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The Effect of Amending Soil with Waste Elemental Sulfur on the Availability of Selected Macroelements and Heavy Metals

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Abstract: Elemental sulfur of waste origin may be a valuable sulfur source for plants. However, assessing the suitability of environmental use of a waste material should confirm there is no harmful effect of the material on soil environment. The purpose of the incubation experiment was to assess the availability of selected elements (P, K, Ca, Mg, Fe, Mn, Zn, Cu, Cr, Ni, Pb, Cd) in soils supplemented with waste elemental sulfur. The research was conducted on two soils: light and heavy, and with three sulfur doses applied to each soil. Available forms of elements in the soils were extracted 60 days after the waste introduction, with three reagents: 0.01 mol L⁻¹ CaCl₂, Mehlich 3 and 1 mol L⁻¹ HCl. Additionally, to determine the impact of the introduced sulfur on soil acidification, soil pH was periodically checked during the experiment. The sulfur addition intensified acidification of the light soil, and, to a lesser extent, of the heavy soil. The acidifying effect was stronger when the sulfur dose was higher. The content of available forms of elements in the soils depended mainly on the strength of the used extractants (generally, the highest amounts were extracted with 1 mol L⁻¹ HCl and the lowest with 0.01 mol L⁻¹ CaCl₂). The effect of sulfur introduction on element availability was small. No harmful effect on element availability in soils was stated.

Keywords: sulfur pulp; macroelements; heavy metals; pH; acidification

1. Introduction

Rapidly increasing urbanization and subsequent effect of growing municipal wastewater production increase the attention in sewage sludge management. The most common approach is anaerobic digestion resulting in production of biogas, constituting the energy source, as well as of waste materials that can be used as fertilizers or soil amendments [1,2].

The recently observed growth in the application of technologies of anaerobic digestion may be due to its suitability for simultaneous organic waste management and energy production, at reduced costs. Although anaerobic digestion is a technology of great significance in organic waste stabilization, the degradation of sulfur-containing molecules generates undesirable hydrogen sulfide gas (H₂S) [3]. Municipal sewage sludge contains from 11 to 17 g S kg⁻¹ d.m. [1]. This element occurs in inorganic (as sulfate and sulfide) and organic (as sulfoxide, sulfonic acid, aromatic sulfur and aliphatic sulfur) forms. Organic forms in raw sludge occur in higher concentrations than the inorganic forms [4]. Sulfur-containing biomolecules undergo assimilatory or dissimilatory transformations, which results in H₂S formation during biogas production [3]. However, in addition to H₂S, organic sulfur compounds (e.g., mercaptans, organic sulfides) may also be in biogas [5,6]. For further processing, H₂S must be removed from biogas (H₂S limits biogas utilization and constitutes an environmental

pollutant) [3]. Methods of biogas desulfurization may involve in situ chemical precipitation, absorption, adsorption, as well as certain biotechnological strategies, using specific microorganisms [3]. A large group of methods is based on using iron-containing reagents [3]. With the use of Fe^{3+} /EDTA (EDTA-ethylenediaminetetraacetic acid), H_2S is oxidized to elemental sulfur and Fe^{3+} is reduced to Fe^{2+} [3]. Oxygenation of Fe^{3+} /EDTA solution allows its regeneration. As a result of desulfurization using Fe^{3+} /EDTA, sludge with a high content of sulfur (even over 90% d.m.) is produced.

Sulfur recovered during biogas desulfurization may be a valuable material enriching soil with this element. The significance of sulfur in plant production has been well explored. The necessity to include this element in the fertilization plan is obvious, since insufficient plant supply with sulfur may result in a decrease in yield quality and quantity decrease, and sulfur deficiency in soils is widespread, both in Poland and globally [7–11]. To maintain high fertility, an agricultural area needs to be recompensed for nutrients losses [12]. For large farms, especially cereal and vegetable producers, the demand for plant nutrients is significant [13]. As Jamal et al. [14] highlighted, to produce 1 Mg of seeds, cereals require from 3 to 4 kg S (variations 1–6), leguminous 8 kg S (variations 5–13), and oilseed crops 12 kg S (variations 5–20). Fertilizing with sulfur in the amount of 20–40 kg ha⁻¹ is currently a standard treatment aimed at optimizing yields on S-deficient soil [15]. Since production of chemical fertilizers is highly energy-consuming, whether it is based on fossil fuels or fossil ore deposits, the reuse of waste materials as a source of nutrients in agriculture seems to be a suitable way considering economically and environmentally friendly approach [12,16]. Such an approach corresponds with the concept of circular economy highlighting the necessity to use by-products from one production process as secondary raw materials in another one. While this approach is broadly discussed, both in scientific and politics arena, its application in practice is low [16].

