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EFFECT OF THE FERTILIZER APPLICATION METHOD ON SOIL ABUNDANCE IN AVAILABLE SULFUR[1]

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ABSTRACT

Efficient increase in the content of available forms of elements in soil depends not only on their total content introduced to soil material, but also on the technology of its application. Technology consists of techniques and date of application as well as agronomic practices aimed at maintaining proper conditions for element transformations. The method of application of waste elemental sulfur and ground phosphate rock was assessed. Doses of 20 and 40 mg S as well as 40 and 80 mg P·kg^{-1}d.m. were added to medium soil; 30 and 60 mg S as well as 60 and 120 mg P·kg^{-1}d.m. were added to heavy soil. The soil samples were collected on the day of application of materials and after 15, 30, 60 and 90 days. The soil pH value decreased during the incubation. An increase in available sulfur content was observed in both soils after elemental sulfur application; the sulfur content in the medium soil depended on the dose of waste. The soils with the addition of a double dose of ground phosphate rock had the highest content of available phosphorus.

Introduction

In 2015, 92% Polish arable soils had a low content of sulfate sulfur; the average sulfate sulfur content in 2015 was 10 mg·kg^{-1}, and the median was 8 mg·kg^{-1} (Monitoring…). For comparison, the average content of available sulfur in 1995 was 13.8 mg·kg^{-1}, and the median was 12.5 mg·kg^{-1} and these were the highest values of these parameters between 1995 and 2015. Limiting the emission of sulfur compounds from anthropogenic sources (mainly from combustion processes) into the atmosphere is one of the main causes of sulfur deficiency in soils (Vega et al., 2018). The total emission of sulfur dioxide in Poland in 1990 was 3210 Gg, in 2000 – 1511 Gg, in 2010 – 866 Gg, and in 2016 – 582 Gg (Environment, 2008, 2018). Other reasons of sulfur deficiency include: removal of this element with plant yields (winter rape and wheat take up approximately 20 kg·ha^{-1}, and maize – 40 kg·ha^{-1}), reduced consumption of organic fertilizers and mineral fertilizers containing sulfur as ballast (e.g. single superphosphate), and sulfur leaching deep into the soil profile (generally from several to several dozen kg·ha^{-1}·year^{-1}) (Boreczek, 2001; Kaczor and Zuzańska, 2009;

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McNeill et al., 2015). Mineral fertilizers enriched with sulfur as well as waste materials rich in this element (both in sulfate form that is directly available for plants and in the elemental form that is available after oxidation to sulfate sulfur) can be the source of sulfur for plants. Sulfur waste is generated, among other things, during desulfurization of combustion gases and biogas (obtained during organic waste fermentation) (Żarczyński et al., 2015).

Effectiveness of the use of waste materials depends, among other things, on the application method. Restrictions as to the method of application and doses of waste, and also the rate and direction of changes in soil properties after waste application, result, among other things, from the physical form of waste. It is possible to use materials in the liquid form and as solids with various degrees of fineness and hydration (Borek et al., 2015; Caputo et al., 2013; Glæsner et at., 2019; Wróbel et al., 2016; Zhu et al., 2013). Efficiency of waste application can be increased by using waste mixtures – simultaneous application of elemental sulfur and ground phosphate rock increases phosphorus availability (Jazaeri et al., 2016). This is beneficial especially when deficiency of available forms of phosphorus in soils occurs. In 2015, almost a half the arable land in Poland had a low or a very low content of available phosphorus (Monitoring…). In terms of application techniques and possibilities of using commercially available and commonly used fertilizer spreaders, searching for methods of waste processing to obtain proper physical properties is essential.

The aim of the research was to assess the efficiency of simultaneous application of waste elemental sulfur and ground phosphate rock in the context of increasing soil abundance in sulfur and phosphorus as well as simplifying the application by using commercially available fertilizer spreaders. The research was conducted under laboratory conditions, on two soils with a different soil category.

