] provide that, in accordance with the requirements of WHO the man should diet receive 2–3 mg Cu per day. 200 g potato consumption covers up to 30% of the demand for this element.

Zinc (Zn) is a pervasive microelement that plays a catalytic or a structural role in more than 200 enzymes involved in digestion, metabolism, reproduction, and wound healing. In addition, zinc has a critical role in immune response, and is an important antioxidant. In recent years, interest in the occurrence of human zinc deficiency, in particular among children, has been growing strongly. In various studies, in different parts of the world, zinc deficiency has been shown to be associated with increased morbidity and mortality, in particular from diarrhea, possibly also from malaria, and also with reduced child growth [Hotz and Brown 2004, Gupta 2005].

Chemical properties of potato tubers are variety characters. However, many other authors also show exterior factors as: locations, climatic factor, cultivation, fertilization [Karam et al. 1998; Zarzecka and Gugała 2005, Gugała and Zarzecka 2008]. Clean air acts led to a drastic decrease of SO_2 emissions in Western Europe including Poland and macroscopic sulfur deficiency has become a widespread nutrient disorder in agricultural production [Schnug 1998; Haneklaus et al. 2003, Balik et al. 2009]. Sulphur is now viewed as the fourth major plant nutrient which crops absorb in amounts comparable to that of phosphorus. Sulphur metabolism provides several efficient mechanisms by which plants are able to tackle abiotic (e.g., xenobiotics and increasing surface ozone levels) and biotic (e.g., pests and diseases) stress, particularly via the glutathione metabolism which again is closely related to the S supply of the plants [Haneklaus et al. 2003]. Other mechanisms involved in response to plant pathogens include the production of S containing compounds in the secondary metabolism of the agriculturally important *Brassica* species, the release of volatile S compounds, the production of S rich proteins, localized deposition of elemental S and the production of phytochelatines, which detoxify heavy metals by forming complexes [Schnug 1998]. The resistance of the crops to certain plant diseases is also improved by the S supply and could therefore minimize the input of pesticides [Klikocka et al. 2005, Grzebisz and Haerdter 2006]. An insufficient supply of S to the crop does not only reduce its economic yield, but it has also a decisive influence on the quality of the crop. Nurzyńska-Wierdak [2009] reported that the leaves of plants nourished with K_2SO_4 contained more nitrates and less Ca, Mg, Mn and Mo, as compared to KCl fertilization, which results from antagonistic effect of sulfates upon the uptake of molybdenum. Generally, it is not a growth-limiting nutrient, since sulfate, the oxidized anion, is relatively abundant in the environment. Sulfur fertilization increased yield of potato tubers, improved tuber quality (increased content of protein, starch, carotene, vitamin C, macro- and microelements) and resistance against *Streptomyces scabies* and *Rhizoctonia solani* [Klikocka et al. 2005, Klikocka 2009a, 2009b, 2010, Mishra and Srivastava 2004/5, Kumar et al. 2007]. Sulfur is an essential element in mineral nutrition of plants, especially high demand for sulphur, as: rape, onions, garlic, sugar beet [Klikocka 2010].

So far, however, no more information is available about the influence of the S supply on quality of potato tuber. Thus, it has been attempted to determine the effect of kind (sulphate and elemental) and dose (0, 25, 50 kg·ha^{-1}) of sulphur application on the content of Cu, Zn, Mn and Fe in the dry mass and uptake these elements by yield of dry mass of potato tuber.

MATERIALS AND METHODS

Field experiments with potatoes were conducted in the years 2004–2006 in a split plot design in fourfold repetition at Malice (N 50°42'; E 23°15'), a village near Zamość in Poland. The experiment was carried out on a leached brown earth with loamy silty soil texture (clay – 13%). Reaction of the soil, pH value = 5.2. Total-C content was on average 7.4 g·kg^{-1}. Total-N – 0.7 g·kg^{-1}; P – 41.7 mg·kg^{-1} and K – 76.8 mg·kg^{-1}; Mg – 30.8 mg·kg^{-1} and S-SO_4 – 10.1 mg·kg^{-1}.

Surface plots for planting and observation was 30 m^2, in contrast for harvesting was 19,5 m^{-2} (3.0 m · 6.5 m). The 'Irga', medium-early, edible variety was used. The fore-crop was Triticale in all of years of experimentation.

Precipitation (April – September) were similar than the long-term average during tuber kindation in 2005–2006 years of experimentation. The sum of long-term average precipitation (1971–2005) is 329.8 mm, while in 2005 and 2006 values of 315.2 and 329.8 mm were determined. In 2004 sum of precipitation were higher than the long-term (fewer 54.3 mm). The sum of mean month temperatures (April – September) in analyzed period was higher than long-term. The sum of mean month temperatures 2901°C in the 2004 and 2949°C in 2005 and 3142°C in 2006; the long-term average is 2687°C. To characterize the weather conditions in years of research 2004–2006 calculated hydro-thermal coefficient of Sielianinow, which was accordingly: 2004 – 1.3 (quite dry), 2005 – 1.1 (quite dry), 2006 – 1.0 (dry), long-term 1971–2005 – 1.5 (quite wet).

The following S treatments were tested: 0, 25 and 50 kg S·ha^{-1} as K_2SO_4 and 0, 25 and 50 kg S·ha^{-1} as elemental S. The K supply was balanced by using KCl in adequate rates. Elemental S originated from the sulfur mine „Jeziórko" in Poland and was fine-ground in a mortar.