The method of biogas desulphurization involving the use of Fe^{3+} /EDTA is one of the methods often used in the plants involved in the production and processing of sewage sludge [3,17]. However, the popularity of this method is not followed by the environmental use of the generated waste containing high content of elemental sulfur. There are also few sources describing the broadly understood effects of introducing waste elemental sulfur into the environment and the details of the waste application [18–21]. One of the important aspects concerning the availability of elements in soils after waste application is discussed in this paper. Waste sulfur may be a valuable material enriching soils with this element [19,20]. However, the assessment of the suitability of waste material for fertilization requires investigating its effect on soil properties and crop yield quantity and quality—it is expected that the applied material will provide satisfactory quality and quantity of yields, but what is also significant is that it will not lead to negative changes in the soil environment. Considering the latter, those changes may result directly from the properties of the waste material (e.g., load of nutrients and trace elements introduced with the material) and indirectly from the effect of the material on processes occurring in soil (e.g., transformation of element availability due to soil pH changes). Therefore, the aim of this model study was to determine the effect of waste elemental sulfur application on the availability of selected macroelements (P, K, Ca, Mg) and heavy metals (Fe, Mn, Zn, Cu, Cr, Ni, Pb, Cd) in soils. The research was conducted as an incubation experiment, on two soils: light and heavy, and with three sulfur doses applied to each soil. Waste sulfur pulp (a by-product of desulfurization of biogas obtained during anaerobic digestion of sewage sludge) was the source of sulfur. Available forms of elements (P, K, Ca, Mg, Fe, Mn, Zn, Cu, Cr, Ni, Pb, Cd) in soils were extracted 60 days after sulfur introduction, with three reagents of different extraction strength: 0.01 mol L⁻¹ CaCl_2 , Mehlich 3 and 1 mol L⁻¹ HCl. Moreover, during incubation, soil pH was periodically checked to characterize the impact of the introduced waste sulfur on soil acidification.

2. Materials and Methods

2.1. Properties of the Soil Material

The experiment was established on two soils: the first one was classified to the agronomic category of light soils and the second one to the category of heavy soils (Table 1). The soil material was collected from southeastern Poland, from a 0–20 cm layer of arable fields, and then air-dried and sifted (to remove stones and plant parts) in order to prepare for the experiment.

Table 1. Selected properties of soil before establishing the experiment.

Soil	Soil Texture, %			Maximum Water Capacity, %	pH _{KCl}	Total N, g kg ⁻¹ d.m.	Total C, g kg ⁻¹ d.m.	Available S, mg kg ⁻¹ d.m.				
	1–0.1 mm	0.1–0.02 mm	<0.02 mm									
Light soil	77	16	7	24.4	5.98	0.32	3.99	4.9				
Heavy soil	8	49	43	35.7	6.04	0.92	9.5	9.2				
Available forms, mg kg ⁻¹ d.m. (extraction with 0.01 mol L ⁻¹ CaCl ₂)												
	P	K	Ca	Mg	Fe	Mn	Zn	Cu	Cr	Ni	Pb	Cd
Light soil	2.04	26.6		9.02	0.506	1.50	0.580	traces	traces	traces	traces	traces
Heavy soil	traces	25.2		149	1.06	3.10	traces	traces	traces	traces	traces	traces
Available forms, mg kg ⁻¹ d.m. (extraction with Mehlich 3)												
	P	K	Ca	Mg	Fe	Mn	Zn	Cu	Cr	Ni	Pb	Cd
Light soil	135	22.7	514	28.7	250	34.2	10.9	2.08	0.262	0.853	6.10	0.138
Heavy soil	35.6	107	3117	235	401	88.6	3.08	3.56	0.486	1.17	4.06	0.095
Available forms, mg kg ⁻¹ d.m. (extraction with 1 mol L ⁻¹ HCl)												
	P	K	Ca	Mg	Fe	Mn	Zn	Cu	Cr	Ni	Pb	Cd
Light soil	130	89.3	464	20.9	355	37.0	7.911	0.549	0.695	0.603	5.61	0.103
Heavy soil	79.2	175	2969	413	1432	148	8.34	4.64	2.31	2.44	8.24	0.127

2.2. Model Incubation Experiment

For the assessment of availability of selected elements in soils after sulfur application, the model incubation experiment was conducted. Three sulfur doses were considered for each soil: S-I, S-II, S-III (Table 2). Soil with no sulfur pulp addition was the control (S-0). Each treatment was repeated three times. Sulfur doses were established based on sulfate sulfur content in the soil before establishing the experiment and according to Polish guidelines on the assessment of sulfur content in soils [22]. According to these guidelines, there are three levels of natural sulfur content in soils: low, medium and high. Fourth level is found in soils with anthropogenically elevated sulfur content. Prior to the experiment, both soils had a low content of sulfate sulfur-Table 1. Elemental sulfur, which undergoes biological oxidation into sulfates, was used as a source of sulfur. However, assuming that the entire waste elemental sulfur applied was transformed into sulfates, introducing sulfur in doses S-I, S-II and S-III would change the sulfate sulfur level in both soils into medium, high and anthropogenically elevated, respectively.

