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EFFECT OF FERTILISATION WITH NITROGEN MACROELEMENTS ON THE CONTENT OF SULPHUR AND THE ACTIVITY OF ARYLSULPHATASE IN SOIL

WPŁYW NAWOŻENIA MIKROSKŁADNIKAMI NA ZAWARTOŚĆ SIARKI ORAZ AKTYWNOŚĆ ARYLOSULFATAZY W GLEBIE

Abstract: The aim of the present research was to determine the effect of mineral fertilisation only on the activity of arylsulphatase (EC 3.1.6.1.) and the content of total sulphur and its fraction in soil under winter wheat. The soil was sampled from a field experiment set up on the area of the Agricultural Experiment Station at Grabow on the Vistula by the Institute of Soil Science and Plant Cultivation (IUNG) in Pulawy twice in the vegetation period of winter wheat in 2008. The experiment involved only mineral fertilisation: increasing rates of ammonium nitrate (0, 40, 80, 120, 160 kgN · ha^{-1}) and fertilisation with P – 70 kgP_2O_5 · ha^{-1}, K – 90 kgP_2O_5 · ha^{-1}, Ca – 200 kgCaO · ha^{-1}, Mg – 70 kgMgO · ha^{-1} and S in fertilisation forms with other elements. The activity of arylsulphatase was determined following the Tabatabai and Bremner method, and sulphate sulphur – compliant with the Bardsley–Lancaster method modified by COMN-IUNG. The fertilisation with ammonium nitrate determined the content of total sulphur and its fraction as well as the activity of arylsulphatase in Luvisol. The optimum nitrogen rate for the application of which the soil was identified with the highest content of total and organic sulphur was the rate of 80 kgN · ha^{-1}. The Luvisol investigated demonstrated a low richness with sulphur and it should be enriched with that nutrient to facilitate the plants producing the yield adequate in both the quality and the size. A decrease in the activity of arylsulphatase when exposed to complete fertilisation with nutrients in a form of mineral salts points to an inactivating effect of ions of those elements on the activity of the enzyme in the soil.

Keywords: arylsulphatase activity, sulphur, soils, makroelements

In the early 1980s numerous ecological actions were taken to reduce the emissions of sulphur compounds to the atmosphere. As a result of its decreased supply from the air accompanied by a limited consumption of sulphur-containing fertilisers there were observed deficits of that element in field crops, *eg* in Great Britain, Germany and Denmark [1–3]. Similarly in Polish agriculture there occur symptoms which point to

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sulphur deficits [4–6]. There is a risk that the NPK fertilisation applied will not be balanced and that sulphur deficit can limit the use of the other nutrients, mostly nitrogen. The metabolism of those elements is interconnected and the deficit of one of them inhibits the effect of the other. An insufficient nutrition of plants with sulphur is seen in the plant look, similarly as when exposed to nitrogen deficit [7]. The difference in the comparison to the nitrogen deficit symptoms is that with nitrogen deficit older leaves get lighter in colour and yellow initially and when exposed to sulphur deficit – those are young leaves which yellow. In such plants there are found considerable amounts of nitrogen in a non-protein form, the content of reducing sugars decreases and the content of starch and hemicelullose increases [3].

The aim of the present paper was to determine the effect of exclusively mineral fertilisation with nitrogen, potassium, phosphorus, calcium, magnesium and sulphur on the content of total sulphur and its fractions as well as the activity of arylsulphatase (EC 3.1.6.1.) in the soil under winter wheat.