After gathering of spring Triticale its used of 3 t·ha^{-1} straw from spring Triticale (as organic fertilization) and 46 kg N·ha^{-1} (urea $CO(NH_2)_2$) – for stabilization in ratio C:N) and were perkinded ploughing (20 cm, second or third decade of August). Spring field works were perkinded in the third decade of March, where shallow ploughing is used (15 cm). Every year, mineral fertilization in kg·ha^{-1} was applied pre-planting: N (as ammonium nitrate) – 100; P (as mineral superphosphate) – 40; K (as potassium sulphate) – 116. Potato planting was carried out in the second decade of April. Row-space was 67.5 cm with 44.000 tubers per 1 ha planted.

Potato planters are equipped with attachments to apply materials to control *Rhizoctonia solani* by metyl tolchlofos (Rizolex, 500 g a.i.·kg^{-1}, Sumitomo) in dose 10 g a.i. per 100 kg of tubers. Weed control was mechanical-chemical: mechanical treatments from potato planting until germination (harrowing, earthing up, and weeding). After germination was used herbicide metribuzin (Sencor 70 WP, 700 g a.i.·kg^{-1}, Bayer) in dose 0.350 g a.i.·ha^{-1} (Sencor – C_8H_{14}-ON_4S contained 15.0 % of S, in this case is used 0.05 kg S·ha^{-1}).

Chemical application of fungicides for the control of *Phytophthora infestans* (late blight) and other foliage diseases were perkinded four times:

1. oksadiksyl + mancozeb (Sandofan Manco 64 WP, 80 g a.i.·kg^{-1} of oksadiksyl + 560 g a.i.·kg^{-1} of mancozeb, Syngenta) in dose 160 g a.i.·ha^{-1} + 1120 g a.i.·ha^{-1},
2. Cooper (oxachloride kind) (Miedzian 50 WP, 500 g a.i.·kg^{-1}, Organika) in dose 1250 g a.i.·ha^{-1},
3. mancozeb (Dithane 75 WG 750 g a.i.·kg^{-1}, Dow AgroSciences) in dose 1500 g a.i.·ha^{-1},
4. fentin (hydroxide kind) (Brestanid 502 SC., 502 g a.i.·kg^{-1}, Aventis) in dose 251 g a.i.·ha^{-1}.

The control of potato-beetle (*Leptinotarsa decemlineata*) was obtained by triple application of safe, economical insecticides:

1. teflunenzuron (Nomolt 150 S.C., 150 g a.i.·L^{-1}, BASF) in dose 37,5 g a.i.·ha^{-1},
2. deltametryna (Decis 2,5 EC, 25 g a.i.·L^{-1}, Aventis) in dose 7.5 g a.i.·ha^{-1},
3. acetamiprid (Mospilan 20 SP, 200 g a.i.·kg^{-1}, Nippon Soda) in dose 20 g a.i.·ha^{-1}.

Chemical practices (suitably the second and the third) against late blight and chrysometids and fertlization feeding were perkinded jointly in order to reduce the number of crossings through the field (the preparations were mixed: Miedzian 50WP with Decis 2.5 EC) (2) and Dithane 75 WG with Mospilan 20 SP (3). The fourth protective treatment, a joint one, was carried out three weeks before potato harvest. Brestanid 502 S.C. (for the protection of tubers against the spores of potato blight) with dikwat desiccant (in ion kind) (Reglone Turbo 200 SL, 200 g s.a.·L^{-1}, Syngenta) in dose 600 g s.a.·ha^{-1}. Pesticides were applied by a 12-m-wide tractor-mounted sprayer that delivered 200 l·ha^{-1} spray solutions through 80–02 flat fan nozzles (model PILMET – P-412, Polen) at a spray pressure of 200 kPa. Tubers were harvested in the second decade of September.

Data analysis. Every year pH of soil (potentiometrically in 0.01 M $CaCl_2$) and content of soluble kinds of Cu, Zn, Mn and Fe in dry mass of potato tubers were determined (extraction with 2N HCl, determined by atomic absorption spectrophotometry (AAS).

The ANOVA was based on the Tukey's HSD test at a significance level of $p < 0.05$ [Trętowski and Wójcik 1988].

RESULTS AND DISCUSSION

Generally sulphur fertilization have positively changed the tuber yield of potato (5.9%) and decreased content of dry mass (3.7%). However, there has been no independent effect of dose and kind of sulphur fertilization. Only the interaction of dose and kind sulphur fertilization statistically a significant affect the value of traits (tab. 1). The highest tuber yield was found when 25 kg·ha^{-1} was applied in sulphate kind and 50 kg·ha^{-1} applied regardless of the kind. The dose of the elemental sulphur in dose of 25 kg·ha^{-1} cause increase in yield of tubers, although not confirmed this statistically. The yield of dry matter of tubers was highest when 25 kg·ha^{-1} was applied in sulphate kind, in another case was not changed by sulphur fertilization. The content of dry mass of potato tubers was highest in the case of control fertilization (without S).

The positive impact of sulphur fertilization (in the kind of: potassium sulphate, ammonium sulphate, sufran plus, single superphosphate, gypsum and elemental sulphur) on potato yields has multiple authors: Lalitha et al. [1997], Grocholl and Scheid [2002], Carew et al. [2009]. El-Fayoumy and El-Gamal [1998], Pickny and Grocholl [2002] recommend the use of elemental sulphur for potatoes in dose from 36 to 80 kg·ha^{-1}. However, some studies have shown a reduction in the yield of potato tubers as a result of the application of elemental sulphur [Eppendorfer and Eggum 1994]. Singh et al. [1995] argue that fertilization increases the sulphur content of dry matter in tubers, and also affects the increase in tubers, calcium, magnesium, sulphur, copper and iron. In addition, the authors you have demonstrated an increase in tubers available and free protein in amino acids. Eppendorfer and Eggum [1994] demonstrated that sulphur fertilization reduces tubers content cyst- + methionine-S, cyst and leucine, and increases the content of glutamic acid and arginine. Wang et al. [2008] says that in S-deficient soil, application of S fertilizer can significantly increase tuber yield and starch content of potato, while leading to a decrease in tuber N concentration due to an increase in dry matter production. While Kumar et al. [2007] reported that tuber dry matter percentage did vary with K-sources and sulphate and nitrate sources of K gave higher values than K-chloride.

