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TOTAL SULFUR AND ITS FRACTIONS AS WELL AS ACTIVITY OF ARYLSULFATASE IN SOIL DEPENDING ON WASTE ORGANIC MATERIALS AND LIMING

Soil samples were collected after the 4th crop of grass in the second year of pot experiment, in which the influence of liming (according to 1 H_h) and organic fertilization (sewage sludge and poultry droppings) were examined. Total sulfur content and its fractions (in the form of SO_4^{2-}, available sulfur, and sulfur from humus compounds) were determined in soil samples. The organic materials applied caused a significant increase in total sulfur content in the soil and considerably increased the amount of sulfur in organic compounds. Liming did not exert any influence on total and available sulfur content, while it decreased the level of sulfur in humus compounds. Arylsulfatase activity in the soil significantly depended on the organic material and liming applied.

1. INTRODUCTION

Content of total sulfur oscillates within wide range in Polish soils; however, it does not exceed 0.2 g · 100 g^{-1} of soil and depends mainly on an abundance of organic matter in soil [1]. An amount of sulfur available for plants in soil ploughing layer ranges from 0.3 to 52 mg · 100 g^{-1} of soil. Therefore, the symptoms of sulfur deficiency can be observed in plants from the areas with the surplus of light soils [2]. At the same time, utilization of waste organic materials such as sewage sludge or poultry droppings for agricultural purposes becomes more and more common [3], which is consistent with EU policy [4]. However, the transformations of organic substances introduced into the soil along with organic materials, including sulfur compounds, mineralized among others by arylsulfatase, have not been well recognized yet [5].

The present study was aimed at the sequential analyzing of organic and inorganic sulfur compounds in the soil fertilized with waste organic material as well as at determining the arylsulfatase activity.

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2. MATERIAL AND METHODS

An experimental material consisted of soil samples collected after the 4th crop of grass in the second year of pot experiment set in completely randomized pattern, in which the influence of the following factors was examined:

I – liming (according to 1 H_h of soil using $CaCO_3$);

II – organic fertilization: sewage sludge from the treatment plant in Siedlce (municipal sewage (85%) and industrial sewage (15%)), sewage sludge from the treatment plant in Łuków (municipal sewage (70%) and industrial sewage (30%)), poultry droppings from laying-hen and broiler-chicken farms.

The organic fertilization was applied once by introducing 0.5 g of sulfur into the pot filled with 10 kg of soil. The humidity on the level of 60% field water capacity was maintained during the whole vegetation period. Orchard grass was the test plant, whose four crops were harvested in each vegetation season. Total sulfur content in the soil was determined by means of ICP-AES after a wet digestion in the mixture of HNO_3 and H_2O_2. Applying sequential method, the following sulfur fractions were analyzed:

- SO_4^{2-} from water extract [6];
- available sulfur in 0.25 M KCl extract at 40 °C [7];
- in humus compounds from 0.1 M NaOH extract.

The arylsulfatase activity was assayed according to TABATABAI and BREMNER [8].

The content of sulfur in particular fractions was determined applying ICP-AES technique. The quantity of sulfur that had not been extracted was calculated from the difference between total sulfur content and the sum of extracted sulfur fractions.

The results obtained were statistically processed by means of variance analysis applying F-Fisher–Snedecor's distribution and using Anal. Var 4.1 software, while $LSD_{0.05}$ values were calculated according to Tukey's test. The simple correlation between total sulfur content, sulfur fractions, and arylsulfatase activity in the soil tested was also calculated.

3. RESULTS AND DISCUSSION

The soil used in the experiment was collected from 0–20 cm ploughing layer of podzolic soils with granulometric composition of strong loamy sand. Before the experiment, pH_{KCl} was 5.6, whereas total nitrogen, 0.98 $g \cdot kg^{-1}$; organic carbon, 7.9 $g \cdot kg^{-1}$; total sulfur, 1.42 $g \cdot kg^{-1}$; available phosphorus, 69 $mg \cdot kg^{-1}$; and available potassium, 75 $mg \cdot kg^{-1}$.

The chemical composition of organic materials used in pot experiment is given in table 1. Organic materials contained different amounts of the elements being determined. The highest content of nitrogen was determined in sludge from Siedlce, and the lowest in the broiler droppings, while in the case of phosphorus, these relations were inverse. The highest content of potassium was contained in laying-hen droppings and, the lowest – in sludge from Siedlce. Of all organic materials analysed the slightest differentiation of the content was found for sulfur. The highest content of sulfur was determined in sludge from Siedlce, and the lowest – in broiler droppings.