Material and methods

The soil was sampled from a field experiment set up at the Agricultural Experiment Station at Grabów nad Wisłą, by the Institute of Soil Science and Plant Cultivation (IUNG) in Puławy twice in the vegetation period of winter wheat in 2008. The soil is a very good rye complex soil. The experiment involved only mineral fertilisation: increasing rates of ammonium nitrate (0, 40, 80, 120, 160 kgN $\cdot$ ha^{-1}) and fertilisation with P – 70 kgP_2O_5 $\cdot$ ha^{-1}, K – 90 kgP_2O_5 $\cdot$ ha^{-1}, Ca – 200 kgCaO $\cdot$ ha^{-1}, Mg – 70 kgMgO $\cdot$ ha^{-1} and S in fertilisation forms with other elements. The experiment was performed as a split-plot design, the first factor involved increasing rates of nitrogen fertiliser, the second factor – fertilisation with the other macroelements. There were applied six levels of the second factor; the first level involved a fertiliser combination of all the minerals and then one of them was absent in each, respectively; hence the following six treatments:

1. P, K, Ca, Mg, S;
2. –, K, Ca, Mg, S;
3. P, –, Ca, Mg, S;
4. P, K, –, Mg, S;
5. P, K, Ca, –, S;
6. P, K, Ca, Mg, –.

Mineral fertilisation was applied only. In the treatments with S there was used single superphosphate and potassium sulphate, while the treatments without S involved triple superphosphate and high-percentage potassium salt.

The activity of arylsulphatase was determined following the Tabatabai and Bremner method [8], and sulphate sulphur – according to the Bardsley–Lancaster method modified by COMN-IUNG [9]. Organic sulphur was calculated from the difference between the content of total sulphur and S-SO_4^{2-}. For the results of the content of sulphur and the activity of the enzyme, there was performed the analysis of variance with the Tuke'y semi-intervals of confidence ($p = 0.05$).

Results and discussion

The reaction of the soil ranged from 6.37 to 6.84 units for the soil sampled from soil from soil was sampled from a field experiment at Grabów nad Wisłą (Table 1). The reaction of the soils analysed ranged from slightly acid through acid to neutral.

Table 1

Reaction (pH in 1mol KCl · dm^{-3}) of soil the years of investigation

Treatments	Nitrogen fertilization [kg · ha^{-1}]				
	0	40	80	120	160
1. P, K, Ca, Mg, S	6.78	6.77	6.68	6.84	6.62
2. –, K, Ca, Mg, S	6.81	6.76	6.65	6.68	6.65
3. P, –, Ca, Mg, S	6.69	6.63	6.69	6.77	6.58
4. P, K, –, Mg, S	6.67	6.84	6.63	6.65	6.54
5. P, K, Ca, –, S	6.72	6.77	6.61	6.64	6.56
6. P, K, Ca, Mg, –	6.56	6.49	6.42	6.63	6.37

The content of total sulphur in the Luvisol investigated was, on average, for all the experimental treatments 0.05 g · kg^{-1}. The range of occurrence of that element in the soil was quite wide and ranged from 0.015 g · kg^{-1} to 0.103 g · kg^{-1} (Fig. 1a, b). The contents of sulphur recorded in the present research classified the soil, applying the grading scale developed by IUNG, as showing a natural (≤ 0.150 g · kg^{-1}) sulphur content [5, 10].

There was observed an effect of the mineral fertilisation applied on the concentration of that nutrient in the soil analysed. The highest contents of total and organic sulphur were determined in the soil sampled from the plots where complete fertilisation with all the macroelements was applied, where the content of S_{tot} was, on average, 0.066 g · kg^{-1} and S_{org} 59.00 mg · kg^{-1} (Fig. 1b, 2b). The lowest amounts of total sulphur and organic sulphur compounds in the soil, on the other hand, were determined for the treatments with sulphur fertilisation, however, without Ca and Mg fertilisation (Fig. 1b, 2b).

Total sulphur covers a total content of organic and mineral compounds of that element which occurs in soil. In Polish soils organic sulphur is a dominant form of occurrence of that element and its content ranges a lot from 6 to 688 mg · kg^{-1} [5]. The share of that sulphur fraction in total sulphur in the humus horizons of mineral soils accounts for 50–80 % [3]. Liming enhances the release of sulphur *eg* by accelerating the decomposition of organic compounds, leading to the transformation of sulphur into soluble sulphates [9]. Earlier Williams [12] found that the application of $CaCO_3$ results in an increase in the concentration of soluble sulphates and sulphur mineralization up to the value of pH 7.5, above that pH value there occurs a fast process of chemical bonding of sulphates.

