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Article

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Abstract: Sulfur deficiency has been recognized as a limiting factor for crop production in many regions of the world. A 120-day incubation experiment was conducted to assess the effect of the applied waste elemental sulfur on sulfur bioavailability in soil. Four doses of sulfur were applied: 10, 20, 30 and 60 mg S kg⁻¹ dry matter (d.m.) of soil. In order to assess the effect of soil pH adjustment on sulfur oxidation, the research was conducted on two sets of soil samples: one set of soil samples had natural pH, and the second one was limed before sulfur application. Application of waste sulfur slightly affected the soil pH, and increased the content of available sulfur in soil proportionally to sulfur dose. A beneficial effect of waste sulfur application on soil dehydrogenase and catalase activity was found. Liming reduced soil acidity, and significantly increased sulfate content and soil enzymatic activity. Waste elemental sulfur may be an alternative source of sulfur, supplementing the deficiencies of this element in soils. The described way of sulfur waste reuse corresponds with the increasingly common approach to create waste-free technologies in all economy.

Keywords: elemental sulfur; sulfate sulfur; sulfur pulp; soil enzymatic activity

1. Introduction

In the face of the increasing amount of waste generated as a result of human activity, waste management is one of the main economic and environmental issues in the world [1–4]. Sewage sludge is a major byproduct of municipal and industrial sewage treatment. Based on recent data, it has been estimated that some 10 million tons of sewage sludge dry matter are produced in Europe annually, while in China and the United States this figure is 20 million tons and 49 trillion liters, respectively [5,6]. In terms of municipal sewage sludge production, Poland ranked second in Europe in 2017, its production reaching 584 thousand tons of dry matter [7]. Along with economic and demographic growth, sewage sludge production will increase [8,9].

Good quality sewage sludge can be used for soil fertilization and remediation [10–12]. This is a rich source of nutrients and organic matter, it also poses an environmental threat [13]. To convert sewage sludge into an environmentally friendly material, this substance is subjected to thermal, chemical or biological treatment, which includes composting, anaerobic digestion, thermal drying, solar drying, lime stabilization [11]. Anaerobic digestion is considered the most environmentally friendly and cost-effective way of treatment and disposal of sewage sludge [14,15].

Anaerobic digestion is a microbiological process of material decomposition in an oxygen-depleted environment [16]. During this process, organic matter is broken down into less complex chemical compounds, such as methane, carbon dioxide, hydrogen sulfide, and the residue is a nutrient-rich

sludge [17,18]. As a byproduct of anaerobic digestion, a valuable gas fuel —biogas—is created, constituting a clean and renewable source of energy [19,20]. The chemical composition of raw biogas depends on the properties of the degraded material and parameters of the fermentation process. Presence of several trace components (hydrogen sulfide, siloxanes, ammonia, particulate matter, moisture, carbon dioxide) in the raw gas may reduce its quality or even exclude its use.

Hydrogen sulfide is a toxic product of degradation of sulfur-containing compounds. Sulfur occurs in sewage sludge as sulfates, sulfonic acid, sulfoxide, aromatic sulfur, aliphatic sulfur and inorganic sulfide—they amount to 18%, 25%, 9%, 18%, 22%, and 8% of total sulfur, respectively [10]. If hydrogen sulfide is released into the environment, it causes its pollution. Moreover, sulfur oxides resulting from combustion of hydrogen sulfide undergo transformation into sulfuric acids that cause damage in the elements of technological installations and create acid rain. Therefore, hydrogen sulfide removal before further biogas processing is necessary for environmental and technical reasons [21,22]. Different biogas desulfurization methods are used [22,23]. In Poland, one of the most frequently used method of removing hydrogen sulfide from biogas obtained from sewage sludge digestion is the Biosulfex[®] method (PROMIS COMPANY, Warsaw, Poland), with the use of iron and organic ethylenediaminetetraacetic acid (EDTA) ligand [24,25]. As a result, sulfur pulp containing a large amount of elemental sulfur is produced.

Sulfur waste obtained as a byproduct of desulfurization may be recovered and reused [21,26]. However, under Polish law, sulfur pulp produced during Biosulfex[®] desulfurization cannot be used directly to improve soil properties, but it can enrich other materials or fertilizers with sulfur. Insufficient sulfur supply concerns most agriculturally used soils in many regions of the world. The significance of sulfur in agriculture is increasing, and the role of sulfur in crop production is well identified. Sulfur has been recognized as a limiting factor for crop production [27–29]. The problem of sulfur deficiency is observed, among others, in Central, Western and Northern Europe (including Poland) and North America [27,30,31]. Since the end of the 20th century there has been a steady reduction in the amount of sulfur returning to the soil surface as a result of atmospheric deposition. It is estimated that this situation will continue at least until 2050 [32–34]. The exception to this is Asia where large amounts of sulfur dioxide are emitted into the environment (however, actions to reduce the emission are currently being taken there) [35]. Apart from atmospheric deposition, causes of an insufficient sulfur supply also include sulfur removal with plant yield, leaching sulfates into the soil profile and a reduction in the use of organic fertilizers [28,36]. Due to this situation, sulfur fertilization is now gaining importance. An alternative to conventional mineral fertilizers may be the use of sulfur-rich waste materials (generated, among others, during gas desulfurization) and fertilizers prepared based on these materials. This has not only ecological, but also economic significance. The use of waste sulfur generated during biogas desulfurization improves the economic balance of sewage treatment plants. In Europe, the estimated costs incurred by sewage sludge treatment and disposal are approximately 50% of the operating costs of secondary sewage treatment plants [11].