Table 1

The content of N, C, P, K and S in D.M. in organic materials

Macroelement	Sewage sludge from Siedlce	Sewage sludge from Łuków	Laying-hen droppings	Broiler droppings
$g \cdot kg^{-1}$				
N	51.0	41.8	24.7	16.8
C	373	392	420	399
P	7.92	10.3	15.9	18,3
K	2.12	2.65	11,3	7,12
S	8.47	6.96	7,18	6,11

Organic materials were introduced into the soil once in the amount of 0.5 g of sulfur per pot. After 2 years of experiment, total sulfur content (table 2) ranged from 127 $mg \cdot 100\ g^{-1}$ in the pot whose soil was not fertilized and not limed to 141.5 $mg \cdot 100\ g^{-1}$ in the pot with liming and fertilizing with poultry droppings from laying hens. This indicated that fertilizing with waste organic materials significantly increased the total sulfur content both in limed and not limed soil compared to that with no organic fertilization. Liming also increased the quantity of total sulfur in the soil, but to a small extent. The total sulfur content in limed soil was only by 1.60% higher than that in not limed one.

The cold-water extract fraction includes sulfates from soil solution [6], whereas fraction in 0.25 M KCl – sulfates adsorbed in soil and part of sulfur from organic matter being easily mineralized [7]. Therefore, the sum of fractions from water extract and from 0.25 M KCl makes the sulfur available for plants; its amount was the lowest in not limed soil fertilized with sewage sludge from Łuków, while the highest – in limed soil fertilized with broiler-chicken droppings. An average amount of extracted sulfates was 1.55% of the total sulfur, which was confirmed by literature data. According to KALEMBASA and GODLEWSKA [9], sulfate sulfur content in surface layers of podzolic soils oscillates between 5.4 and 13.3 $mg \cdot kg^{-1}$ of soil, which is from 1.5 to 21.3% of total sulfur quantity, respectively. The studies performed by KULCZYCKI and SPIAK [10] revealed that the content of sulfur in the form of SO_4^{2-} in surface soil layers amounts to 4.9 $mg\ S \cdot kg^{-1}$, on average, which gaves 7% of the total sulfur. Also according to TERELAK et al. [2], the amount of sulfur in sulfate form ranges from 0.1 up to 6.3 $mg \cdot 100\ g^{-1}$ of soil, which is from 1.43 to 5.89% of total sulfur.

Table 2

The content of sulfur fractions in soil (mg S · 100 g^{-1} of soil)

Liming	Without liming					Means	Liming according 1 H_h soil					Means
Organic fertilization	Without fertilization	Sludge from Łuków	Sludge from Siedlce	Laying-hen droppings	Broiler droppings		Without fertilization	Sludge from Łuków	Sludge from Siedlce	Laying-hen droppings	Broilers droppings	
Fractions:												
I. H_2O	1.20	0.90	1.20	1.00	0.80	1.02	1.05	1.10	1.30	0.90	1.60	1.19
II. 0.25 M KCl	0.90	0.80	0.90	0.90	1.00	0.90	1.00	0.90	1.05	0.90	1.10	0.99
III. 0.1 M NaOH	10.04	15.90	12.00	12.20	11.60	12.34	6.50	11.70	10.05	9.50	9.90	9.53
Sum of fractions	12.14	17.60	14.10	14.10	13.40	14.27	8.55	13.70	12.40	11.30	12.60	11.8
Total sulfur	127.0	135.2	138.7	139.1	132.7	134.5	128.5	138.2	140.0	141.5	135.4	136.7
Percent of extracted sulfur	9.56	13.02	10.17	10.14	10.10	10.6	6.65	9.91	8.86	8.00	9.30	8.54
Percentage share of fractions of sulfur in extractable sulfur												
Fractions:												
I. H_2O	9.88	5.11	8.51	7.09	5.97	7.31	12.28	8.03	10.48	7.96	12.70	10.29
II. 0.25 M KCl	7.41	4.55	6.38	6.38	7.46	6.44	11.70	6.57	8.47	7.96	8.73	8.69
III. 0.1 M NaOH	82.71	90.34	85.11	86.53	86.57	86.25	76.02	85.40	81.05	84.08	78.57	81.02
Percent of extractable sulfur	100	100	100	100	100	100	100	100	100	100	100	100

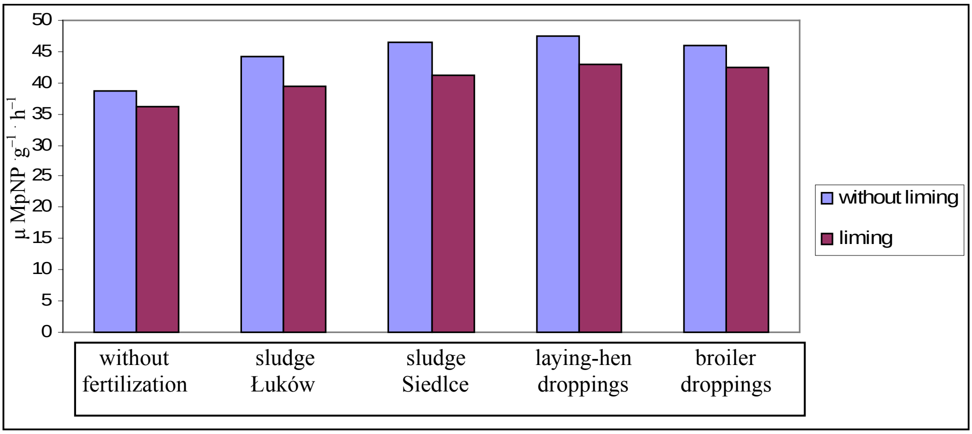
NIR $LSD_{(0.05)}$ for:
liming, 0.362,
organic fertilization, 0.814,
fractions, 0.536,
liming and organic fertilization, n s,
liming and fractions, 0.810,
organic fertilization and fractions, 1.409.