Table 2. Doses of sulfur introduced to the soils (mg kg⁻¹ d.m.).

Sulfur Dose	Light Soil	Heavy Soil
S-0	0	0
S-I	15	20
S-II	30	40
S-III	45	60

Waste sulfur pulp was the source of sulfur for the incubation experiment. The material was obtained from a facility located in southern Poland. The sulfur pulp was produced during biogas desulfurization with the Biosulfex method (PROMIS COMPANY, Warsaw, Poland) using iron and EDTA ligand [23,24]. Sulfur content in the used waste exceeded 90% d.m. (Table 3).

Table 3. Selected chemical properties of sulfur pulp used in the experiment.

Parameter	Value
d.m., %	54.7
Total C, g kg ⁻¹ d.m.	13.5
Total N, g kg ⁻¹ d.m.	0.95
Total P, g kg ⁻¹ d.m.	traces
Total K, g kg ⁻¹ d.m.	traces
Total Ca, g kg ⁻¹ d.m.	traces
Total Mg, g kg ⁻¹ d.m.	traces
Total Na, g kg ⁻¹ d.m.	10.5
Total Fe, g kg ⁻¹ d.m.	2.13
Total S, g kg ⁻¹ d.m.	921
Total Zn, mg kg ⁻¹ d.m.	traces
Total Cu, mg kg ⁻¹ d.m.	traces
Total Ni, mg kg ⁻¹ d.m.	traces
Total Pb, mg kg ⁻¹ d.m.	traces
Total Cd, mg kg ⁻¹ d.m.	traces
Total Mn, mg kg ⁻¹ d.m.	0.96
Total Cr, mg kg ⁻¹ d.m.	4.02

In accordance with the experimental design, soil enriched with sulfur pulp was put into plastic containers (each contained 300 g d.m. of light soil or 250 g d.m. of heavy soil—soil mass differences are a result of different texture, hence different density of the soils were also used). During the experiment, soil moisture was kept constant (60% of the maximum water capacity). This was done by periodically weighing the containers with samples and replenishing water losses. Temperature during incubation was 25 ± 2 °C. Soil samples for pH analysis were collected on the day sulfur was applied as well as 10, 20, 30 and 60 days after application. Analyses of the content of available forms of selected elements (P, K, Ca, Mg, Fe, Mn, Zn, Cu, Cr, Ni, Pb, Cd) were conducted on samples collected 60 days after sulfur introduction. Incubation lasting several weeks may allow oxidation of a greater part of the introduced elemental sulfur. A subsequent increase in sulfate content is not so intense [20,25]. That is why that incubation period (60 days) was chosen to determine the effect of sulfur application on soil properties. Once collected, all samples were dried and sieved to prepare for laboratory analyses.

2.3. Methods of Laboratory Analyses

Soil pH_{KCl} was determined potentiometrically in a 1 mol L⁻¹ KCl suspension (1:2.5 m/v). Available forms of elements (P, K, Ca, Mg, Fe, Mn, Zn, Cu, Cr, Ni, Pb, Cd) were extracted with three reagents of different extraction strengths: (i) 0.01 mol L⁻¹ CaCl₂ (POCH, Gliwice, Poland) (120 min, 30 rpm, 1:10 m/v), (ii) Mehlich 3 (5 min, 30 rpm, 1:10 m/v) and (iii) 1 mol L⁻¹ HCl (Chempur, Piekary Śląskie, Poland) (60 min, 40 rpm, m/v 1:10) [26,27]. Mehlich 3 is an extractant of pH 2.5 ± 0.05 , containing 0.2 mol L⁻¹ CH₃COOH (Chempur, Piekary Śląskie, Poland), 0.25 mol L⁻¹ NH₄NO₃ (Chempur, Piekary Śląskie, Poland), 0.015 mol L⁻¹ NH₄F (Chempur, Piekary Śląskie, Poland), 0.013 mol L⁻¹ HNO₃ (Chempur, Piekary Śląskie, Poland) and 0.001 mol L⁻¹ EDTA (POCH, Gliwice, Poland). Element content in all the obtained extracts was determined using a Optima 7300 DV (Perkin-Elmer, Waltham, MA, USA) inductively coupled plasma optical emission spectrophotometer (ICP-OES method). The wavelengths which were used to determine the concentration of the analyzed elements and detection limits are given in Table S1.