Table 1. The influence of sulphur fertilization on the yield of potato tubers and pH value of soil and content and yield of dry matter
Tabela 1. Wpływ nawożenia siarką na plon bulw oraz zawartość i plon suchej masy oraz wartość pH gleby

S rate Dawka S $kg \cdot ha^{-1}$	S kind Rodzaj nawozu	Tuber yield Plon bulw $t \cdot ha^{-1}$	Content of dry mass Zawartość s.m. %	Yield of D.M. of tubers Plon s.m. $t \cdot ha^{-1}$	pH 0.01 M $CaCl_2$
0 – control – kontrola		25.56	22.7	5.81	5.25–5.33
25	SO_4	28.06	22.4	6.28	5.18–5.40
25	S	26.17	22.1	5.78	5.19–5.32
50	SO_4	27.02	21.5	5.80	5.20–5.42
50	S	27.44	21.5	5.90	5.08–5.21
25	mean	27.12	22.2	6.03	5.21–5.31
50	średnio	27.23	21.5	5.85	5.15–5.32
Mean	SO_4	27.54	21.9	6.04	5.24–5.32
Średnio	S	26.81	21.8	5.84	5.15–5.23
Years Lata	2004	24.68	22.3	5.58	5.26–5.33
	2005	27.42	22.1	5.99	5.26–5.38
	2006	29.24	21.7	5.91	5.23–5.35
*LSD – NIR: Rate – Dawka S		n.s.	n.s.	n.s	n.s.
Kind – Rodzaj S		n.s.	n.s.	n.s	0.08
Rate × Kind S Dawka S × Rodzaj S		1.60	0.3	0.33	0.10
Years – Lata		1.19	0.2	0.24	0.08

* LSD – NIR: ($P < 0.05$) significant difference – istotna różnica; n.s.: not significant – nieistotny

The content of Cu, Zn, Mn and Fe in the dry mass and uptake these elements by yield of dry mass of potato tuber was generally significantly determined by S fertilization (tab. 2). Eppendorfer and Eggum [1994] and Singh et al. [1995] says that S application increased in tuber of total-N, P, K, Na, Ca, Mg, Zn Mn, Cu and Fe contents. Singh and Srivastava [1996] supplemented S for potato in dose of 20 $kg \cdot ha^{-1}$, in the $CaSO_4$ kind and have demonstrated increase of iron in chloroplasts and higher content iron in tubers. Also El-Fayoumy and El-Gamal [1998] have studied that sulphur fertilization increased in tubers: carotene, vitamin C, starch, protein, micronutrients and reduced sugar content.

In presented study generally sulphur fertilization have changed the content of Cu, Zn, Mn and Fe in the dry mass and uptake these elements by yield of dry mass of potato tubers. However, does not in any case changes depend on the direct effect of dose and kind of fertilizer. Only the interaction of factors (except iron) saw changes in the contents of elements in dry mass and its yield of dry mass tubers (tab. 2).

Table 2. The influence of sulphur fertilization on content (A) ($mg·kg^{-1}$) and uptake (B) ($g·ha^{-1}$) of micro-elements by tubers
Tabela 2. Wpływ nawożenia siarką na zawartość (A) ($mg·kg^{-1}$) i pobranie mikroelementów przez bulwy (B) ($g·ha^{-1}$)

S rate dawka S $kg·ha^{-1}$	S kind rodzaj nawozu	Copper Miedź		Zinc Cynk		Manganese Mangan		Iron Zelazo	
		A**	B**	A	B	A	B	A	B
		content and uptake in dry mass – zawartość i pobranie w suchej masie							
0 – Control – Kontrola		11.4	65.5	33.05	191.3	27.4	161.0	90.0	519.4
25	SO_4	7.5	47.1	29.88	186.8	21.7	139.6	105.1	658.8
25	S	9.7	56.6	27.76	159.5	15.9	92.0	112.5	650.1
50	SO_4	8.8	50.8	24.93	144.7	12.0	69.6	117.8	681.5
50	S	13.7	80.1	31.76	186.6	14.9	87.4	112.3	661.7
25	mean	8.6	51.9	28.82	173.2	18.8	115.8	108.8	654.5
50	średnio	11.2	65.4	28.35	165.6	13.4	78.5	115.0	671.6
Mean	SO_4	8.2	48.9	27.40	165.8	16.9	104.6	111.5	670.2
Średnio	S	11.7	68.4	29.76	173.0	15.7	89.7	112.4	655.2
Years Lata	2004	10.2	56.7	29.50	164.9	12.8	71.3	95.6	531.3
	2005	10.9	64.5	38.60	230.2	21.1	125.8	150.1	902.5
	2006	9.6	58.9	20.33	126.3	21.2	132.7	76.9	469.1
*LSD – NIR: Rate – Dawka S		2.4	13.28	n.s.	n.s.	2.9	18.1	n.s.	n.s.
Kind – Rodzaj S		2.2	12.46	2.3	n.s.	n.s.	19.1	n.s.	n.s.
Rate × Kind S dawka S × Rodzaj S		2.6	15.47	3.5	22.4	3.8	25.4	n.s.	n.s.
Years – Lata		n.s.	n.s.	3.3	17.7	2.9	18.1	19.1	109.4