The transformations of organic sulphur to the mineral form do not always result in a considerable increase in the content of sulphates in soil [13]. Most probably considerable amounts of inorganic sulphur are leached deep down the soil profile in winter and at the beginning of the vegetation period, especially in light soils [7, 15].

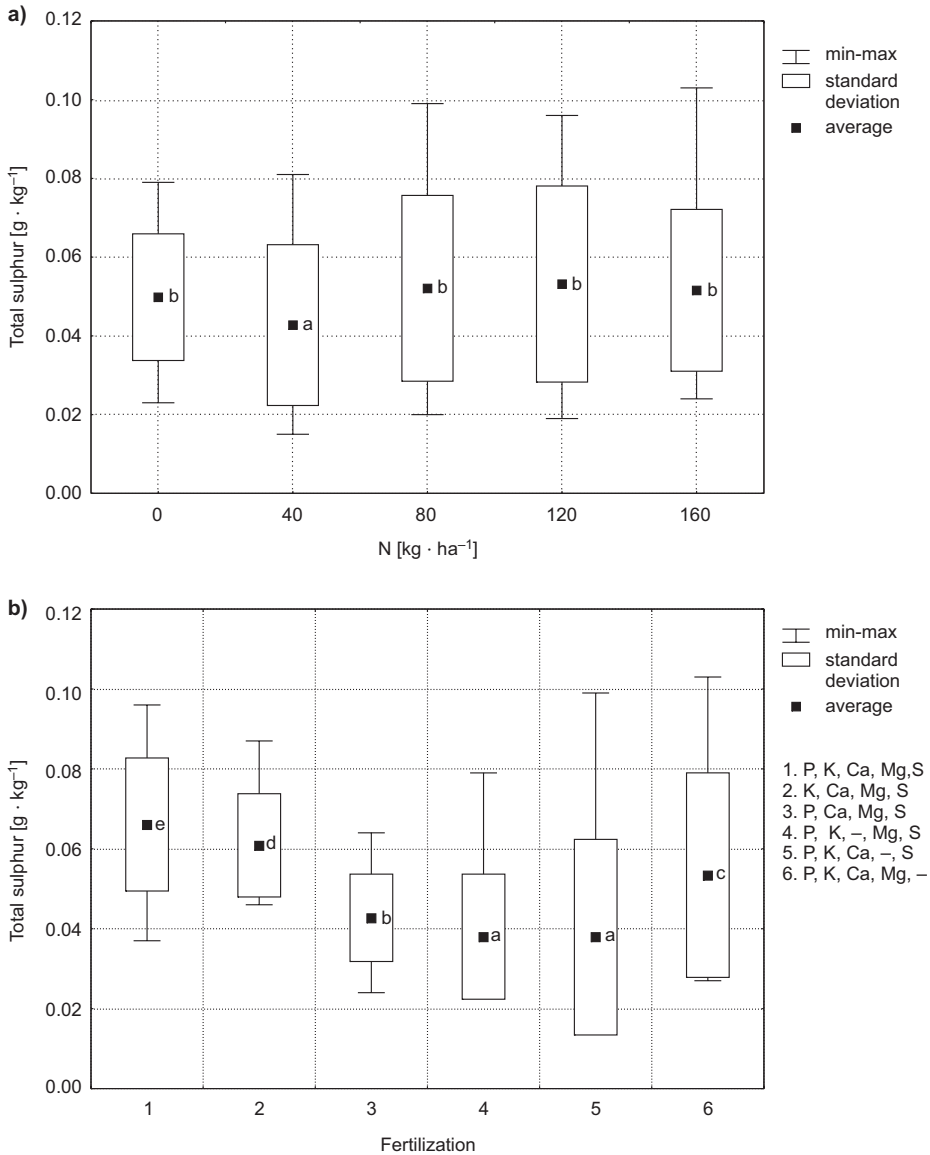

Fig. 1. Content of total sulphur in soil as dependent on fertilization

The fertilisation with ammonium nitrate also modified the content of both sulphur forms. Their lowest amount was reported in the soil sampled from the treatments with the rate of N 40 kgN · ha^{-1} (Fig. 2a, 3a).