To characterize the properties of the soils and sulfur pulp before setting up the experiment, additional analyses were carried out. Soil granulometric composition was determined using the Bouyoucos-Casagrande's aerometric method in Prószyński's modification [28]. This method was applied because it is consistent with the methods of assessing element availability which are used in Poland. Maximum water capacity of the soils was determined by measuring the difference in soil mass before and after moisture conditioning by capillary rise. Total content of carbon and nitrogen

in all samples (soils, sulfur pulp) was determined in a vario MAX cube CNS analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany). Available sulfur was extracted from the soil samples with a $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$. Absolute dry matter of sulfur pulp was determined using the weight method. Total sulfur content in the sulfur pulp was determined after reaction with hydrogen peroxide in an alkaline environment [29]. Total content of other macroelements (P, K, Ca, Mg, Na) and microelements (Fe, Zn, Cu, Ni, Pb, Cd, Mn, Cr) was determined after thermal decomposition and digestion in inorganic acids, under conditions suitable to the properties of the materials. Determination of the content of the analyzed elements in the obtained solutions was done using ICP-OES.

2.4. Statistical Analysis

The results obtained for the element content in soils underwent a two-way statistical analysis of variance (factor 1: sulfur dose, factor 2: extractant), using Dell Statistica (data analysis software system), version 13 (Dell Inc., Tulsa, OH, USA). The significance of differences in mean values was assessed using the Tukey test, with the significance level $\alpha \leq 0.05$.

3. Results and Discussion

3.1. Soil pH_{KCl}

The functionality of the soil ecosystem is shaped by biogeochemical processes occurring in soil. One of the major factors controlling the direction and rate of those processes is pH. It is also a crucial element when considering soil fertility [30]. Since pH affects nutrient availability, water uptake, biological activity and solubility of aluminum and iron ions, soil acidification is a significant indirect yield reducing factor [31].

Throughout the experiment, pH of the light soil was within the range from 5.93 to 5.27 (Figure 1a), which corresponded to slightly acid and acid reaction. The pH of the heavy soil was between 5.97 and 5.79 (Figure 1b), in other words, a slightly acid reaction. During incubation, the pH of the light soil significantly decreased and mostly no significant changes of the pH of the heavy soil were stated (data not shown in the figure). Moreover, the higher the dose of sulfur introduced into the soils, the lower the determined pH of those soils. Similar results were presented by Yang et al. [32], Rahman et al. [33], Skwierawska et al. [34] and Karimizarchi et al. [35]. Matos Castañon et al. [36] concluded that soil pH was decreased linearly with increasing elemental sulfur doses.

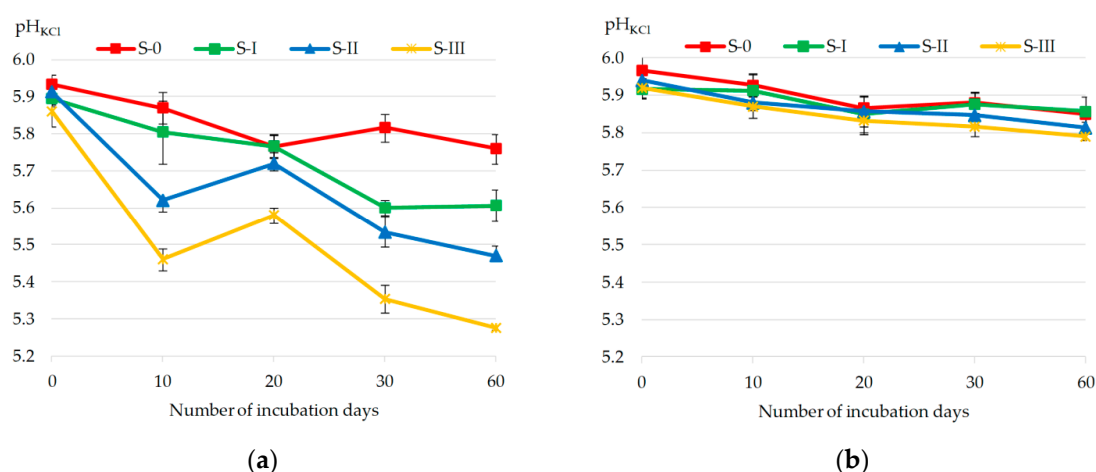


Figure 1. pH_{KCl} value of soils throughout the experiment: (a) light soil; (b) heavy soil. S-0: control soil (with no sulfur addition); S-I: soil with the addition of sulfur pulp at dose I; S-II: soil with the addition of sulfur pulp at dose II; S-III: soil with the addition of sulfur pulp at dose III. Error bars represent standard deviation.