**A: content in d.m. – zawartość w s.m., B: uptake by d.m. of yield of tubers – pobranie z plonem s.m. bulw

The highest content and uptake of Cu in potato dry matter was found when using 50 kg $S·ha^{-1}$ in elemental kind, in relation to the control of growth amounted to respectively: 16.8 and 18.2%. However, the remaining doses and the kind of lowered the contents and the content and uptake of Cu in relation to the control, respectively, on 24 and 22%. The contents and the uptake of Cu by tubers conducive to fertilization in double dose and use elemental kinds. Content and uptake of Zn in potato tubers was highest in control plots (without S) and in case when 50 kg $S·ha^{-1}$ in elemental kind was used. In other cases, sulphur fertilizing has downgraded the Zn content (16.7%) and a uptake of Zn (14.4%) in relation to the control. Regardless from S rate the elemental S kind was favourable for highest content and uptake of Zn (7.9%) as sulphate kind. Content and uptake of Mn in dry mass of potato tubers was highest in control plots (without S) and substantially decreased after each dose and kind S (41.1 and 39.7%). Least Mn contained and accumulated tubers after applying sulphur in dose of 50 $kg·ha^{-1}$. The kind of sulphur had no significant impact on the content and the uptake of Mn by dry mass of tubers. The sulphur fertilization not influenced content and uptake of Fe in dry mass of potato tubers. However, the smallest content and uptake of Fe in potato tubers was in control plots, but the sulphur fertilization increased accumulation of Fe in tubers, although not confirmed this statistically (tab. 2).

Singh and Srivastava [1996] says that S fertilizer (20 kg S·ha^{-1}) increased stem and tuber Fe contents and plant Fe uptake but tuber Fe concentration declined during growth from the dilution effect. Gugała and Zarzecka [2008], Kucharzewski et al. [2002] believe that iron concentration below the average value, ranking from 21 to 58 mg·kg^{-1} d.m., is not harmful because plants take up the element in varying amounts (200–2500 g per 1 ha) and in general, show a marked tolerance to high Fe concentration in tissues. This phenomenon was also seen in the presented studies, where in the year 2005 was iron almost twice more than in the remaining years of the study. Zarzecka and Gugała [2005] stated that the contents of the Cu in tubers affected significantly the herbicide, variety and climate conditions, while substantially lower copper content of the herbicide. The vegetation seasons have significantly changed the content and uptake of micro-nutrients by potato tubers. The highest content and uptake of reported micro-nutrients was in the year 2004 and 2005. The smaller amounts of Cu, Zn and Fe (only Mn) were observed in 2006. These results are compatible with the opinion of Gugała and Zarzecka [2008] and Zarzecka [2004], those who argue that the humid years are particularly conducive to concentration of copper, manganese and iron in potato tubers.

Under the Regulation of the Ministry of Health of April 30, 2004, on permissible levels of food chemical and biological pollution, limiting cooper, zinc, iron and manganese contents in potato tuber has been abandoned due to the present deficiencies of these elements in diets [Wojciechowska-Mazurek et al. 2003]. Also Gembarzewski [2000] in his studies on basic crops found a decreased uptake of Cu, Mn and Fe with potato tuber yield in the years 1966–1970.

In presented study sulphur fertilization in rate 50 kg·ha^{-1} in elemental kind significantly decreased pH value of soil (tab. 1). Significantly negative correlation between pH value of soil and content of Cu and uptake of Cu and Mn observed in 2004. In 2005 no observed significantly interrelation. While in 2006 between pH value of soil and content and uptake of Zn and Mn positive interrelation was observed. Only Fe in tubers not correlated with pH value of soil (tab. 3, 4). El-Fayoumy and El-Gamal [1998] reported that S applications decreased soil pH value and increased micronutrients availabilities in the soil, besides improving nutrient uptake and the elemental status of plant; leaves and tubers. Sillanpää [1982], Garcia-Mina et al. [2004], Kabata-Pendias [2004], Nube and Voortman [2006] says that contents of various micronutrients in plants depend on the total micronutrient supply in soils and on factors controlling their availability to plants. Frossard et al. [2000], White and Broadley [2008] and Smoleń et al. [2010] claims that Zn, Mn and Fe in plant correlated with Zn, Mn and Fe in soil and pH value of soil. The Zn and Mn contents of plants decreased steadily with rising pH value. The phenomenon is also confirmed in the presented studies. The Cu content of plants increases only slightly with increasing soil organic carbon in soils of very low organic matter content, while further increases in organic carbon cause a decrease in the Cu content in plants. However, a clear increasing trend of soil Cu and plant Cu toward alkaline soils can be noticed. Also Vicente et al. [2009] claim that the availability of copper to plants, as with other trace minerals, markedly decreases as pH value rises above seven. At high pH value copper is strongly adsorbed to clays, iron and aluminum oxides, and organic matter. Of the micronutrients required by plants, copper often has the lowest total concentration in soil.

Table 3. Significant correlation coefficients between elements in plant and yield of potato tubers (mean of 2004–2006)
Tabela 3. Istotne współczynniki korelacji pomiędzy plonem bulw a pierwiastkami w bulwach (średnio w latach 2004–2006)

Specification Wyszczególnienie (n = 60)	Yield of tubers Plon bulw	Content of dry mass Zawartość s.m.	Yield of dry mass Plon s.m.	Elements in tubers Pierwiastki w bulwach							
				Cu		Zn		Mn		Fe	
				C.	R.	C.	R.	C.	R.	C.	R.
pH of soil ph gleby	-0.28*	0.44	-	-	-	-	-	-	-	-	-
Yield of tubers Plon bulw	-	-0.44	0.93	-	-	-	-	-	0.27	-	-
Content of dry mass zawartośc suchej masy	-	-	-	-	-	0.31	0.30	0.34	0.31	-	-
Yield of dry mass Plon suchej masy	-	-	-	-	-	-	-	0.31	0.44	-	-

C – content in d.m. of tubers – zawartość w s.m. bulw; R – uptake in yield with d.m. of tubers – pobranie z plonem s.m. bulw;
*Significant coefficients – współczynniki istotne

Also soil Fe seems to have been more affected by the various soil factors than plant Fe. Increases in soil pH value and $CaCO_3$ equivalent values were accompanied by decreases in the extractable soil Fe contents and its availability to plants. Fe and Mn are also strongly affected by oxidation-reduction reactions which largely depend on the soil moisture content [Sillanpää 1982, Garcia-Mina et al. 2004, Kabata-Pendias 2004, Nube and Voortman 2006].