The aim of this research was to determine the bioavailability of sulfur from waste (sulfur pulp) obtained during desulfurization of biogas obtained during anaerobic digestion of sewage sludge. Under the incubation experiment, changes in sulfate sulfur content in the soil after introduction of sulfur pulp were analyzed (to complement the characteristics of the soil, soil acidification and enzymatic activity after sulfur application were also determined). The research was conducted on two sets of soil samples —limed and unlimed—to assess the effect of soil pH adjustment on sulfur oxidation.

2. Materials and Methods

2.1. Properties of the Soil Material

The experiment was set up on soil classified to the agronomic category of medium soils (Table 1). The soil material was collected from southern Poland, from a 0–20 cm layer of an arable field. To prepare

for the experiment, the soil was brought to an air-dry condition and sifted (to remove stones and plant parts).

Table 1. Selected soil properties before setting up the experiment.

Parameter	Value
Soil texture, %	
Fraction 1-0.1 mm	39
Fraction 0.1-0.02 mm	34
Fraction < 0.02 mm	27
Maximum water capacity, %	25.9
pH _{H2O}	6.16
pH _{KCl}	5.35
Hydrolitic acidity, mmol (+) kg ⁻¹ d.m.	15.5
Total N, g kg ⁻¹ d.m.	0.92
Total C, g kg ⁻¹ d.m.	7.69
Total S, mg kg ⁻¹ d.m.	148.3
Sulfate S, mg kg ⁻¹ d.m.	30.0

2.2. Incubation Experiment

For assay of bioavailability of waste sulfur, soil samples were added with different doses of sulfur pulp. Four sulfur doses were considered: 10 (S-I), 20 (S-II), 30 (S-III) and 60 mg S kg⁻¹ d.m. of soil (S-IV). Soil with no addition of sulfur pulp was regarded as control (C). Moreover, in order to compare the rate of oxidation of elemental sulfur and the availability of sulfate sulfur applied with traditional sulfate fertilizer, ammonium sulfate was introduced as a soil treatment with a sulfur dose of 20 mg S kg⁻¹ d.m. of soil (Sas-II). Each treatment was conducted in four replications.

The sulfur doses were established based on sulfate sulfur content in the soil before setting up the experiment and according to Polish guidelines on the assessment of sulfur content in soils. According to these guidelines, there are three levels of natural sulfur content (low, medium and high). There is also a fourth level, which indicates sulfur content elevated as a result of human pressure. Before setting up the experiment, the soil had medium content of sulfate sulfur (Table 1). According to Polish guidelines, increasing the sulfate sulfur content in medium soil by doses I and II would change the abundance of this form of sulfur (to high and elevated as a result of human pressure, respectively). In the conducted research, sulfur pulp was used as a source of sulfur (Figure 1a). This waste contains elemental sulfur (S⁰) which needs to be oxidized to an available sulfate form. That is why additional, increased doses (III and IV) were introduced.



Figure 1. Materials used in the experiment: (a) sulfur pulp; (b) carbide lime.

Before the experiment, the soil had an acid reaction (Table 1). To examine the effect of soil acidity on sulfur oxidation, the research was conducted on two sets of soil samples: the first one was unlimed (0Ca) and the second one was limed (+Ca). To deacidify the soil of the limed set, carbide lime (Figure 1b) had been introduced two months before sulfur application. Lime dose was established so as to neutralize the soil acidification amounting to one hydrolytic acidity.

The waste materials (sulfur pulp and carbide lime) came from a facility located in southern Poland. Sulfur pulp was produced during biogas desulfurization with the Biosulfex® method. The material had a high sulfur content exceeding 90% d.m. (Table 2). Carbide lime was generated during acetylene production with the use of carbide, and its alkalinity reached 67.4% CaO (Table 2).

Table 2. Selected chemical properties of sulfur pulp and carbide lime used in the experiment.

Parameter	Material	
	Sulfur Pulp	Carbide Lime
d.m. (%)	54.7	62.3
Alkalinity (% CaO)	–	67.4
Total C (g kg ⁻¹ d.m.)	13.5	52.4
Total N (g kg ⁻¹ d.m.)	0.95	0.56
Total P (g kg ⁻¹ d.m.)	traces	0.17
Total K (g kg ⁻¹ d.m.)	traces	traces
Total Ca (g kg ⁻¹ d.m.)	traces	395
Total Mg (g kg ⁻¹ d.m.)	traces	1.79
Total Na (g kg ⁻¹ d.m.)	10.5	traces
Total Fe (g kg ⁻¹ d.m.)	2.13	0.764
Total S (g kg ⁻¹ d.m.)	921	0.001
Total Zn (mg kg ⁻¹ d.m.)	traces	5.26
Total Cu (mg kg ⁻¹ d.m.)	traces	5.62
Total Ni (mg kg ⁻¹ d.m.)	traces	3.94
Total Pb (mg kg ⁻¹ d.m.)	traces	traces
Total Cd (mg kg ⁻¹ d.m.)	traces	0.32
Total Mn (mg kg ⁻¹ d.m.)	0.96	32.7
Total Cr (mg kg ⁻¹ d.m.)	4.02	5.28
Total Hg (mg kg ⁻¹ d.m.)	not determined	0.274

According to the experimental design, soil enriched with suitable materials was placed into plastic containers (soil mass was 280 g d.m. in each container). Throughout the experiment, soil moisture was maintained at a constant level (60% of the maximum water capacity) by periodically weighing the containers with samples and replenishing water losses. Incubation was conducted at 25 ± 2°C. Soil for analyses was collected on the day of sulfur application as well as 7, 15, 30, 60 and 120 days after sulfur introduction. Laboratory analyses were conducted on dried and sieved samples (1 mm mesh), excluding determinations of enzymatic activity. Those determinations were conducted on fresh and sieved samples (2 mm mesh) with moisture determined by weight method.