Material and methods

The incubation experiment was conducted on two soils with different soil category: medium and heavy (Tab. 1). Both soils were acid. The content of available forms of sulfur and phosphorus in the medium soil was average and high, respectively, whereas in the heavy soil – low. There was no contamination with heavy metals (basing on the guidelines of Kabata-Pendias et al., (1995). The experiment comprised five treatments (each in triplicates): 1. control soil (with no additions); 2. soil with the addition of sulfur pulp (sulfur dose: S_I); 3. soil with the addition of sulfur pulp (sulfur dose: S_{II}); 4. soil with the addition of sulfur pulp (sulfur dose: S_I) and ground phosphate rock (phosphorus dose: P_I); 5. soil with the addition of sulfur pulp (sulfur dose: S_{II}) and ground phosphate rock (phosphorus dose: P_{II}).

Doses of sulfur and phosphorus were set based on the content of available forms in the soils, guidelines on the limit content of elements in soils, and on the principles of crop fertilization. The medium soil was amended with 20 mg S (S_I) and 40 mg S (S_{II}) as well as 40 mg P (P_I) and 80 mg P (P_{II}), per 1 kg d.m. The heavy soil was amended with 30 mg S (S_I) and 60 mg S (S_{II}) as well as 60 mg P (P_I) and 120 mg P (P_{II}), per 1 kg d.m. Sulfur pulp which is a by-product of biogas desulfurization using the Biosulfex method (biogas is obtained as a result of sewage sludge fermentation) was used in the research. The initial dry matter content in the pulp was 54.7% (the material was partially dehydrated before use), and the sulfur content in dry matter of the waste was 92%. Ground phosphate rock contained 14.5% P. The materials were applied in the solid form. The method of soil application was used. Simultaneous and single-time application of both materials was tested, as a time- and cost-effective method of the new fertilizer application (by using commercially available fertilizer spreaders) in future.

Table 1.
Selected properties of soils before setting up the experiment

Parameter	Medium soil	Heavy soil
Fraction < 0.02, (%)	27	42
pH_{KCl}	5.35	4.65
Available S, ($mg \cdot kg^{-1}$ d.m.)	30.0	10.5
Available P, ($mg \cdot kg^{-1}$ d.m.)	86.0	26.8

The soils were incubated under laboratory conditions (25^{o}C, 60% Max WHC). Soil samples for analyses were collected on the day of introducing the sulfur waste and ground phosphate rock (after their application), as well as after 15, 30, 60 and 90 days of incubation. The soil material was brought to an air-dry condition and sifted through a 1 mm mesh sieve.

The soil pH was determined by potentiometry in 1 $mol \cdot dm^{-3}$ KCl suspension, whereas available sulfur was extracted with 0.03 $mol \cdot dm^{-3}$ acetic acid (10:1 (v:m), 30 min, 40 RPM) (Ostrowska et al., 1991). Available phosphorus was determined by Egner-Riehm method (Ivanov et al., 2012), after extraction with calcium lactate at pH 3.55 (5:1 (v:m), 90 min, 40 RPM). The sulfur and phosphorus content in the solutions was determined using inductively coupled plasma optical emission spectrometry (ICP-OES), using a Perkin Elmer Optima 7300 DV spectrometer. Results of determinations of the content of available sulfur and phosphorus were subjected to statistical analysis. A two-way analysis of variance was carried out (factors: treatment in the experiment, number of incubation days). Significance of variance was determined by Tukey test ($\alpha \leq 0.05$), with the use of Statistica 13 software (Dell Inc.).