Significantly correlation was between pH value of soil and tuber yield (negative) and between pH value of soil and content of dry matter of tuber (positive) (tab. 3, 4). Content and uptake of zinc correlated positively with content of dry mass of tubers. Manganese correlated positively with tuber and dry mass yield, and with content of dry mass (tab. 3).

High positive correlation observed also between content and uptake of: Cu and Mn (respectively: 0.51 and 0.44) in 2004, Cu and Zn (respectively: 0.71 and 0.63), Cu content and Fe uptake (-0.42) in 2005, Cu and Mn content and uptake (respectively: 0.41 and 0.43) Cu and Zn uptake (respectively: 0.46 and 0.56), Cu and Mn uptake (respectively: 0.46 and 0.53), Zn content and Mn content and uptake (respectively: 0.73 and 0.77), Zn uptake and Mn content and uptake (respectively: 0.69 and 0.77) in 2006. In another case, on the same element between content and uptake was observed, that correlation coefficients was also significant (tab. 4). Sillanpää [1982], Frossard et al. [2000], Starck [2002], Nube and Voortman [2006], White and Broadley [2009] reported that good correlation between the plant contents of two micronutrients depended on availability of these micronutrients and is controlled by the same soil factor (e.g. pH value of soil) or factors. The best example is negative correlation between Mo and Mn. While the Mn contents of plants decrease greatly with rising pH value the Mo content increase and deficiencies of both Mn and Mo can therefore hardly exist in same soil. In Mn and Zn case the soil pH value exercises the leading effect on the availability of these micronutrients to plants, also other soil factors e.g. texture and organic carbon content, which correlate with plant Mn much as they do with plant Zn. Therefore between extractable soil Mn and Zn, these factors may contribute to the good plant Mn-Zn correlation. Sillanpää [1982], Starck [2002], Nube and Voortman [2006] says that for the correlations between the plant contents of Fe and Zn, Fe and Cu and Fe and Mn the common soil factors are not defined, since the Fe contents of plants were less strongly affected any of the soil factors studied than were the other micronutrients. In all three cases, Fe-Zn, Fe-Cu, and Fe-Mn, the extractable soil contents are correlated to a degree similar to the plants content. In general, taking into account the very small concentrations of micronutrients in soils, the possibility that one micronutrient directly affects the availability of another seems less likely than that their mutual relationships are indirectly determined by other soil factors affecting their behavior. Nube and Voortman [2006] claims that chemically, zinc has some similarities with iron and magnesium, and in plant uptake there can be competition between these elements. Furthermore, high levels of phosphate in soils can strongly reduce zinc availability. As for iron, there is large variation in zinc contents of foods. For example, most green vegetables are rather rich in zinc, but zinc contents of root crops such as cassava and yams are very low [Nube and Voortman 2006]. It should be noted that in developing countries cereals are generally the main source of dietary zinc intake. Furthermore, with respect to crop zinc contents it is important to note that, according to some studies, problems of zinc deficiency have been aggravated in the process of the green revolution [Dar 2004], and several studies report lower levels of micronutrients, including zinc, in modern varieties of rice and wheat in comparison with traditional varieties [Cakmak 2002]. Both greenhouse studies and field experiments have shown, for various food crops, that fertilization with zinc can result in significant increases in yields. For example, in field experiments in Turkey application of zinc resulted in wheat yield increases up to 500%, depending on local soil conditions and method of zinc application [Cakmak 2002]. While leaf application of zinc fertilizer (e.g. $ZnSO_4$) had the largest positive effect, simple addition of zinc fertilizer to soils can already have a significant yield increasing effect.

Cakmak [2002] and Dar [2004] reported that plant with restricted growth (low yields) contain more micronutrients per unit plant mass produced in relation to available soil micronutrients than do the plants growing more rapidly (high yields). The principles of these relations, called here as concentration-dilution phenomenon. When is high yields, the plants are apparently unable to absorb micronutrients from soil in quantities related to the mass of DM produced. Consequently, portions of the micronutrients already absorbed are diluted in the increased DM mass and the micronutrients contents of the plants in relation to available micronutrients in soil decrease with increasing yields. This phenomenon in the presented studies significantly not confirmed.

Table 4. Significant correlation coefficients between elements in plant and pH
Tabela 4. Istotne współczynniki korelacji pomiędzy pierwiastkami w bulwach a pH gleby

Specification Wyszczególnienie (n = 20)	Yield of tubers Plon bulw	Elements in tubers Pierwiastki w bulwach							
		Cu		Zn		Mn		Fe	
		C.	R.	C.	R.	C.	R.	C.	R.
pH of soil									
2004	-0.44	-0.42	-0.46	-	-	-	-0.41	-	-
2005	-	-	-	-	-	-	-	-	-
2006	-	-	-	0.42	0.44	0.41	0.41	-	-

An Explanation in tab. 3 – wyjaśnienie w tab. 3.