The optimal value of pH for the growth and development of many crops ranges from 6 to 7 [37]. It is assessed that acidic soils (characterized by topsoil pH < 5.5) cover nearly 30% and 50% of the world's total land and arable land area, respectively. Over 67% of acidic sites are not suitable for crop production [31,38]. Generally, soils are strongly buffered and show a high ability to resist abrupt pH changes. Natural acidification process is slow and may take from 100 to 1000 years. However, human activities, including farming practices, accelerate soil acidification [39]. It is well known that using conventional nitrogen and sulfur fertilizers causes formation of strong inorganic acids, and as a result lowers soil pH [37,40]. Application of elemental sulfur may also decrease soil pH. Sulfur transformation by S-oxidizing microorganisms (mainly chemolithotrophic *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans*) results in production of acidifying ions, H^+ and SO_4^{2-} , and in $CaCO_3$ solubilization [32]. Microbiological oxidation of 500 mg kg^{-1} elemental sulfur leads to formation of $31 \text{ mmol } (H^+) \text{ kg}^{-1}$ soil. Formed hydrogen ions would not reduce pH in soil rich in free carbonates, since 0.16% $CaCO_3$ is sufficient for neutralizing the acid charge. On the other hand, in non-calcareous soil with low buffering capacity, a significant pH decrease after elemental sulfur application may be observed [41]. In the conducted research, acidification of the light soil was much stronger than that of the heavy soil, despite higher sulfur doses introduced to the heavy soil than to the light soil. Those differences result from differences in buffer capacity. Over the pH range 4.0–6.5, there is a connection between soil pH buffering capacity and organic matter content and clay content [42]. The higher the soil pH buffering capacity, the slower the pH change [43]. A low percentage of clay and organic matter in sandy soil results in, among other things, its lower buffering capacity and ability to retain nutrients and water. Clay material has higher capacity to bind ions than sandy soil [44,45].

Introduction of S-containing fertilizers or materials to acidic soil may escalate the problem of its acidification. Therefore, sulfur application could be more effective in combination with liming or other agricultural measures [20,31]. In soils with high pH, fertilization with elemental sulfur may alleviate micronutrient shortages [32].

3.2. Availability of Selected Elements in Soils

The content of available forms of the examined elements in both soils is provided in Tables 4–7. Generally, the introduced waste elemental sulfur had no significant impact on the content of available forms of macroelements in both tested soils, regardless of sulfur dose. Significant changes in the content of available forms of heavy metals as a result of sulfur application were observed only for some of the examined heavy metals and used reagents. However, no clear positive relation between waste sulfur dose and heavy metal availability was observed.

Table 4. Content of available forms of selected macroelements in light soil 60 days after sulfur introduction (mg kg^{-1} d.m. $\pm$ SD).

Extractant	Treatment	P	K	Ca	Mg
0.01 mol L ⁻¹ CaCl ₂	S-0 ¹	0.98 a ² $\pm$ 0.06	3.10 a $\pm$ 0.77		44.4 b $\pm$ 5.9
	S-I	1.06 a $\pm$ 0.05	3.68 a $\pm$ 0.99		44.1 b $\pm$ 4.4
	S-II	1.19 a $\pm$ 0.06	4.77 a $\pm$ 0.78		40.9 b $\pm$ 3.4
	S-III	1.22 a $\pm$ 0.08	4.22 a $\pm$ 0.57		42.1 b $\pm$ 1.8
Mehlich 3	S-0	116 b $\pm$ 6	14.6 b $\pm$ 1.2	490 a $\pm$ 71	23.2 a $\pm$ 0.7
	S-I	123 bc $\pm$ 12	17.0 b $\pm$ 0.4	470 a $\pm$ 49	26.1 a $\pm$ 1.9
	S-II	132 bc $\pm$ 7	16.4 b $\pm$ 1.6	515 ab $\pm$ 68	27.2 a $\pm$ 1.2
	S-III	127 bc $\pm$ 4	18.0 b $\pm$ 0.5	445 a $\pm$ 2	26.2 a $\pm$ 2.2
1 mol L ⁻¹ HCl	S-0	128 bc $\pm$ 6	58.7 c $\pm$ 3.9	637 bc $\pm$ 61	62.3 c $\pm$ 3.3
	S-I	126 bc $\pm$ 13	57.1 c $\pm$ 1.6	633 bc $\pm$ 27	75.8 d $\pm$ 1.3
	S-II	138 c $\pm$ 3	59.4 c $\pm$ 2.5	695 c $\pm$ 39	78.8 d $\pm$ 6.4
	S-III	125 bc $\pm$ 4	54.7 c $\pm$ 0.1	662 c $\pm$ 33	83.5 d $\pm$ 4.9

SD-standard deviation. ¹ S-0: control soil (with no sulfur addition); S-I: soil with the addition of sulfur pulp at dose I; S-II: soil with the addition of sulfur pulp at dose II; S-III: soil with the addition of sulfur pulp at dose III. ² for a given element, mean values marked with the same letters do not differ statistically significantly at the significance level $\alpha \leq 0.05$; according to Tukey test.

Table 5. Content of available forms of selected heavy metals in light soil 60 days after sulfur introduction (mg kg⁻¹ d.m. ± SD).