The content of the sulphur form available to plants ranged from 2.368 g · kg^{-1} to 14.42 g · kg^{-1} (Fig. 3a, b). In most soils under agricultural use the content of sulphate sulphur in Poland does not exceed 25 mg · kg^{-1} of soil. In most soils, namely

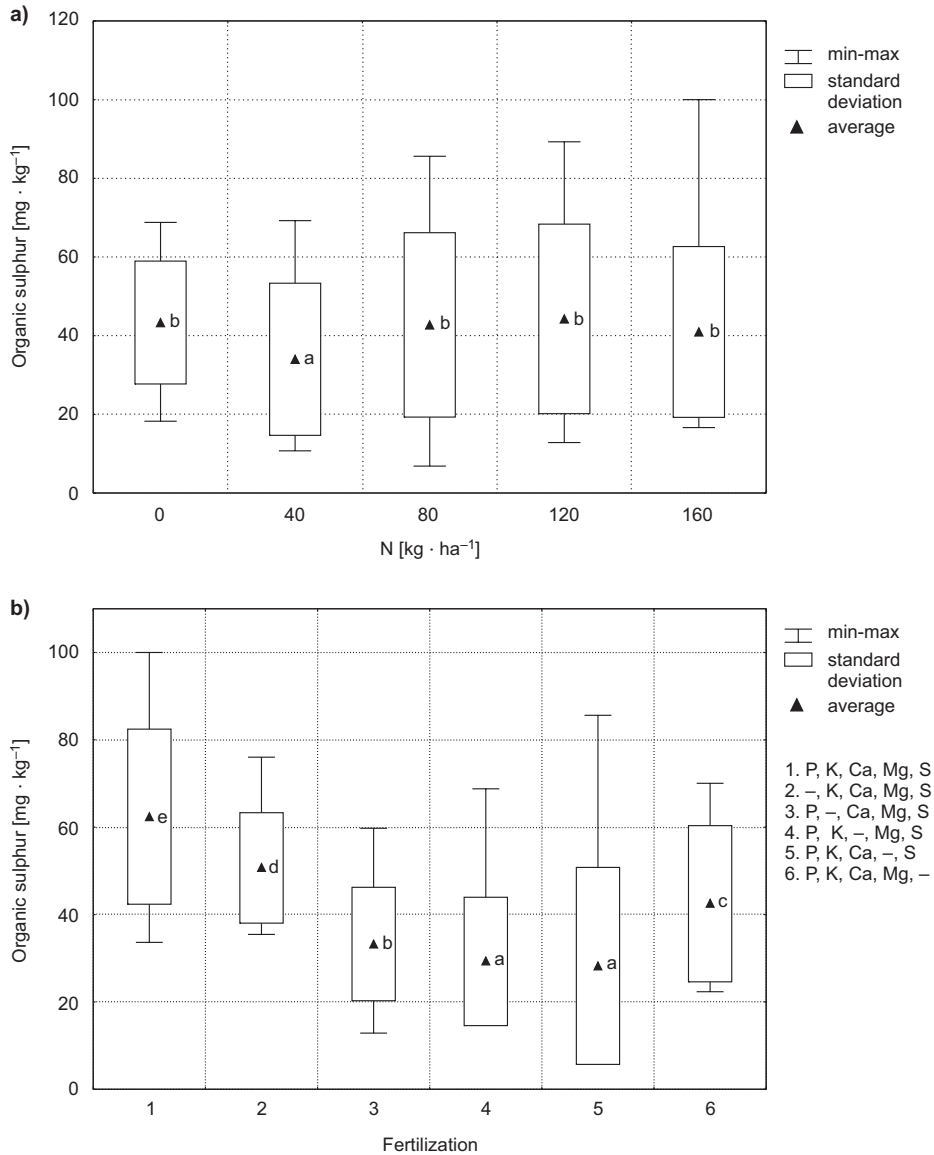

Fig. 2. Content of organic sulphur in soil as dependent on fertilization

70 % of the agricultural acreage, the content of that sulphur fraction ranges from 5.0 to 20.0 mg · kg^{-1} [14]. The content of sulphate sulphur was, on average, 8.219 mg · kg^{-1}. Such soil richness with available sulphur is considered low and wheat, although found to represent the group of plants of low sulphur requirements, needs supplementary sulphur fertilisation [15]. There was noted an effect of the mineral fertilisation applied on the content of that sulphur fraction in the soil from Grabow. The highest content of