Scherer [2001], Aulakh [2003], Reszel et al. [2004], Jaggi et al. [2005] reported that the S deficiency in soils in several parts of the world led to the use of fertilizer S to enhance the production and quality of crops. Among S-containing fertilizers, elemental S (S^o) is becoming increasingly popular in field crops. Use of S^o helps to reduce leaching and run-off losses, leaving prolonged residual effects on the S nutrition of the succeeding crop. The biochemical oxidation of S^o produces H_2SO_4, which decreases soil pH value and solubilizes $CaCO_3$ in alkaline calcareous soils to make soil conditions more favorable for plant growth, including the availability of plant nutrients [Jaggi et al. 2005, Klikocka 2005a, 2010]. Thus, application of S^o to alkaline-calcareous soils could assist in correcting iron chlorosis. Soil pH is known to regulate bioactivity and availability of nutrients to plants, because H^+ protons are involved in chemical equilibrium [Jaggi et al. 2005]. The use of S^o in alkaline soils reduces soil pH value, which may create favorable conditions for the availability of plant nutrients, especially P [Aulakh 2003, Kulczycki 2003]. As reported in the presented research sulphur fertilization, especially in the elemental kind resulted in lowering the pH value and the important increase of content and download cooper and iron by tubers of potatoes. This phenomenon was in the presented studies. Therefore, you should recommend supplementation of mineral fertilization under potatoes in sulphur, particularly in elemental kind.

CONCLUSIONS

The yield of tubers and content and yield of dry matter depend substantially on the interaction of the dose and kind of fertilizer. The highest tuber yield was found when 25 $kg \cdot ha^{-1}$ S was applied in sulphate kind and 50 $kg \cdot ha^{-1}$ S applied in sulphate and elemental kind. The yield of dry matter was highest when 25 $kg \cdot ha^{-1}$ was applied in sulphate kind.

The content of Cu, Zn, Mn and Fe in the dry mass and uptake these elements by yield of dry mass of potato tuber was significantly determined by S fertilization. The highest content and uptake of Cu, Zn was found when using 50 kg $S \cdot ha^{-1}$ in elemental kind and in control plots. Content and uptake of Mn by dry mass of tubers was decreased generally by S-fertilization. The S-fertilization increased amount and uptake of Fe in dry mass of potato tubers (although not confirmed this statistically).

Sulphur fertilization in rate 50 kg·ha^{-1} in elemental kind significantly decreased pH value of soil. Is stated significantly interrelation between pH value of soil and content and uptake (only Fe) of Cu (negative), Zn (positive) and Mn (different values depending on years of research). Significantly correlation was between pH value of soil and tuber yield (negative) and between pH value of soil and content of dry matter of tuber (positive). Zn and Mn correlated positively with content of dry matter. High positive correlation observed also between content and uptake by tubers of: Cu and Zn, Cu and Mn, Zn and Mn.

REFERENCES

Aulakh M.S., 2003. Crop responses to sulphur nutrition. [In:] Abrol YP, Ahmad A. (eds.), Sulphur in plants. Kluwer, Boston, 341–358.

Arredondo M., Nunez M.T., 2005. Iron and copper metabolism. Mol. Aspects Med., 26, 313–327.

Balik J., Kulhanek M., Černy J., Szakova J., Pavlikova D., Čermak P., 2009. Differences in soil sulfur fractions due to limitation of atmospheric deposition. Plant Soil Environ., 55(8), 344–352.

Cakmak I., 2002. Plant nutrition research: Priorities to meet human needs for food in sustainable ways. Plant and Soil 247, 3–24.

Carew R., Khakbazan M., Mohr R., 2009. Cultivar Developments, Fertilizer Inputs, Environmental Conditions, and Yield Determination for Potatoes in Manitoba. Am. J. Pot Res. 86, 442–455.

Copenhagen Consensus., 2004. http://www.copenhagenconsensus.com.

Dar W.D., 2004. Macro-benefits from micronutrients for grey to green revolution in agriculture, IFA international symposium on micronutrients, 23–25 February 2004, New Delhi, India.

Dzwonkowski W., Szczepaniak J., Zalewski A., Chotkowski J., Rembeza J., Mieczkowski M., 2010. Rynek ziemniaka – stan i perspektywy. Wyd. IERiGŻ, ARR, MRiRW Warszawa.

El-Fayoumy M.E., El-Gamal A.M., 1998. Effects of sulphur application rates on nutrients availability, uptake and potato quality and yield in calcaerous soil. Egypt. J. Soil Sci. 38(1–4), 271–286.

Eppendorfer W.H., Eggum B.O., 1994. Sulphur deficiency of potatoes as reflected in chemical composition and in some measures of nutritive value. Norweg. J. Agr. Sci. Supplement. 15, 127–134.

Frossard E., Bucher M., Mächler F., Mozafar A., Hurrell R., 2000. Potential for increasing the content and bioavailability of Fe, Zn and Ca in plants for human nutrition. J. Sci. Food Agr. 80, 861–879.

Garcia-Mina J.M., Antolin M.C., Sanchez-Diaz M., 2004. Metal-humic complexes and plant micronutrient uptake: a study based on different plant species cultivated in diverse soil types. Plant and Soil 258, 57–68.

Gembarzewski H., 2000. Stan i tendencje zmian zawartości mikroskładników w glebach i roślinach z pól produkcyjnych w Polsce. Zesz. Probl. Post. Nauk Rol., 471, 171–179.

Graham R.D., Welch R.M., Bouis H.E., 2001. Addressing micronutrient malnutrition through enhancing the nutritional quality of staple foods: principles, perspectives and knowledge gaps. Adv. Agron. 70, 77–142.

Graham R.D., Welch R.M., Saunders D.A., Ortiz-Monasterio I., Bouis H.E., Bonierbale M., de Haan S., Burgos G., Thiele G., Liria R., et al., 2007. Nutritious subsistence food systems. Adv. Agron. 92, 1–74.