2.3. Methods of Laboratory Analyses

The soil pH_{KCl} was determined by potentiometry in a 1 mol L⁻¹ potassium chloride suspension (m/v 1:2.5). To calculate the mean pH, pH values of four replicates were converted into hydrogen ion [H⁺] concentrations, then the arithmetic mean was calculated and converted into pH according to the formula: pH = -log[H⁺].

Sulfate sulfur was extracted from the soil samples with a 0.03 mol L⁻¹ acetic acid solution (30 min, 40 rpm, m/v 1:10). This extractant allows to assess the amount of sulfur readily available to plants [37]. Sulfur concentration in the soil extracts was determined using an Optima 7300 DV inductively coupled plasma optical emission spectrophotometer (ICP-OES method, Perkin-Elmer Waltham, MA, USA). The emission value was determined at 181.975 nm in axial mode. The gas flow in the plasma was 15 L min⁻¹, the shield gas flow was 0.2 L min⁻¹, and the gas flow in the atomizer was 0.6 L min⁻¹. The quantification limit of the method used was 0.031 mg L⁻¹.

Sulfur mineralization occurring in indigenous organic matter and its immobilization by microorganisms take place simultaneously during elemental sulfur oxidation. Owing to this fact, determination of sulfate content in the soil solution does not reflect the net S⁰ oxidation [38]. Due to this

reason, sulfur oxidation after 120 days of incubation was referred to as apparent oxidation (S^0_{apparent}), which was calculated using the following equation:

$$S^0_{\text{apparent}}(\%) = (S_{\text{treatment}} - S_{\text{control}}) \times 100 / S_{\text{dose}} \quad (1)$$

where: $S_{\text{treatment}}$ and S_{control} are the S-SO₄ concentrations in soil with and without elemental sulfur application, respectively, and S_{dose} is the amount of elemental sulfur introduced to the soil.

Determination of soil enzymatic activity involved measurement of catalase and dehydrogenase activity. The CAT activity was measured using hydrogen peroxide as a substrate. The soil material (2 g) suspended in 40 mL of distilled water was shaken with 5 mL of 0.3% hydrogen peroxide at room temperature (20 min, 30 rpm). Excess hydrogen peroxide was back titrated with aqueous solution of potassium tetraoxomanganate (VII) in the environment of sulfuric acid. The CAT activity was expressed as μmol of H₂O₂ per g d.m. soil per minute. The DEH activity was determined by the transformation of colorless, water-soluble 2,3,5-triphenyltetrazolium chloride (TTC) into red water-insoluble 1,3,5-triphenylformazan (TPF). In a test-tube, 5 g of soil material and 5 mL of 1.0% TTC were mixed. TTC was prepared in a tris(hydroxymethyl) aminomethane hydrochloride (TRIS-HCL) buffer, pH 7.4. The tubes were sealed and incubated in the dark for 96 h at 30 °C. After that, TPF was extracted with 20 mL of methanol and quantified by the colorimetric method at the wavelength of 485 nm on a UV/VIS DU 640 spectrophotometer (Beckman, Fullerton, CA, USA). The DEH activity was expressed as μmol of TPF per g d.m. soil per 24 h.

To characterize the properties of the soil and the applied waste materials (sulfur pulp and carbide lime) before the experiment, additional analyses were conducted. The soil granulometric composition was determined by the Bouyoucos-Casagrande's aerometric method in Prószyński's modification [39]. This method of determining the granulometric composition was applied because it is in accordance with the method of assessing sulfur content in soils that is used in Poland. Maximum water capacity of the soil was determined by measuring the difference in soil mass before and after moisture conditioning by capillary rise. The soil pH_{H2O} was determined potentiometrically in water suspension (m/v 1:2.5). Hydrolytic acidity was determined by Kappen method after extraction with 1 mol L⁻¹ sodium acetate (1 h, 40 rpm, 2:5 m/v). Total content of carbon and nitrogen in all samples was determined with a vario MAX cube CNS analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany). Total sulfur content in the soil and in the carbide lime was determined by ICP-OES method after binding sulfur by magnesium nitrate, dry mineralization (12 h, 450 °C) and after dissolving the residue in a nitric acid solution. Absolute dry matter of the waste materials was determined by the weight method. Alkalinity of carbide lime was determined after reaction with hydrochloric acid and back titration of the acid with sodium hydroxide. Total sulfur content in the sulfur pulp was determined after reaction with hydrogen peroxide in an alkaline environment [40]. Total content of other macroelements (P, K, Ca, Mg, Na) and microelements (Fe, Zn, Cu, Ni, Pb, Cd, Mn, Cr) in both materials was determined after incineration and dissolving the remains in inorganic acids, under conditions suitable to the properties of the materials. The content of the analyzed elements in the obtained solutions was determined by ICP-OES. Total mercury content in the carbide lime was determined on AMA-254 (Altec Ltd., Praha, Czech Republic) apparatus.

2.4. Statistical Analysis

The obtained results of sulfate sulfur content in the soil and of soil enzymatic activity were statistically analyzed by performing a three-way analysis of variance (factor 1: liming, factor 2: treatment, factor 3: incubation time), with the use of PQStat, ver 1.6 statistical package (PQStat Software, Poznań, Poland). The least significant differences (LSD) were calculated by Fisher's test ($\alpha = 0.05$). Moreover, a principal component analysis (PCA) was applied to show relationships between the analyzed parameters and treatments. The data analysis software system Statistica, ver. 13 (TIBCO Software Inc., Palo Alto, CA, USA) was used to conduct the PCA analysis.