Results and Discussion

Sulfur waste (technologically unprocessed) used in the Authors' own research is problematic in respect of its application and impact on soil properties in terms of increasing abundance in this element. The used material is sludgy and currently on the market there are no effective methods of its application. One of the most important factors limiting the use of waste in agriculture is its physical form, unsuitable for the currently used machines. Occurrence of elements in chemical forms that are not directly available to plants is also important. Introduction of a new fertilizing product into the market in the present-day world must be connected with creating a technology for its application and analyzing its precise impact on soil properties, both in the long-term and short-term context. Waste sulfur, which is the subject of this research, despite considerable fertilizer potential, can be a problem due to its chemical form. Elemental sulfur introduced to soil must be oxidized to the sulfate form, because only this form is available to plants. Combining ground phosphate rock with sulfur pulp created a product which, after thorough homogenization, can be a suitable material for granulation. Granulation is one of the main factors that increase fertilizer chances for market success (Tur-Cardona et al., 2018) and fits into the widely understood technical progress in agriculture (Borusiewicz et al., 2016). Moreover, using technological additions that allow for an increase in effectiveness of fertilizers based on waste materials is a modern approach in creating waste-free technologies not only in agriculture, but in the whole economy (Wróbel et al., 2016).

The pH of the medium soil during the experiment ranged from 4.99 to 5.74, which corresponds to acid and slightly acid reaction (Fig. 1). The pH of the heavy soil ranged from 4.42 to 4.75, which indicated very acid and acid reaction. During the incubation, a decrease in pH values of both soils was observed (higher in the medium soil), regardless of the treatment. As a rule, the soil with the addition of double dose of sulfur pulp had the lowest pH, but diversity between the treatments was not considerable.

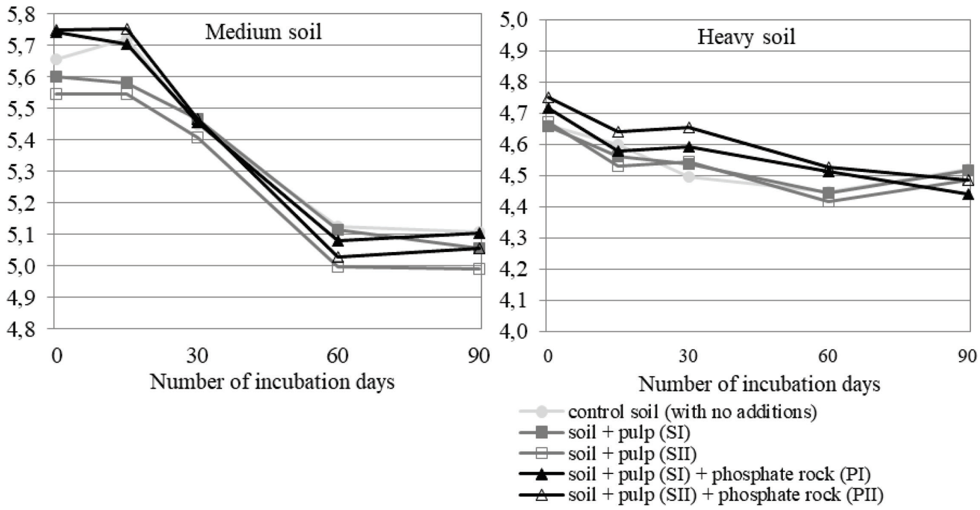

Figure 1. Soil pH_{KCl} during the incubation

Previous studies confirmed soil acidification after sulfur application (Bobowiec and Tabak, 2018; Kulczycki, 2015; Yang et al., 2010). Such acidification can be limited by liming; adjustment of the soil reaction is also beneficial for the activity of sulfur oxidizing microorganisms (Bobowiec and Tabak, 2018). Stanisławska-Glubiak et al., (2012) did not state that application of mixtures of phosphate rock and sulfur had a stronger acidifying effect than application of phosphate rock exclusively, especially when the sulfur dose was not very high. The authors explained that by the fact that calcium (present in these mixtures as tricalcium phosphate) stabilized soil pH.