Grocholl J., Scheid L., 2002. Effect of sulfur on potato yield and quality. 15th Triennial Conf. EAPR. 14–19.07.2002. Hamburg. Abstracts, 240

Grzebisz W., Haerdter R., 2006. Kizeryt – naturalny siarczan magnezu w produkcji roślinnej. Verlagsgesselschaft für Ackerbau mbH, Kassel, Niemcy.

Gugała M., Zarzecka K., 2008. Effect of weed control operations and tillage simplifications on iron content and uptake with potato tuber yield. J. Elementol. 13(3), 321–327.

Gupta A.P., 2005. Micronutrient status and fertilizer use scenario in India. J. Trace. Elem. Med. Biol. 18, 325–331.

Haneklaus S., Bloem E., Schnug E., 2003. The global sulphur cycle and its links to plant environment. [In:] Y.P. Abrol, A. Ahmad, (eds.), Sulphur in Plants, Kluwer Academic Publishers, Dordrecht, 1–28.

Hotz C., Brown K.H., 2004. Guest Editors, Assessment of the risk of zinc deficiency in populations and options for control, IZiNCG Technical Document 1. Food and Nutrition Bull. 25, Suppl. 2.

Jaggi R.C., Aulakh M.S., Sharma R., 2005. Impacts of elemental S applied under various temperature and moisture regimes on pH and available P in acidic, neutral and alkaline soils. Biol. Fertil. Soils 41, 52–58.

Kabata-Pendias A., 2004. Soil-plant transfer of trace elements-an environmental issue. Geoderma 122(2–4), 143–149.

Karam N.S., Ereifej K.I., Shibli R.A., AbuKudais H., Alkofahi A., Malkawi Y., 1998. Metal concentrations, growth, and yield of potato produced from in vitro plantlets or microtubers and grown in municipal solid-waste-amended substrates. J. Plant Nutrition 21(4), 725–739.

Klikocka H., Haneklaus S., Bloem E., Schnug E., 2005. Influence of sulfur fertilization on infection of potato tubers with *Rhizoctonia solani* and *Streptomyces scabies*. J. Plant Nutrition 28(05), 1–14.

Klikocka H., 2009a. The Influence of enriched NPK fertilization with S, Mg, and conteined of micronutrients liquid fertilizer Insol 7 on potato tubers yield (*Solanum tuberosum* L.) and infestation of tubers with *Streptomyces scabies* and *Rhizoctonia solani.* J. Element. 14(2), 271–288.

Klikocka H., 2009b. Sulfur supply in Polish agriculture. [w:] Sulfur Metabolism in Plants. Ed. Sirko A., De Kok L.J., Haneklaus S., Hawkesford M.J., Rennenberg H., Saito K., Schnug E., Stulen I. Backhuys Publishers, Leiden, The Netherlands, Margraf Publishers, Weikersheim, Germany, 45–48.

Klikocka H., 2010. Znaczenie siarki w biosferze i nawożeniu roślin. Przem. Chem. 89/7, 903–908.

Kucharzewski A., Nowak L., Dmowski Z., Markowski J., 2002. Zawartość metali ciężkich i siarki w ziemniakach na Dolnym Śląsku. Zesz. Probl. Post. Nauk Rol., 480, 491–497.

Kulczycki G., 2003. Wpływ nawożenia siarką elementarną na plon i skład chemiczny roślin oraz właściwości gleby. Nawozy Nawoż. 5, 4, 17, 151–159.

Kumar P., Pandev S.K., Singh B.P., Singh S.V., Kumar D., 2007. Influence of Source and Time of Potassium Application on Potato Growth, Yield, Economics and Crisp Quality. Potato Res. 50, 1–13.

Lalitha B.S., Sharanappa, Hunsigi G., 1997. Balance sheet of available potassium and sulphur as influenced by K and S application in seed tuber and true potato seed raised crop. J. Indian. Potato Ass. 24(3–4), 171–173.

Leszczyński W., 2000. Jakość ziemniaka konsumpcyjnego. Żywność 4 (25), 5–27.

Mishra K.K., Srivastava J.S., 2004/5. Soil amendments to control common scab of potato. Potato Res. 47, 101–109.

Nube M., Voortman R.L., 2006. Simultaneously addressing micronutrient deficiencies in soils, crops, animal and human nutrition: opportunities for higher yields and better health. Staff Working Paper WP-06-02. Stichting Onderzoek Wereldvoedselvoorziening van de Vrije Universiteit. Centre for World Food Studies. 1–41.

Nurzyńska-Wierdak R., 2009. Growth and yield of garden rocket (*Eruca sativa* Mill.) affected by nitrogen and potassium fertilization. Acta Sci. Pol., Hortorum Cultus 8(4), 23–33.

Pickny J., Grocholl J., 2002. Kartoffelschorf-Lässt sich der Befall durch eine Schwefeldüngung vermindern? Kartoffelbau. 3(53), 76–78

Reszel R., Reszel H., Pęcek J., Hadam B., 2004. Heavy metals and sulphur in the soils of farmlands in protected areas of the Podkarpacie region. Environ Prot Eng. 4, 113–121.

Rozporządzenie Ministra Zdrowia z dnia 30 kwietnia 2004 r. w sprawie maksymalnych poziomów zanieczyszczeń chemicznych i biologicznych w żywności. Dz.U. nr 120, poz. 1257.

Schnug E. (Ed.), 1998. Sulphur in Agroecosystems. Kluwer Academic Publishers. The Netherlands.

Scherer NW., 2001. Sulphur in crop production. Eur. J. Agron. 14, 81–111.

Singh J.P., Marwaha R.S., Srivastava O.P., 1995. Processing and nutritive qualities of potato tubers as affected by fertilizer nutrients and sulphur application. J. Indian Potato Ass. 22(1–2), 32–37.