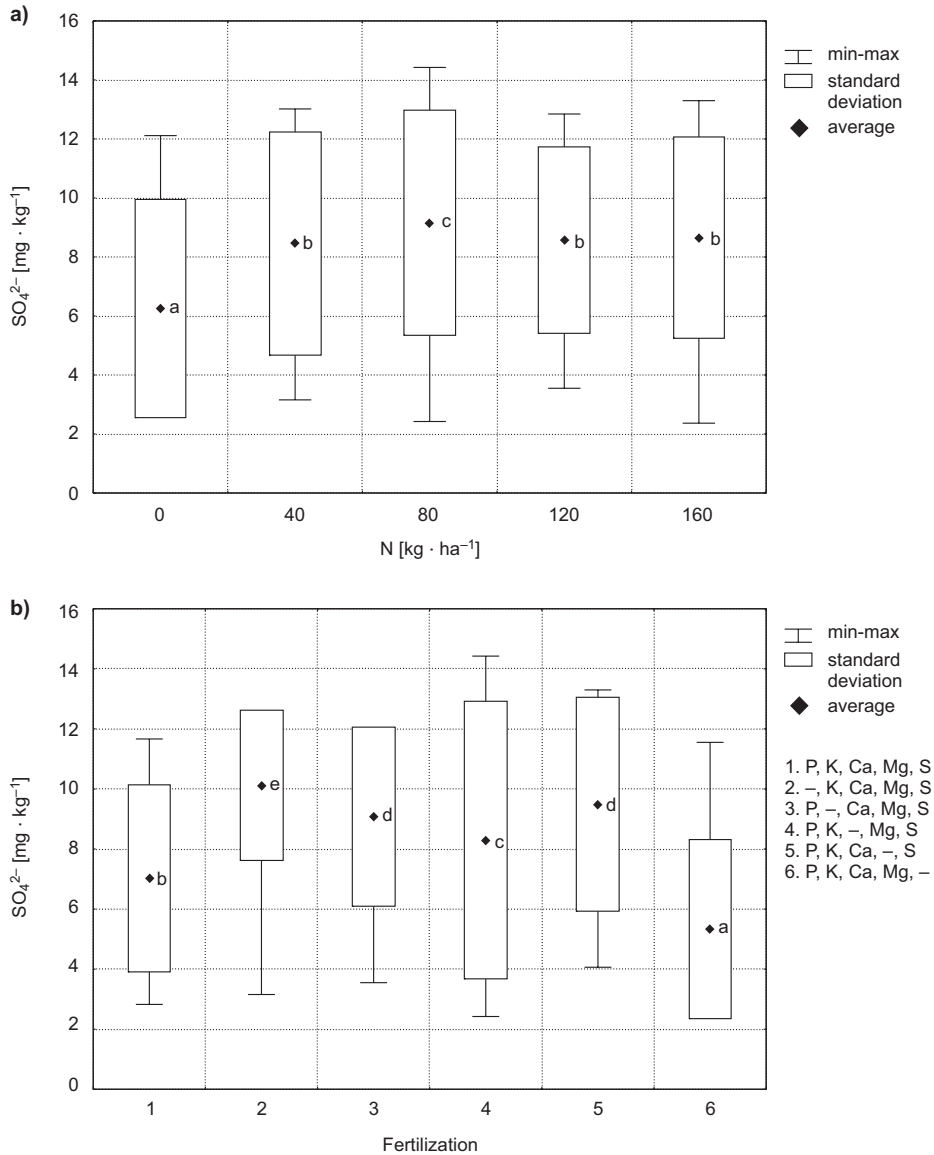

Fig. 3. Content of sulphate sulphur(VI) in soil as dependent on fertilization

sulphate sulphur was recorded in the soil sampled from the treatments with nitrogen fertilisation at the rate of 80 kg · ha^{-1} (Fig. 3a).

The increase in the nitrogen rate to 120 and 160 kg · ha^{-1} resulted in a decrease in the content of the sulphur form available to plants. There was observed an effect of fertilisation with the other macronutrients on the content of S-SO_4^{2-}. The highest content of sulphur available to plants was noted in the soil sampled from the treatments