3. Results and Discussion

3.1. Soil pH_{KCl}

Soil reaction is an important parameter that shapes physicochemical and biological processes occurring in soil, thus regulating the possibility of plant growth and development. Soil pH is characterized by variability resulting from the influence of external factors. Under natural conditions, the rate of soil acidification is generally slow [41,42].

During the incubation experiment, the pH of the unlimed soil ranged from 4.68 to 5.14, and of the limed soil from 5.59 to 5.98 (Figure 2a,b). These values correspond to acid and slightly acid reaction, respectively. Liming reduced soil acidity. A similar trend, as a result of applying carbide lime, is also presented by Lalande et al. [43]. Liming not only neutralizes soil acidity and improves its chemical properties, but it also influences sulfur regime in soil. It can also reduce the amount of mobile fraction of this element in soil up to 7–8 times [44].

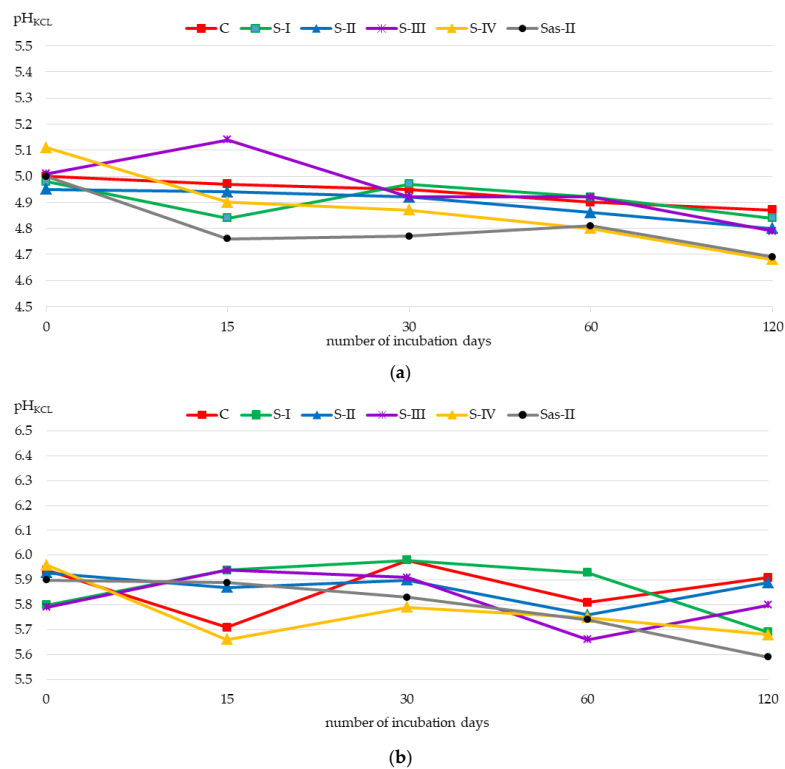


Figure 2. pH_{KCl} value of soil during the experiment: (a) unlimed soil; (b) limed soil. C: control soil (with no additions); S-I: soil with the addition of sulfur pulp (sulfur dose: I); S-II: soil with the addition of sulfur pulp (sulfur dose: II); S-III: soil with the addition of sulfur pulp (sulfur dose: III); S-IV: soil with the addition of sulfur pulp (sulfur dose: IV); Sas-II: soil with the addition of ammonium sulfate (sulfur dose: II).

During the experiment, the diversity of soil pH resulting from sulfur application was relatively small, indicating only slight influence of the applied sulfur on soil pH. At the same time, during incubation, a slight decrease in pH of the unlimed soil of all treatments was observed, while the effect of sulfur application on pH of the limed soil did not have a clear direction. Similar results related to a decrease in soil pH as a result of elemental sulfur application have been reported in other studies [38,45–47].

Fertilization with elemental sulfur may cause slow soil acidification, which is a result of microbial oxidation of sulfur [47,48]. Oxidation of 500 mg kg^{-1} of elemental sulfur results in production of $31 \text{ mmol [H}^+] \text{ kg}^{-1}$ soil. In soil abundant with free carbonates, this would not decrease pH, since $0.16\% \text{ CaCO}_3$ suffices to neutralize the acid formed. However, in soil with low buffering capacity, oxidation of

elemental sulfur can induce a significant pH reduction [49]. On the other hand, applying conventional mineral fertilizers containing nitrogen can also accelerate soil acidification (especially NH_4^+ - or R- NH_2 -based fertilizers) [42,50,51]. Infertility of acid soils can be ameliorated by application of deacidifying materials such as waste lime. In addition to increasing pH, this material is a source of calcium and magnesium—essential nutrients for plant growth and development [43,52,53].

3.2. Sulfate Sulfur Content in Soil

Elemental sulfur is not directly available to plants; inorganic sulfate ions SO_4^{2-} are the available form [36,54]. The microbiological oxidation of elemental sulfur consists of the following steps: $\text{S}^0 \rightarrow \text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} \rightarrow \text{SO}_4^{2-}$ [36]. The gradual release of the ionic form of sulfur may bring benefits when using elemental sulfur on soils susceptible to leaching. Additionally, due to gradual release of sulfates, elemental sulfur fertilization can be performed every few years [38,47].

During incubation, sulfate sulfur content in the unlimed soil ranged from 23.2 mg to 69.8 mg kg^{-1} d.m., and in the limed soil—from 24.9 mg to 63.2 mg kg^{-1} d.m. (Table 3). Despite the similar ranges of content, liming significantly increased sulfate content in the soil, particularly in the initial stage of incubation (up to day 30) and after application of larger doses of sulfur.

Table 3. Sulfate sulfur content in soil during the experiment [mg S- SO_4^{2-} kg^{-1} d.m. of soil].