Extractant	Treatment	Fe	Mn	Zn	Cu
0.01 mol L ⁻¹ CaCl ₂	S-0 ¹	traces	0.629 a ² ± 0.039	traces	traces
	S-I	traces	0.928 a ± 0.057	traces	traces
	S-II	traces	1.013 a ± 0.097	traces	traces
	S-III	traces	1.235 a ± 0.119	traces	traces
Mehlich 3	S-0	219 a ± 15	29.7 b ± 1.7	1.59 b ± 0.23	0.680 d ± 0.102
	S-I	231 a ± 9	31.0 bc ± 2.0	1.35 ab ± 0.20	0.522 bc ± 0.069
	S-II	243 a ± 11	32.8 bcd ± 1.5	1.22 a ± 0.07	0.609 cd ± 0.047
	S-III	240 a ± 3	31.9 bcd ± 0.4	1.21 a ± 0.12	0.646 cd ± 0.074
1 mol L ⁻¹ HCl	S-0	333 b ± 11	35.6 de ± 1.8	2.16 d ± 0.06	0.412 ab ± 0.022
	S-I	326 b ± 24	34.6 cde ± 2.3	1.90 cd ± 0.02	0.518 bc ± 0.018
	S-II	355 b ± 25	37.0 e ± 1.0	1.63 bc ± 0.05	0.389 ab ± 0.015
	S-III	316 b ± 20	32.8 bcd ± 1.4	1.63 bc ± 0.01	0.348 a ± 0.011
		Cr	Ni	Pb	Cd
0.01 mol L ⁻¹ CaCl ₂	S-0	traces	traces	traces	traces
	S-I	traces	traces	traces	traces
	S-II	traces	traces	traces	traces
	S-III	traces	traces	traces	traces
Mehlich 3	S-0	0.218 a ± 0.011	0.277 b ± 0.009	1.96 a ± 0.07	traces
	S-I	0.217 a ± 0.003	0.265 b ± 0.017	1.85 a ± 0.10	traces
	S-II	0.227 ab ± 0.013	0.258 b ± 0.014	1.85 a ± 0.13	traces
	S-III	0.222 a ± 0.015	0.271 b ± 0.028	1.79 a ± 0.04	traces
1 mol L ⁻¹ HCl	S-0	0.280 c ± 0.011	0.169 a ± 0.009	2.46 b ± 0.05	0.046 c ± 0.002
	S-I	0.274 c ± 0.016	0.174 a ± 0.006	2.30 b ± 0.14	0.041 b ± 0.002
	S-II	0.329 d ± 0.027	0.203 a ± 0.034	2.31 b ± 0.11	0.042 bc ± 0.002
	S-III	0.269 bc ± 0.018	0.163 a ± 0.008	2.01 a ± 0.05	0.036 a ± 0.001

SD-standard deviation. ¹ S-0: control soil (with no sulfur addition); S-I: soil with the addition of sulfur pulp at dose I; S-II: soil with the addition of sulfur pulp at dose II; S-III: soil with the addition of sulfur pulp at dose III. ² for a given element, mean values marked with the same letters do not differ statistically significantly at the significance level $\alpha \leq 0.05$; according to Tukey test.

Table 6. Content of available forms of selected macroelements in heavy soil 60 days after sulfur introduction (mg kg⁻¹ d.m. ± SD).

Extractant	Treatment	P	K	Ca	Mg
0.01 mol L ⁻¹ CaCl ₂	S-0 ¹	traces	15.0 a ² ± 0.6	-	106 a ± 2
	S-I	traces	17.6 a ± 0.5	-	114 a ± 6
	S-II	traces	14.8 a ± 1.7	-	112 a ± 8
	S-III	traces	15.6 a ± 0.5	-	107 a ± 6
Mehlich 3	S-0	40.8 a ± 3.4	120 b ± 8	3442 b ± 90	254 b ± 6
	S-I	40.7 a ± 0.5	135 b ± 11	3687 b ± 125	272 c ± 11
	S-II	40.3 a ± 1.8	129 b ± 4	3721 b ± 162	282 bc ± 14
	S-III	41.9 a ± 2.7	129 b ± 6	3774 b ± 144	283 bc ± 3
1 mol L ⁻¹ HCl	S-0	77.4 b ± 5.6	156 c ± 9	2856 a ± 164	435 d ± 22
	S-I	74.3 b ± 2.3	152 c ± 4	2922 a ± 44	437 d ± 4
	S-II	72.3 b ± 2.0	154 c ± 4	2856 a ± 79	444 d ± 7
	S-III	69.8 b ± 1.2	152 c ± 3	3039 a ± 211	446 d ± 9

SD-standard deviation. ¹ S-0: control soil (with no sulfur addition); S-I: soil with the addition of sulfur pulp at dose I; S-II: soil with the addition of sulfur pulp at dose II; S-III: soil with the addition of sulfur pulp at dose III. ² for a given element, mean values marked with the same letters do not differ statistically significantly at the significance level $\alpha \leq 0.05$; according to Tukey test.

Table 7. Content of available forms of selected heavy metals in heavy soil 60 days after sulfur introduction (mg kg^{−1} d.m. ± SD).