Singh J.P., Srivastava O.P., 1996. Accumulation and distribution pattern of iron in potato plant and influence of sulphur fertilization. J. Indian Potato Ass. 23(1–2), 68–71.

Sillanpää M., 1982. Micronutrients and the nutrient status of soils: a global study. FAO Soils Bull. Rome, 9–12.

Smoleń S., Sady W., Ledwożyw-Smoleń I., 2010. Quantitative relations between the content of selected trace elements in soil extracted with 0.03 M CH_3COOH or 1 M HCl and its total concentration in carrot storage roots. Acta Sci. Pol., Hortorum Cultus 9(4), 3–12.

Starck Z., 2002. Składniki mineralne w roślinach. [In:] J. Kopcewicz, S. Lewak (eds.). Fizjologia roślin. PWN Warszawa, 228–239.

Trętowski J., Wójcik A.R., 1988. Metodyka badań rolniczych. WSRP Siedlce, 124–215.

Uriu-Adams J.Y., Keen C.L., 2005. Copper, oxidative stress, and human health. Mol. Aspects Med., 26, 268–298.

Vicente A.R., Manganaris G.A., Sozzi G.O., Crisisto C.H., 2009. Nutritional Quality of Fruits and Vegetables. [In:] W.J. Florkowski, R.L. Shewfelt, R. Brueckner, S.E. Prussia (eds.). Postharvest Handing: A Systems Approach. Elsevier INC., 81–86.

Wang Zhao-Hui, Li Sheng-Xiu, Malhi S., 2008. Effects of fertilization and other agronomic measures on nutritional quality of crops. J. Sci. Food Agric. 88, 7–23.

Welch, R.M., Graham, R.D., 2002. Breeding crops for enhanced micronutrient content. Plant and Soil 245, 205–210.

Welch R.M., Graham R.D., 2005. Agriculture: the real nexus for enhancing bioavailable micronutrients in food crops. J. Trace Elem. Med. Biol. 18, 299–307.

White P.J., Broadley M.R., 2005. Biofortifying crops with essential mineral elements. Trends Plant Sci. 10, 586–593.

White P.J., Broadley M.R., 2009. Biofortification of crops with seven mineral elements often lacking in human diets – iron, zinc, copper, calcium, magnesium, selenium and iodine. New Phytol. 182, 49–84.

WHO, 2001. Iron deficiency anemia, Assessment, Prevention, and Control, A guide for programme managers, Unicef/UNU/WHO, WHO/NHD/01.3, Geneva.

Wojciechowska-Mazurek M., Starska K., Brulińska-Ostrowska E., Karłowski K., 2003. Maksymalne dopuszczalne poziomy metali szkodliwych dla zdrowia w żywności. Przem. Spoż. 2, 44–51.

Zarzecka K., 2004. Zawartość żelaza i manganu w bulwach ziemniaka w zależności od sposobu zwalczania chwastów. Acta Sci. Pol., Agricultura 3(1), 165–173.

Zarzecka K., Gugała J., 2005. Wpływ sposobów regulacji zachwaszczenia na zawartość miedzi i żelaza w bulwach ziemniaka jadalnego. J. Element. 10(3), 615–623.

WPŁYW DAWKI I RODZAJU SIARKI NA ZAWARTOŚĆ I POBRANIE MIKROELEMENTÓW PRZEZ BULWY ZIEMNIAKA (*Solanum tubersosum* L.)

Streszczenie. W warunkach niedoboru siarki w glebie nawożenie tym pierwiastkiem ma istotny wpływ na plonowanie roślin i ich jakość. Celem pracy była ocena wpływu dawki i rodzaju siarki na zawartość w suchej masie i pobranie przez plon suchej masy bulw ziemniaka Cu, Zn, Mn i Fe. Doświadczenie polowe z ziemniakiem prowadzono w latach 2004–2006, stosując różne rodzaje siarki (siarka elementarna i K_2SO_4) i dawki (0, 25 i 50 kg·ha^{-1}). Aplikacja siarki istotnie wpłynęła na zwiększenie plonu bulw. Jednakże nie zaobserwowano niezależnego wpływu dawki siarki i rodzaju nawozu. Dopiero w przypadku ich współdziałania stwierdzono, że najwyższy plon bulw nastąpił, gdy zastosowano 25 kg·ha^{-1} siarki w postaci siarczanowej i 50 kg·ha^{-1} siarki niezależnie od rodzaju nawozu. Plon suchej masy bulw był największy, gdy stosowano 25 kg·ha^{-1} siarki w postaci siarczanowej. Zawartość w suchej masie bulw i pobranie w plonie suchej masy bulw Cu, Zn, Mn (z wyjątkiem Fe) zależało generalnie od nawożenia siarką. Dodatek siarki w dawce 25 kg·ha^{-1} w postaci siarczanowej obniżał zawartość i pobranie mikroelementów w suchej masie bulw. Najwyższa zawartość i pobranie Cu i Zn przez bulwy była po zastosowaniu 50 kg S·ha^{-1} w postaci elementarnej i na poletkach kontrolnych (bez siarki). Zawartość i pobranie Mn było ograniczane nawożeniem siarką, natomiast zawartość i pobranie Fe przez bulwy zwiększało się w wyniku zwiększania dawki siarki (choć nie potwierdzono tego statystycznie). Nawożenie siarką elementarną w dawce 50 kg·ha^{-1} istotnie zmniejszyło wartość pH gleby. Stwierdzono istotną korelację między wartością pH gleby a zawartością i pobraniem Cu (ujemną), Zn (dodatnią) i Mn (różne wartości w zależności od lat badań).

Słowa kluczowe: bulwy ziemniaka, siarka siarczanowa i elementarna, miedź, cynk, mangan, żelazo

Accepted for print – Zaakceptowano do druku: 15.03.2011