Treatment		Incubation Time						
		0	15	30	60	120	Mean	
Mean for 'liming' variable	C ¹	32.6	30.6	25.6	37.0	30.7	31.3	
	S-I	34.4	29.3	27.0	43.2	32.9	33.3	
	S-II	34.8	25.7	26.5	40.2	41.2	33.7	
	S-III	35.3	27.4	26.4	44.0	43.9	35.4	
	S-IV	35.3	31.3	30.4	58.6	67.2	44.6	
	Sas-II	60.3	40.1	43.9	63.5	52.2	52.0	
	Mean	38.8	30.7	30.0	47.8	44.7	38.4	
LSD _{0.05} for:								
treatment					1.5			
incubation time					1.4			
treatment x incubation time					3.4			
Liming	0Ca	C	30.2	34.3	26.4	44.2	32.1	33.4
		S-I	30.7	25.9	28.5	43.6	35.4	32.8
		S-II	33.2	23.2	25.7	39.2	40.0	32.3
		S-III	31.5	23.3	23.5	43.1	44.6	33.2
		S-IV	29.9	27.0	26.7	60.4	69.8	40.8
		Sas-II	57.4	39.9	39.7	65.8	52.1	51.0
		Mean	35.5	28.9	28.4	47.7	45.7	37.2
	+Ca	C	35.1	26.9	24.9	29.9	29.3	29.2
		S-I	38.0	32.6	25.5	42.8	30.3	33.9
		S-II	36.4	28.3	27.4	41.2	42.4	35.1
		S-III	39.1	31.5	29.3	44.9	43.1	37.6
		S-IV	40.7	35.7	34.1	66.8	64.7	48.4
		Sas-II	63.2	40.3	48.0	61.2	52.3	53.0
		Mean	42.1	32.6	31.5	47.8	43.7	39.5
LSD _{0.05} for:								
liming					0.9			
treatment x liming					2.1			
incubation time x liming					1.9			
treatment x incubation time x liming					4.8			

¹ see Figure 2.

Regardless of liming, application of sulfur in the elemental and ionic form significantly increased the content of sulfates in the soil compared to the content determined in the soil with no additions (Table 3). As a rule, soil treated with ammonium sulfate had a high content of available sulfur throughout the whole incubation. The effect of elemental sulfur application became more visible over time (the effect of the introduction of sulfur pulp on sulfate sulfur content in the soil was clearly visible on later sampling days—60th and 120th day) and as the dose of sulfur increased. After 120 days of incubation, the soil without additions and with the addition of sulfur pulp at dose I (10 mg kg⁻¹ d.m. of soil) had the lowest content of sulfate ions. Application of sulfur pulp at dose II (20 mg kg⁻¹ d.m. of soil) increased sulfate content, but not to the level after application of the same dose in sulfate form. Application of successive doses (in particular dose IV: 60 mg kg⁻¹ d.m. of soil) also increased sulfate content in soils. It must be highlighted that introducing very high doses of sulfur to soil may have a negative effect, leading to strong acidification of the environment and leaching of sulfates.

Oxidation of elemental sulfur is positively related with soil pH, owing to the fact that pH value affects both the abundance and activity of S-oxidizing microorganisms [49,55]. As a rule, soils with high pH (5.4–8.0) have a high oxidative capacity [56], and an addition of calcium compounds (e.g., CaCO₃) to acid soil increases the oxidation of elemental sulfur [57]. The beneficial effect of higher soil pH on sulfur oxidation was confirmed by Zhao et al. [55]. The authors, in an incubation experiment with 10 soils (with pH ranging from 4.4 to 8.5) collected from various agro-ecological zones, found that soils with the highest pH (8.5) showed the highest oxidation rate of the applied elemental sulfur. Zhao et al. [49], at the end of a 96-day incubation experiment, also found that more than 96% of the applied elemental sulfur (1000 mg kg⁻¹) was oxidized in soils with pH ranging from 7.3 to 7.5, 85% in soils with pH ranging from 6.2 to 6.7, 66–77% in soils with pH ranging from 4.6 to 5.1, and only 21% in soil with pH 4.0. As the authors highlighted, after 48 days of incubation, oxidation slowed down in soils with pH value of 5.1–6.2, due to the acidification resulting from oxidation of the introduced elemental sulfur.

The findings presented in this study clearly indicate that application of elemental sulfur has a positive impact on sulfate content in soil, which corresponds with our previous results [58] and with results presented by other authors [30,47,59].

Agricultural use of waste sulfur pulp will lead to an improvement of sulfur balance in soils. Due to the common sulfur deficiency in soils in many regions of the world, it is legitimate to use waste sulfur pulp for the production of fertilizers. There are many reports on the effectiveness of elemental sulfur in improving production (biomass quality and quantity) of plants that are important both globally and regionally [60–63]. However, there is little research on the fertilizer use of waste elemental sulfur, and this issue needs further investigation.

The significance of sulfur in plant nutrition result from the fact that limited availability of this element causes both direct and indirect production loss. The obvious direct effect of sulfur deficiency is biomass reduction due to sulfur participation in the primary metabolism of plants [61]. While indirect effects are revealed by reduced tolerance of plants to biotic and abiotic stresses. This is related to the function sulfur plays in the pathway of the synthesis of sulfur-containing defense compounds—metabolites that are involved in the plant physiological response to stress factors [64]. Yield losses due to sulfur deficiency in plants can reach as much as 50% in cereals [65]. Moreover, sulfur constitutes a key component of enzymes involved in nitrogen metabolism. Fertilization with sulfur increases nitrogen uptake and recovery, allowing to maintain a high level of nitrogen efficiency. Thus, nitrate losses are reduced, which is particularly important in soil susceptible to leaching [66]. What is more, fertilizing plants with sulfur-containing waste in combination with other organic wastes may be considered as enhancing factors of plant efficiency in terms of bioactive compounds production [67]. In many crop species, especially those with high sulfur requirements, treatment with sulfur may increase its antioxidant actions.