The fraction extracted in 0.1 M NaOH is organic sulfur contained in humus compounds. Its lowest levels were determined in soil from the pot without organic fertilization and without liming (6.5 mg · 100 g^{-1} of soil), while the highest – in not limed soil fertilized with sewage sludge from Łuków (15.9 mg · 100 g^{-1} of soil).

The highest quantities of extractable sulfur, i.e. 17.6 mg · 100 g^{-1} of soil, making up 13.02% of total sulfur, were recorded in not limed soils fertilized with sludge from Łuków. The lowest content of extractable sulfur was found in limed soil without organic fertilization. This content amounted to 8.55 mg · 100 g^{-1} of soil, making up 6.65% of total sulfur.

Fraction extracted with 0.1 M NaOH makes up the largest percent share of extractable sulfur, which is justifiable, because sulfur contained in the soil is mainly released from organic compounds, while the fraction of adsorbed sulfates, sulfates dissolved in the soil solution and the sulfur released due to organic matter mineralization and extracted with 0.25 M KCl made up the lowest percentage. Moreover, the proportions of fraction extracted with H_2O and 0.25 M KCl were on comparable levels.

Statistical analysis revealed a significant influence of all the factors studied on the fractions of extracted sulfur compounds in the soil. Organic fertilization with every waste material increased considerably the content of sulfur extracted both from limed and not limed soil as compared with the pots without fertilization.



Arylsulfatase activity, depending on organic fertilization and liming.
$LSD_{0,05}$ for: fertilization – 1.473, liming – 0.631, fertilization and liming – 2.084

Sulfur content in the fraction extracted with 0.1 M NaOH was significantly higher in not limed soil compared with limed one, both in fertilized and not fertilized pots. The quantity of sulfur in its sulfate form did not depend on liming, i.e. on pH of the soil, which was confirmed by numerous studies [11]–[13]. However, some authors [14], [15] report a positive dependence of the content of sulfate sulfur on a soil acidity.

The activity of arylsulfatase (figure) in the soil tested was 42.2 μ MpNP $\cdot g^{-1} \cdot h^{-1}$, which significantly depended on both organic material and liming. Considerably higher activity of the enzyme in relation to the control was observed in the soil samples fertilized with organic material. Liming significantly decreased the arylsulfatase activity in the soil. KOPER and SIWIK-ZIOMEK [16], when examining the arylsulfatase activity in the soils fertilized with manure and NPK, recorded its lower values that ranged from 16.9 to 30.8 μ MpNP $\cdot g^{-1} \cdot h^{-1}$. The values of the coefficient of correlation (table 3) between the parameters determined prove that sulfur quantities in humus compounds (fraction extracted with 0.1 M NaOH) was significantly correlated with arylsulfatase activity in the soil studied.

Table 3

The coefficients (r) of correlation between arylsulfatase activity and the content of different sulfur determinated in different fractions

	Arylsulfatase activity	Fractions of sulfur determined in extract of:			Total content of sulfur
		H_2O	KCl	NaOH	
Arylsulfatase activity	1				
Fractions of sulfur determined in extracts of:					
H_2O	–0.25331	1			
KCl	–0.22620	0.59787	1		
NaOH	0.63322	–0.29187	–0.62212	1	
Total content of sulfur	0.54061	0.00034	–0.08953	0.03076	1

The critical value of $r = + 0.6319$.

The results obtained in the present paper in terms of environmental engineering and protection have clearly shown a strong possibility of utilizing waste materials in order to increase sulfur content in soil, especially of the organic compounds of sulfur extracted with 0.1 M NaOH. This shows that the sulfur occurs in soil humic substances and that it is not easy to remove it from soils by leaching. Independently of the materials used, the highest content of sulfur compounds was extracted from soil fertilized with the sludge undergoing mechanical-biological stabilization in the Łuków sewage-treatment plant. Additional liming significantly decreased the content of sulfur in extractable compounds which testified to the very stable compounds of sulfur in soil.

4. CONCLUSIONS

1. Waste organic materials significantly increased the total sulfur content in the soil studied, among others in the soil fertilized with laying-hen droppings.

2. Organic fertilization considerably increased the sulfur content in organic compounds in soil fertilized with sludge from Łuków (it was produced by mechanical-biological method).

3. Liming had not any influence on the sulfur content in the fraction extracted with H_2O and 0.25 M KCl, while it significantly decreased that content in the fraction extracted with 0.1 M NaOH.

4. The parameters studied in the present experiment significantly differentiated the arylsulfatase activity in soil.

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