The content of available sulfur in the soils with the addition of pulp increased during the experiment (Tab. 2). The highest amount was determined in soils with the addition of sulfur pulp and ground phosphate rock (especially when the double dose was used). After the experiment, medium soil abundance in available sulfur (after pulp application) increased up to an anthropogenically elevated content, which was a result of the dose of pulp and relatively high soil abundance prior to commencement of the experiment (Tab. 2). Heavy soil abundance after sulfur application was at least medium (the highest after application of the double dose of sulfur and ground phosphate rock – anthropogenically elevated).

Table 2.
Available sulfur content in soils after simultaneous application of sulfur pulp and ground phosphate rock, ($mg \cdot kg^{-1}$ d.m.)

Soil	Treatment	Number of incubation days				
		0	15	30	60	90
Medium soil	control soil (with no additions)	30.1 ab*	34.4 abcd	39.7 cdefg	39.3 cdefg	28.0 a
	soil + pulp (S_I)	33.6 abcd	43.1 efgh	34.4 abcd	36.8 bcde	45.6 fghi
	soil + pulp (S_{II})	38.4 cdefg	32.5 abc	36.8 ab	52.0 ij	55.9 j
	soil + pulp (S_I) + phosphate rock (P_I)	34.6 abcd	40.1 defg	33.7 abcd	49.5 hij	46.4 ghi
	soil + pulp (S_{II}) + phosphate rock (P_{II})	39.1 cdefg	42.6 efgh	37.0 bcde	54.9 j	67.0 k
Heavy soil	control soil (with no additions)	11.3 a	14.8 abc	10.7 a	9.9 a	14.9 abc
	soil + pulp (S_I)	10.7 a	22.8 e	12.4 ab	18.9 bcde	35.0 f
	soil + pulp (S_{II})	12.2 ab	12.7 ab	22.2 de	30.2 f	32.0 f
	soil + pulp (S_I) + phosphate rock (P_I)	15.6 abcd	16.2 abcde	21.5 cde	33.1 f	48.1 g
	soil + pulp (S_{II}) + phosphate rock (P_{II})	16.9 abcde	22.5 de	30.1 f	54.8 gh	59.7 h

* mean values for a given soil in the columns marked with the same letters do not differ statistically significantly at $\alpha \leq 0.05$; according to the Tukey test

An increase in soil abundance in sulfate sulfur after application of elemental sulfur has been recorded earlier (Bobowiec and Tabak, 2018; Kulczycki, 2015; Stanisławska-Glubiak et al., 2012). Intensity of elemental sulfur oxidation depends on temperature, moisture and pH of soil (optimum: 20-30ºC, moisture approximately 60%, pH 6.0-7.0) (Hoffman et al., 2014), activity of oxidizing bacteria (*Acidithiobacillus thiooxidans*), and also on properties of sulfur material (including the size of particles, which determines the degree of contact with soil).

During the experiment, the soils with the addition of a double dose of phosphate rock had the highest content of available phosphorus (Tab. 3). As a rule, application of a single dose of phosphate rock did not increase soil abundance in phosphorus, despite simultaneous sulfur addition. Application of the double dose of phosphate rock increased the medium soil abundance from high to very high, and the heavy soil abundance from low to medium.

Stanisławska-Glubiak et al., (2012) found an increase in available phosphorus content after application of phosphorus-sulfur mixtures, but no sooner than in the second year of research. Phosphorus availability modification is a result of elemental sulfur oxidation. Produced sulfates react with phosphate rock, transforming tricalcium phosphate into monoand dicalcium phosphate (Stanisławska-Glubiak et al., 2012). In addition, sulfate ions increase soil acidification, and as a result increase solubility of phosphorus compounds. A decrease in soil pH also modifies the availability of other elements (Bobowiec and Tabak, 2018). Evans et al., (2006) indicated the possibility of using sulfur to increase phosphorus availability in organic farming, including conditions of low soil moisture. However, application of mixtures of a small ratio of phosphate rock to sulfur may be a threat to the environment (because of phosphate leaching), and mixture granulation slows down changes in soil properties (Stanisławska-Glubiak et al., 2012, 2015). High nutrient-release efficiency can be ensured by mixing fractions of different particle sizes (Rafael et al., 2018).