Agricultural use of waste is also in line with the increasingly common approach to create waste-free technologies in the whole economy [68,69]. Attention should be drawn to one more aspect associated

with using sulfur for the production of fertilizers. The physical properties of pulp (water presence, low particle size) significantly hinder its application, especially on a large scale. During fertilizer production, it would be possible to transform waste (e.g., through granulation) into a form allowing application with commercially available and commonly used spreaders.

Apparent S⁰ Oxidation

Apparent S⁰ oxidation was calculated to assess the net S⁰ sulfur oxidation. After 120 days of incubation, the apparent S⁰ oxidation in the unlimed soil was 33.1%, 39.6%, 41.8% and 62.8% for elemental sulfur doses I, II, III, IV, respectively. After 120 days of incubation, the apparent S⁰ oxidation in the limed soil was: 10.5%, 65.8%, 46.3%, 59.0% for elemental sulfur doses I, II, III, IV, respectively. It needs to be highlighted that elemental sulfur oxidation starts at temperatures > 5° C, and shows optimum rates in the range of 30 to 40°C. Elemental sulfur oxidation under field conditions will therefore be significantly lower than in incubation experiments [38]. The rate of oxidation also depends on the elemental sulfur dose, and generally increases with the amount of sulfur introduced [70].

Oxidation of elemental sulfur has been assessed in many studies as an increase in concentration of oxidation products, mainly sulfate. Nevertheless, in some cases this may result in underestimation of sulfur oxidation due to sulfate immobilization and adsorption into organic matter or minerals, respectively [71,72]. A short-term incubation may result in a greater underestimation of the oxidation rate, due to a higher ratio of predicted-to-measured values. This could either be related to the lag-time for the oxidation or more sulfate being immobilized in a short period of time [71,73]. He et al. [71] measured oxidation of elemental sulfur in 4 cultivated soils (amended with 200 mg S kg⁻¹) and stated that at a short incubation time (1 week and less), only 13–55% of oxidized elemental sulfur was extractable as sulfate. At a longer incubation time (>5 weeks), 34–75% of oxidized elemental sulfur was extractable as sulfate. Zhao et al. [74] found that in soil (with varied pH) incubated with elemental sulfur at a dose of 200 mg kg⁻¹ d.m. of soil, approximately 40% of introduced sulfur was oxidized in week 2, and 90% in week 14. As He et al. [71] pointed out, there is a limited capacity for sulfur immobilization into organic matter. Relatively more sulfur may be immobilized within short periods, when only a small amount of sulfur is oxidized to sulfate.

3.3. Soil Enzymatic Activity

The availability of elemental sulfur in soil is governed by sulfur oxidation rate, which depends principally on soil microbiological activity. Thus, the factors that affect soil microbiological activity are also likely to influence the oxidation of elemental sulfur [47,56].

Activity of soil enzymes is a sensitive indicator of changes occurring in the soil environment. This parameter is considered to be an indicator for measuring the quality and fertility of soil, and thus the degree of its degradation [75–77].

CAT activity is very stable in soil. Not only is it an intracellular enzyme, but it is also sorbed by clay minerals and organic colloids. CAT is an anti-oxidant enzyme responsible for breakdown of hydrogen peroxide (H₂O₂) into water and molecular oxygen. That mechanism reduces harmful effects of H₂O₂ on living organisms and is beneficial for organic carbon accumulation in soil [78–80]. DEH plays a significant role in biological oxidation of soil organic matter due to transferring hydrogen from organic substrates to inorganic acceptors. These enzymes are considered to exist as an integral part of cells and do not accumulate extracellularly in soil. The DEH activity shows the total activity of soil microbial population and is commonly used to assess the effects of different factors on soil microorganisms [81–84].

During incubation, the CAT activity in the unlimited and limed soil ranged from 2.04 μmol to 4.57 μmol H₂O₂ g⁻¹ d.m. of soil min⁻¹ and from 3.36 μmol to 7.16 μmol H₂O₂ g⁻¹ d.m. of soil min⁻¹, respectively. The DEH activity ranged from 0.81 μmol to 7.46 μmol TPF g⁻¹ d.m. of soil 24 h⁻¹ and from 3.01 μmol to 17.84 μmol TPF g⁻¹ d.m. of soil 24h⁻¹, respectively. Liming significantly increased the soil activity of both examined enzymes (Tables 4 and 5).

Table 4. Soil catalase activity during the experiment [$\mu\text{mol H}_2\text{O}_2 \text{ g}^{-1} \text{ d.m. of soil min}^{-1}$].