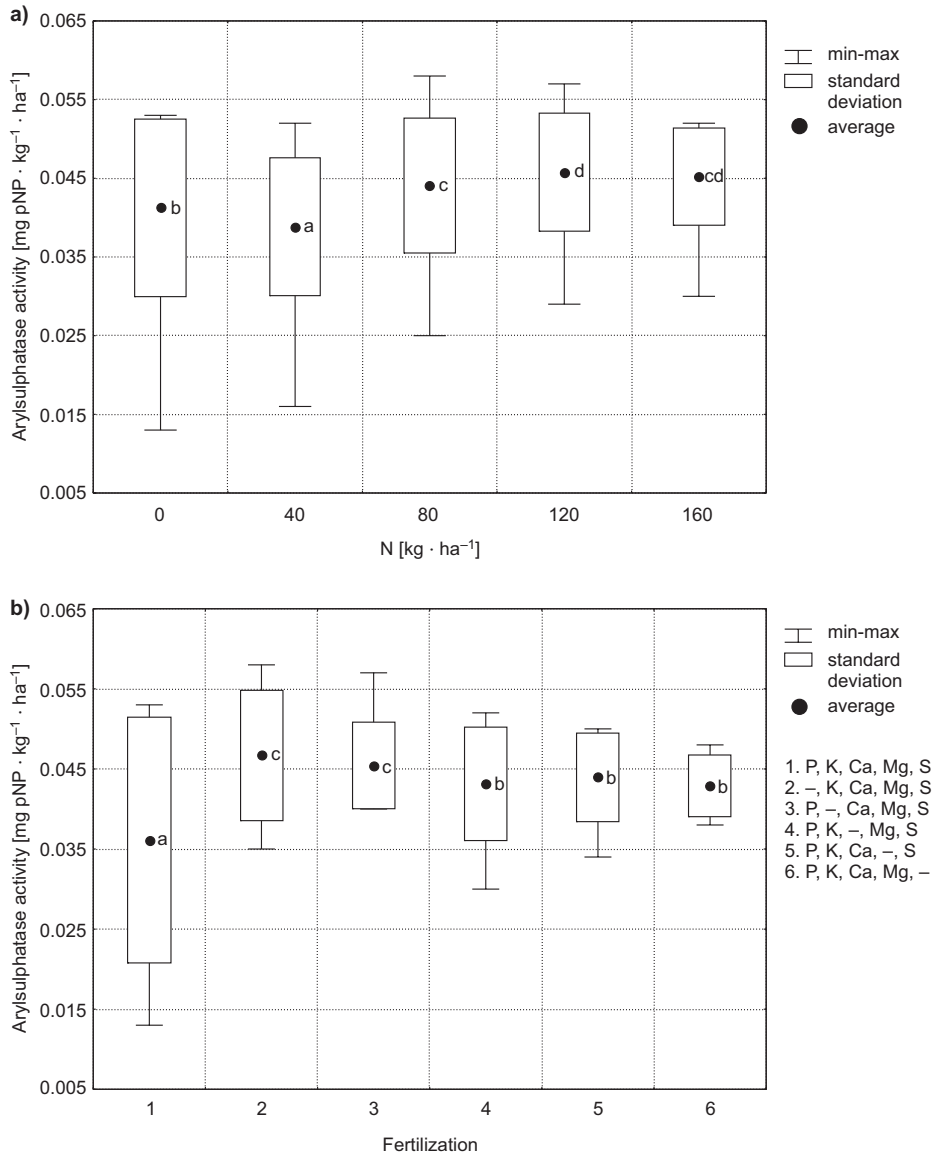

Fig. 4. Arylsulphatase activity in soil as dependent on fertilization

without P fertilisation (treatment 2), a slightly lower – for the treatments without K and Ca (treatments 3 and 5) (Fig. 3b). The lowest amount of S-SO_4^{2-}, on the other hand, was obviously reported in the soil where no fertilisation with that nutrient was used (Fig. 3b).

There was observed an effect of the mineral fertilisation on the activity of arylsulphatase (Fig. 4a, b). The activity of the hydrolase investigated in the soil sampled

from the plots fertilised with nitrogen at the rate of 120 kg · ha^{-1} was highest, while its lowest activity was noted in the soil sampled from the treatments fertilised with ammonium nitrate at the rate of 40 kg · ha^{-1}. As for the control treatment, the activity of hydrolase was 5 % higher. One can thus assume that there must have occurred an inhibition of the activity of that enzyme. The applicable literature [16, 17] reports on a negative effect of ions (NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, Cl^-) on the enzymatic activity of soil. The present research also report on an inhibiting effect of mineral salts on the activity of arylsulphatase. Its lowest activity was assayed in the soil sampled from the treatments with complete mineral fertilisation.

Conclusions

1. The fertilisation with ammonium nitrate determined the content of total sulphur and its fraction in Luvisol. The optimum rate of nitrogen in a form of mineral salt was the rate of 80 kg N · ha^{-1}. Higher amounts of that macroelement introduced into soil did not result in an increase in the content of sulphur and its fraction in soil.