Extractant	Treatment	Fe	Mn	Zn	Cu
0.01 mol L ^{−1} CaCl ₂	S-0 ¹	traces	2.99 a ² ± 0.05	traces	traces
	S-I	traces	3.37 a ± 0.08	traces	traces
	S-II	traces	3.80 a ± 0.14	traces	traces
	S-III	traces	3.89 a ± 0.23	traces	traces
Mehlich 3	S-0	450 a ± 28	102 b ± 2	3.59 a ± 0.39	2.93 a ± 0.13
	S-I	446 a ± 6	104 b ± 1	4.43 a ± 0.55	3.17 a ± 0.05
	S-II	446 a ± 20	100 b ± 5	3.95 a ± 0.56	3.17 a ± 0.38
	S-III	447 a ± 6	102 b ± 1	4.42 a ± 0.25	3.12 a ± 0.32
1 mol L ^{−1} HCl	S-0	1356 c ± 38	135 cd ± 3	7.54 b ± 0.45	4.19 b ± 0.38
	S-I	1350 c ± 21	138 d ± 2	8.49 b ± 0.60	4.02 b ± 0.02
	S-II	1310 bc ± 70	130 cd ± 8	7.95 b ± 0.55	4.06 b ± 0.13
	S-III	1227 b ± 9	126 c ± 2	7.45 b ± 0.48	3.94 b ± 0.08
		Cr	Ni	Pb	Cd
0.01 mol L ^{−1} CaCl ₂	S-0	traces	traces	traces	traces
	S-I	traces	traces	traces	traces
	S-II	traces	traces	traces	traces
	S-III	traces	traces	traces	traces
Mehlich 3	S-0	0.542 a ± 0.034	1.41 a ± 0.02	4.62 a ± 0.39	0.103 a ± 0.002
	S-I	0.512 a ± 0.001	1.44 a ± 0.04	4.67 a ± 0.10	0.109 ab ± 0.006
	S-II	0.547 a ± 0.018	1.41 a ± 0.09	4.58 a ± 0.11	0.107 ab ± 0.005
	S-III	0.559 a ± 0.045	1.42 a ± 0.04	4.67 a ± 0.13	0.106 ab ± 0.001
1 mol L ^{−1} HCl	S-0	2.32 c ± 0.30	2.37 c ± 0.13	7.97 b ± 0.38	0.112 ab ± 0.008
	S-I	1.60 b ± 0.03	2.05 bc ± 0.09	7.78 b ± 0.16	0.118 b ± 0.006
	S-II	1.61 b ± 0.02	2.00 bc ± 0.33	7.64 b ± 0.31	0.109 ab ± 0.002
	S-III	1.85 b ± 0.09	2.02 b ± 0.13	7.42 b ± 0.07	0.107 ab ± 0.004

SD-standard deviation. ¹ S-0: control soil (with no sulfur addition); S-I: soil with the addition of sulfur pulp at dose I; S-II: soil with the addition of sulfur pulp at dose II; S-III: soil with the addition of sulfur pulp at dose III. ² for a given element, mean values marked with the same letters do not differ statistically significantly at the significance level $\alpha \leq 0.05$; according to Tukey test.

Element availability is determined by soil factors, such as pH, quality and quantity of organic matter, moisture and temperature [46]. Phosphorus is affected the most by pH, and its availability in acidic conditions may be reduced by up to 90% [31]. For phosphorus, the optimal soil pH varies from 6.5 to 7.5. Nitrogen, potassium and sulfur are less affected by hydrogen ion activity. The optimum pH value is 6–8 for nitrogen and >6 for potassium and sulfur [47]. Slightly acidic conditions favor microelement availability, and toxic heavy metal concentration increases as pH decreases [39,47]. As Blake and Goulding [48] reported, cadmium and lead bioavailability increases at pH 6–5.5 and <4.5, respectively. Mobility of zinc, nickel, manganese and copper is enhanced at pH 5.0. Furthermore, excess hydrogen ions in soil solution decrease the availability of basic cations (calcium, potassium, sodium and magnesium). Moreover, under low pH (<4.5), the toxic character of aluminum and manganese is revealed and may lead to plant root damage and yield reduction [49].

Introduction of elemental sulfur through microbial oxidation may reduce soil pH and, as a result, affect nutrient release [21,50]. Kaya et al. [51] reported that the content of plant available nitrogen, iron, copper, manganese and calcium increased and zinc and potassium concentration decreased, whereas magnesium levels did not change after elemental sulfur treatment. The authors concluded that this practice had a beneficial effect on element uptake by tested plants. Skwierawska et al. [34] indicated a varied impact of elemental sulfur on nutrient mobility in soils. Matos Castañón et al. [36], under a pot experiment, found that increasing doses of elemental sulfur did not affect the content of available phosphorus, potassium or magnesium, despite a pH decrease in the examined soil. In the conducted research, no harmful effect on element availability in the tested soils was stated 60 days after waste sulfur introduction. The observed slight effect of introduced waste sulfur on trace element availability

may result from the low impact of sulfur application on soil pH and low concentration of elements other than sulfur (occurring as impurities) in the utilized waste.