Treatment		Incubation Time						
		0	15	30	60	120	Mean	
Mean for 'liming' variable	C ¹	3.87	3.70	3.89	4.17	3.21	3.77	
	S-I	4.16	3.57	4.43	5.82	2.97	4.19	
	S-II	4.57	3.94	4.30	4.91	3.48	4.24	
	S-III	4.20	3.80	4.18	4.86	3.36	4.08	
	S-IV	4.30	3.51	4.13	4.12	3.07	3.83	
	Sas-II	4.44	3.75	4.04	4.41	3.15	3.96	
	Mean	4.26	3.71	4.16	4.71	3.21	4.01	
LSD _{0.05} for:								
treatment					0.15			
incubation time					0.14			
treatment x incubation time					0.34			
Liming	0Ca	C	3.58	3.53	3.66	3.33	2.78	3.38
		S-I	3.89	3.37	4.11	4.48	2.04	3.58
		S-II	4.05	3.70	3.98	4.04	2.96	3.74
		S-III	3.63	3.39	3.85	4.57	3.11	3.71
		S-IV	3.86	3.18	3.87	4.15	2.79	3.57
		Sas-II	4.28	3.57	3.60	3.20	2.91	3.51
		Mean	3.88	3.46	3.84	3.96	2.76	3.58
	+Ca	C	4.15	3.86	4.12	5.01	3.63	4.15
		S-I	4.43	3.78	4.75	7.16	3.90	4.81
		S-II	5.08	4.17	4.63	5.78	4.01	4.74
		S-III	4.77	4.20	4.51	5.15	3.61	4.45
		S-IV	4.74	3.85	4.38	4.10	3.36	4.09
		Sas-II	4.61	3.93	4.47	5.62	3.40	4.41
		Mean	4.63	3.97	4.48	5.47	3.65	4.44
LSD _{0.05} for:								
liming					0.09			
treatment x liming					0.22			
incubation time x liming					0.20			
treatment x incubation time x liming					0.49			

¹ see Figure 2.**Table 5.** Soil dehydrogenase activity during the experiment [$\mu\text{mol TPF g}^{-1} \text{ d.m. of soil 24h}^{-1}$].

Treatment		Incubation Time					
		0	15	30	60	120	Mean
Mean for 'liming' variable	C ¹	8.94	4.97	5.59	4.49	2.20	5.24
	S-I	10.13	4.73	7.06	5.09	2.43	5.89
	S-II	12.88	3.94	6.90	5.34	2.92	6.40
	S-III	12.32	5.21	5.63	6.87	2.87	6.58
	S-IV	10.43	4.65	7.99	4.86	2.74	6.13
	Sas-II	7.50	5.61	5.40	3.51	2.21	4.85
	Mean	10.37	4.85	6.43	5.03	2.56	5.85
LSD _{0.05} for:							
treatment					0.56		
incubation time					0.51		
treatment x incubation time					1.25		

Table 5. Cont.

Treatment		Incubation Time					Mean	
		0	15	30	60	120		
Liming	0Ca	C	6.18	3.19	3.03	2.59	1.13	3.22
		S-I	8.46	4.82	5.60	4.92	1.58	5.08
		S-II	8.30	4.36	5.03	4.41	2.45	4.91
		S-III	6.79	4.61	4.08	5.26	2.72	4.69
		S-IV	7.46	3.49	5.67	3.16	1.49	4.26
		Sas-II	5.40	3.41	2.40	3.23	0.81	3.05
		Mean	7.10	3.98	4.30	3.93	1.70	4.20
	+Ca	C	11.70	6.76	8.14	6.39	3.27	7.25
		S-I	11.80	4.65	8.53	5.27	3.27	6.70
		S-II	17.47	3.53	8.78	6.26	3.40	7.89
		S-III	17.84	5.82	7.17	8.48	3.01	8.46
		S-IV	13.40	5.80	10.3	6.55	3.99	8.01
		Sas-II	9.59	7.81	8.40	3.79	3.60	6.64
		Mean	13.63	5.73	8.55	6.12	3.43	7.49
LSD _{0.05} for:								
liming					0.32			
treatment x liming					0.79			
incubation time x liming					0.72			
treatment x incubation time x liming					1.76			

¹ see Figure 2.

Regardless of liming, a significant effect of different sulfur doses on soil CAT and DEH activity was observed (Tables 4 and 5). As a rule, during incubation, the lowest activity of both enzymes was recorded in the unlimed soil without sulfur addition and after application of sulfate sulfur. During the first 15 days of incubation, a strong decrease in DEH activity was observed. A decrease in DEH activity was also observed on the successive dates of analyses, particularly in relation to the unlimed soil. Changes in CAT activity during incubation were lower. A beneficial effect of application of sulfur pulp on CAT and DEH activity was observed (the strength of this effect depended on duration of the experiment and on soil pH).

The activity of various soil enzymes depends on many factors, e.g., organic matter content, pH, temperature, moisture, aeration state, fertilization. Organic and mineral fertilizers have been reported to have positive, neutral and negative effect on soil enzyme activities [85–87]. Wang et al. [88] as well as Zhao et al. [54] observed that long-term mineral fertilization enhanced soil CAT activity. However, soil treated with bio-organic fertilizers had higher values of this enzyme. Zakaruskaitė et al. [89] observed inhibition of DEH activity as an effect of long-term application of mineral fertilizers, while Liang et al. [85] and Šimon and Czako [90] showed no negative effect. Fernández-Calviño et al. [91] suggested that soil acidity suppressed potential DEH activity, and Zhao et al. [92] showed that fertilization with elemental sulfur enhanced CAT activity, and indicated that 30 mg S kg⁻¹ is the suitable sulfur dose to increase CAT activity. According to Wang et al. [93], CAT activity is generally higher in soils of higher quality, and it may decrease or cease due to the occurring extremes of soil pH, temperature or nutrient content. A decrease in DEH activity could be, among other things, a result of deficiency of carbon substrates which are prone to decomposition [94,95], and of intensifying soil acidification. It is assumed that pH may affect the mechanism and rate of enzymatic reactions [75]. The optimal pH for efficient DEH activity is close to the neutral value (pH of 7). Low soil pH also favors the growth of fungi. These microorganisms are not metabolically active and use resources to a greater extent [96,97].