2. Complete balanced fertilisation with nitrogen, phosphorus, potassium, magnesium, calcium and sulphur created favourable soil conditions to the occurrence of sulphur of organic compounds and total sulphur in soil.

3. The highest amount of sulphate sulphur (VI) was noted in the soil samples fertilised with potassium, magnesium, calcium and sulphur, however, non-fertilised with phosphorus.

4. The Luvisol investigated showed a low richness with sulphur and, as such, it should be enriched with that nutrient to make it possible for the plants to produce the yield adequate in both the quality and the size.

5. A decrease in the activity of arylsulphatase when exposed to complete fertilisation with nutrients in a form of mineral salts points to an inactivating effect of the ions of those elements on the activity of arylsulphatase in soil.

References

[1] Richards IR. Sulphur as a crop nutrient in the United Kingdom. Sulphur Agric. 1990;14:8-9.
[2] Gupta AK, Paulsen HM, Haneklaus S, Schung E. Comparative efficacy of selected S sources. Sulphur Agric. 1997;20:15-20.
[3] Schung E, Haneklaus S. Sulphur in agroecosystems. Amsterdam: Schung Kluwer Academic Publishers; 1998.
[4] Motowicka-Terelak T, Terelak H. Sulphur in soils and plant of Poland. Folia Uni Agri Stetin. 2000;81:7-16.
[5] Motowicka-Terelak T, Terelak H. Sulphur in soils of Poland – the status and the risks. Warszawa: Bibl Monit Środ; 1998.
[6] Grzebisz W, Przygocka-Cyna K. Current problems of sulphur in Poland. Fertiliz Fertilizat. 2003;4:64-75.
[7] Scherer HW. Sulfur in soils. J Plant Nutr Sci. 2009;172:326-335. DOI:10.1002/jpln.200900037.
[8] Tabatabai MA, Bremner JM. Factors affecting soil arylsulfatase activity. Soil Sci Soc Am Proc. 1970;34:427-429.
[9] Bardsley CE, Lancaster JD. Determination of reserve sulfur and soluble sulfates in soil. Soil Soc Am Proc. 1960;24:265-268.