Table 3.
Available phosphorus content in soils after simultaneous application of sulfur pulp and ground phosphate rock, (mg·kg^{-1} d.m.)

Soil	Treatment	Number of incubation days				
		0	15	30	60	90
Medium soil	control soil (with no additions)	95.0 abcd*	102.2 bcde	89.0 abcd	82.3 abc	86.0 abcd
	soil + pulp (S_I)	91.9 abcd	85.7 abcd	88.2 abcd	91.3 abcd	75.4 ab
	soil + pulp (S_{II})	82.8 abc	93.3 abcd	87.1 abcd	79.1 abc	75.6 ab
	soil + pulp (S_I) + phosphate rock (P_I)	102.7 bcde	84.8 abc	104.2 cde	72.2 a	79.7 abc
	soil + pulp (S_{II}) + phosphate rock (P_{II})	112.2 de	125.6 e	128.8 e	102.3 bcde	105.0 cde
Heavy soil	control soil (with no additions)	22.8 abcde	18.0 abc	22.9 abcde	19.5 abcd	20.5 abcd
	soil + pulp (S_I)	25.2 abcde	14.0 a	23.1 abcde	23.5 abcde	24.8 abcde
	soil + pulp (S_{II})	29.4 bcdef	23.4 abcde	16.1 ab	21.7 abcde	22.7 abcde
	soil + pulp (S_I) + phosphate rock (P_I)	33.2 defgh	33.2 defgh	35.8 efgh	26.3 abcde	31.8 cdefg
	soil + pulp (S_{II}) + phosphate rock (P_{II})	42.4 fghi	47.0 hi	52.1 hi	41.0 fghi	45.2 ghi

* as in Table 2

Conclusions

Using ground phosphate rock as an addition to sulfur waste can be an important technological element of manufacturing fertilizers based on the waste in question. The conducted research allows to positively verify it in the context of producing a fertilizer that can be applied with the use of standard fertilizer spreaders. It was established that the proposed application method had a positive effect on the use value of the new product; it increased soil abundance in available sulfur. Application of waste sulfur pulp increased the sulfate sulfur content in both soils. Additionally, the sulfur content in the medium soil depended on the pulp dose. Application of double dose of ground phosphate rock increased soil abundance in phosphorus.

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WPŁYW METODY APLIKACJI NAWOZU NA ZASOBNOŚĆ PRZYSWAJALNYCH FORM SIARKI W GLEBIE

Streszczenie. Efektywne zwiększanie zawartości przyswajalnych form pierwiastków w glebie jest związane nie tylko z sumaryczną ich ilością wprowadzaną do gleby, ale także z technologią aplikacji. Na technologię składają się techniki i termin aplikacji oraz zabiegi agrotechniczne mające na celu utrzymanie właściwych warunków przemian pierwiastków. Oceniono metodę aplikacji odpadowej siarki pierwiastkowej i mączki fosforytowej. Do gleby średniej wprowadzono 20 i 40 mg S oraz 40 i 80 mg P, a do gleby gleby ciężkiej 30 i 60 mg S oraz 60 i 120 mg $P \cdot kg^{-1}$. Próbki gleb pobrano w dniu wprowadzenia materiałów oraz po 15, 30, 60 i 90 dniach. W trakcie inkubacji stwierdzono zmniejszenie wartości pH obu gleb. W obu glebach stwierdzono zwiększenie zawartości siarki przyswajalnej po aplikacji siarki pierwiastkowej; w glebie średniej zawartość siarki zależała od dawki odpadu. Najwięcej fosforu przyswajalnego zawierały gleby z dodatkiem podwójnej dawki mączki fosforytowej.

Słowa kluczowe: siarka elementarna, siarka siarczanowa, siarka przyswajalna, fosfor przyswajalny, odpady

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