3.4. Relationships between pH, Sulfate Sulfur Content and Enzymatic Activity of Soil under Various Sulfur Doses and Incubation Time

Relationships between primary variables and obtained principal components are presented in Figure 3. PCA of the data for unlimed soil indicated that the first three principal components (PCs), accounted for 85.81% of the total variability (PC1: 53.55%, PC2: 19.63%, PC3: 12.63%). For limed soil, the first three PCs accounted for 78.95% of the total variability (PC1: 38.18%, PC2: 24.76%, PC3: 16.01%). The PCA ordination of soil characteristics and conditions of conducting the experiment (S dose and incubation time) suggested that S dose and incubation time can reduce the soil enzymatic activity (CAT and DEH) and decrease the pH value, but increase the sulfate sulfur content in soil.

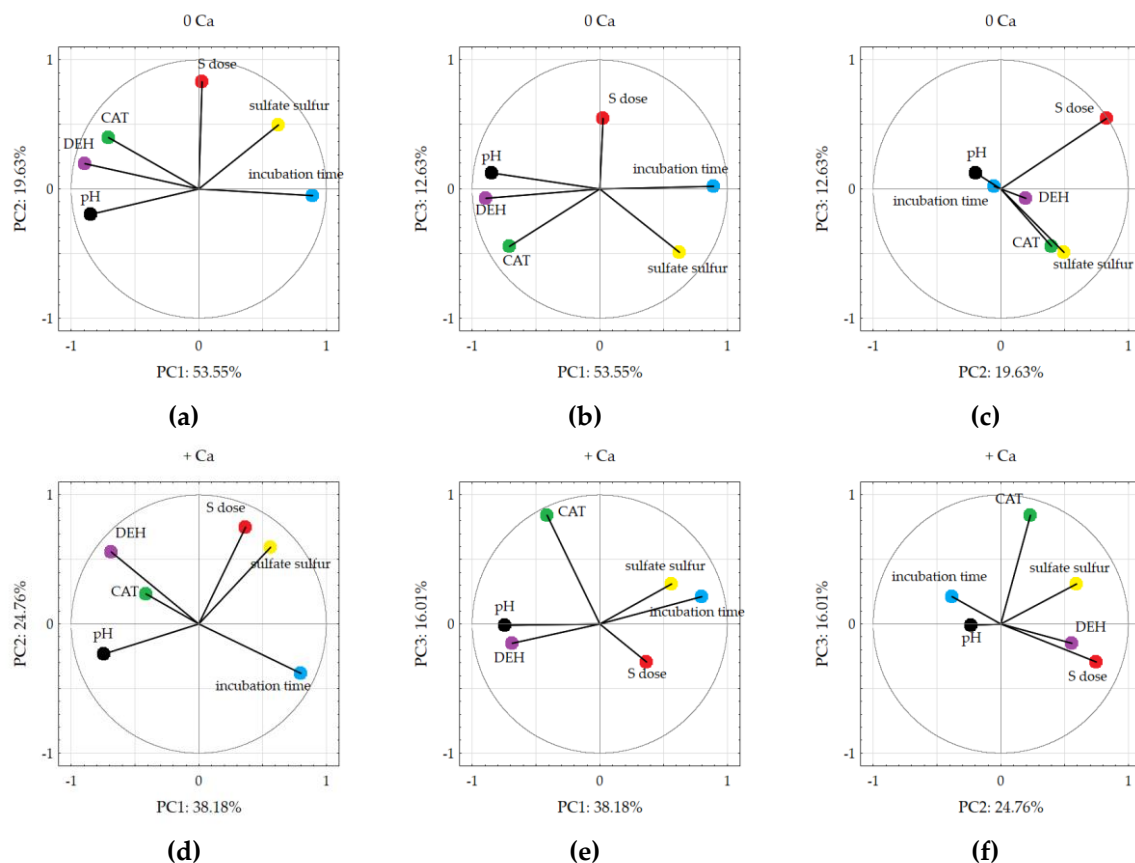


Figure 3. Principal component analysis (PCA) showing relationships between the examined parameters, incubation time and sulfur doses: (a) principal components PC1 and PC2 for unlimed soil; (b) principal components PC1 and PC3 for unlimed soil; (c) principal components PC2 and PC3 for unlimed soil; (d) principal components PC1 and PC2 for limed soil; (e) principal components PC1 and PC3 for limed soil; (f) principal components PC2 and PC3 for limed soil.

Adjustment of soil pH decreased the correlation between the studied variables. Both positive correlation between enzyme activity and pH value, and negative correlation between enzyme activity and incubation time, were distinctly stronger for unlimed soil. The positive correlation between DEH and CAT was also stronger for unlimed soil. The positive correlation between incubation time and sulfate sulfur content was stronger for unlimed soil. However, liming increased correlation between S dose and sulfate sulfur content.

Similar results have been presented by other authors. Mattiello et al. [98] highlighted a significant negative correlation between soil pH and sulfate sulfur content, similar to Hanousek et al. [99]. Filipek-Mazur et al. [100] showed a significant negative correlation between soil acidification and activity of DEH and CAT, as well as a positive correlation between sulfate sulfur content and CAT

activity, resulting from sulfur fertilization. Zhao et al. [49] concluded that the rate of elemental sulfur oxidation was positively correlated with soil pH.

4. Conclusions

The study reveals that soil application of waste sulfur pulp increases the content of available form of sulfur in soil. The effect of pulp application becomes more visible over time and as the dose of sulfur increases. However, introducing very high doses of sulfur to soil may have a negative effect, increasing acidification of the environment. Adjusting the soil pH (liming) before sulfur application reduces this negative effect, and has a positive effect on soil enzymatic activity and the rate of sulfur oxidation.

Based on the obtained results, it can be concluded that sulfur pulp may be an alternative source of sulfur in soils with deficiency of this element, especially in soils with adjusted pH. Moreover, finding a way to use this material to enrich soils with sulfur (e.g., by using waste for the production of sulfur-containing fertilizers) will help to reduce the environmental and economic burden associated with this waste disposal.

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