[10] Kabata-Pendias A, Piotrowska A, Motowicka-Terelak T, Maliszewska-Kordybach B, Filipiak K, Krakowiak A, et al. Podstawy oceny chemicznego zanieczyszczenia gleb. Metale ciężkie, siarka i WWA. Warszawa: PIOŚ; 1995.
[11] Kopeć M, Gondek K. The effect of long-term diversifield fertilization on sulphur contents in soil and sward of a mountain meadow. Fertiliz Fertilizat. 2004;1(18):62-74.
[12] Williams CH. Some factors affecting the mineralisation of organic sulphur in soils. Plant Soil. 1967;26:205-223.
[13] Kiepul J. The after-effect of simulated sulphur immision and liming the balance of sulphur in soil. Zesz Probl Post Nauk Roln. 1999;467:539-545.
[14] Lipiński W, Terelak H, Motowicka-Terelak T. Suggestion for limiting values of sulphate sulphur content in mineral soils for fertilization advisory needs. Roczn Glebozn. 2003;LIV(3):79-84.
[15] Eriksen J. Organic manures as sources of fertiliser sulphur. Fertiliz Fertilizat. 2003;3(16):52-70.
[16] Ganeshamurthy AN, Nielsen NE. Arylsulpatase and the biochemical mineralization of soil organic sulphur. Soil Biol. Biochem. 1990;22(8):1163-1165.
[17] Germida JJ, Wainwright M, Gupta VVSR. Biochemistry of sulphur cycling in soil. Soil Biochem. 1992;7:1-53.

WPŁYW NAWOŻENIA MIKROSKŁADNIKAMI NA ZAWARTOŚĆ SIARKI ORAZ AKTYWNOŚĆ ARYLOSULFATAZY W GLEBIE

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Abstrakt: Celem pracy było określenie wpływu wyłącznie mineralnego nawożenia na aktywność arylosulfatazy (EC 3.1.6.1.) oraz zawartość siarki ogółem i jej frakcji w glebie spod uprawy pszenicy ozimej. Próbki gleby pobrano z doświadczenia polowego założonego na terenie RZD w Grabowie nad Wisłą, przez IUNG w Puławach dwukrotnie w sezonie wegetacyjnym pszenicy ozimej w 2008 r. W doświadczeniu zastosowano tylko nawożenie mineralne: wzrastające dawki saletry amonowej (0, 40, 80, 120, 160 kgN · ha^{-1}) oraz nawożenie P – 70 kgP_2O_5 · ha^{-1}, K – 90 kg P_2O_5 · ha^{-1}, Ca – 200 kgCaO · ha^{-1}, Mg – 70 kg MgO · ha^{-1} i S w formach nawozowych z innymi pierwiastkami. Aktywność arylosulfatazy oznaczono wg metody Tabatabai i Bremnera, a siarkę siarczanową zgodnie z metodą Bardsleya–Lancastera w modyfikacji COMN-IUNG. Nawożenie saletrą amonową determinowało zawartość siarki ogółem i jej frakcji oraz aktywność arylosulphatazy w płowej glebie. Optymalną dawką azotu, przy zastosowaniu której stwierdzono w glebie największą ilość siarki ogółem i organicznej, była ilość 80 kgN · ha^{-1}. Badana gleba płowa wykazywała niską zasobność w siarkę i powinna być wzbogacona w ten składnik, by umożliwić roślin wydanie plonu o odpowiedniej jakości i ilości. Zmniejszenie aktywności arylosulfatazy przy pełnym nawożeniu składnikami pokarmowymi w postaci soli mineralnych wskazuje na inaktywujący wpływ jonów tych pierwiastków na aktywność enzymu w badanej glebie

Słowa kluczowe: arylosulphataza, siarka, gleba, makroskładniki