Total element content in soil is not a suitable indicator of their bioavailability [52,53]. In a soil environment, elements occur in water soluble, exchangeable, and non-exchangeable fractions [52]. Elements existing as soluble components in the soil solution and which are readily solubilized or desorbed, considered as readily available for crop uptake, constitute only a part of the total element content in the environment [54]. In environmental studies, determination of available fractions of elements is important due to possible harmful effects of elements entering the food chain.

One group of procedures used for determination of metal bioavailability includes simple one-step extractions. There are three main classes of single extractants: (i) weak salts, for example, calcium chloride (CaCl_2), magnesium chloride MgCl_2 , sodium nitrate (NaNO_3) and ammonium nitrate (NH_4NO_3); (ii) solutions of strong or weak acids, for example, hydrochloric acid HCl ; and (iii) chelating agents, for example, ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) [55]. When using weak salt solutions, metals bound to soil solid-phase exchange sites are transferred into solution. These reactants mainly dissolve the cation exchangeable fraction [54]. Therefore, the extracted metal content may be considered as available. However, in some cases, extraction with weak salts does not reflect the plant-available pool of metals [56]. Hydrochloric acid, belonging to the second class of single extraction solutions, is a strong extractant which separates elements bound to the exchangeable and carbonate fraction, with iron and manganese oxides and organic matter particles. Using acid solutions can show the results of environmental acidification. Extraction with $1 \text{ mol L}^{-1} \text{ HCl}$ does not reflect the content of elements which may be readily absorbed by plant. This solution was proposed as a standard metal contamination assessment method [57,58]. Chelating reagents like EDTA and DTPA react with extracted elements from the solid phase and form stable and soluble metal-organic complexes. These reagents are used to extract available forms of metals-exchangeable and carbonate fractions in soils [58,59]. Extraction with chelating agents may be used to predict element uptake by plants [56]. It can provide information about potential hazards from future metal mobilization [60]. Extractants used for the assessment of element bioavailability may be composed of several reagents. Mehlich 3, which contains CH_3COOH , NH_4NO_3 , NH_4F , HNO_3 and EDTA, is one example of these extractants. Mehlich 3 is a universal method of extraction of a wide range of elements from acidic soils [61]. Since Mehlich 3 is a multicomponent reactant, several extraction mechanisms can be observed. Acetic acid and ammonium fluoride release P from calcium and aluminum phosphates. Other macronutrients (K, Ca, Mg) are extracted with nitric acid and ammonium nitrate. Ammonium nitrate and EDTA dissolve and complex heavy metals [62,63].

Extraction strength of the used reagents influences the amounts of eluted elements [52,54,55,63]. At the same time, soil properties, especially the content of clay, organic carbon, oxides of iron, manganese and aluminum, as well as pH and cation exchange capacity, also influence the extraction of elements [63]. In the conducted research, two soils differing in composition and texture (Table 1) were amended with waste sulfur. The incubation experiment was carried out at $25 \pm 2 \text{ }^\circ\text{C}$. Sulfur doses amounted to 15, 30 and $45 \text{ mg kg}^{-1} \text{ d.m.}$ of the light soil and 20, 40 and $60 \text{ mg kg}^{-1} \text{ d.m.}$ of the heavy soil. After 60 days from sulfur introduction, element availability in both soils was established. When considering the reagent strength, the significantly lowest amounts of the examined elements were extracted with $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$, then with Mehlich 3, and significantly the highest amounts were extracted with $1 \text{ mol L}^{-1} \text{ HCl}$ (Tables 4–7). Only some minor exceptions were observed: from the light soil, higher amounts of Mg were extracted with CaCl_2 than with Mehlich 3 and higher amounts of Cu and Ni were extracted with Mehlich 3 than with HCl . A larger amount of Ca was extracted with Mehlich 3 than with HCl from the heavy soil.

4. Conclusions

The use of waste elemental sulfur increased acidification of the light soil. The acidifying effect of sulfur was stronger when sulfur dose was higher. The impact of sulfur on acidification of the heavy soil was small.

The content of available forms of macroelements and trace elements in soils depended mainly on the strength of the used extractants. Generally, the reactants used extracted elements in the following descending order: 1 mol L⁻¹ HCl > Mehlich 3 > 0.01 mol L⁻¹ CaCl₂.

The waste elemental sulfur, introduced in doses based on sulfur content in that waste and on soil properties and plant needs, did not affect the content of available forms of macroelements in both tested soils significantly, regardless of sulfur dose. Moreover, no clear positive relation between waste sulfur dose and heavy metal availability was stated.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2227-9717/8/10/1245/s1>, Table S1: Wavelengths and quantification limits for the ICP-OES method.

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