

Article

The Use of Carbonate-Clay Flour, Sewage Sludge and Waste Sulfate Sulfur as Fertilizer Agents

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Abstract

Macro- and microelements in waste can be returned to the soil as fertilizers and their sustainable use can reduce the need to extract natural resources. For example, the use of carbonate-clay flour, sewage sludge and waste sulfate sulfur to improve soil properties enables the natural recycling of the nutrients contained in these materials. Soil physico-chemical properties with the application of waste and the bioavailability of nutrients and trace elements were assessed before and after a 3-month incubation period. This study showed that when carbonate-clay flour was applied alone or together with sewage sludge and waste sulfur, it improved the properties of the soil, inducing a reduction in acidification and an increase in the content of available P, K and Mg. Sewage sludge also provided Zn, Cu, Ni and Cr in addition to organic carbon. Sulfate did not cause soil acidification. The results indicate that the use of carbonate-clay flour alone, as well as with the addition of sewage sludge and sulfate sulfur, can be recommended for the deacidification of soil and serve as a remediation tool for, for example, the precipitation of chemical pollutants. The valorization of the waste used fits into the circular economy approach.

Keywords: waste; recycling; sustainable resource management; fertilizer; bioavailability of elements



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1. Introduction

Most soils in Europe range between pH 4.0 (very acid) and pH 8.5 (very alkaline). northern Europe tends to have lower pH values due to its acidic soils, while southern Europe has higher pH values, often influenced by carbonate-rich soils. Very low pH values (pH < 3) were observed in Bavaria (Germany), in the sandy soils of the “Landes” department in France, and in Belgium, Spain, Portugal and the UK. Higher pH measurements (pH = 9) were observed in soils in Puglia (Italy) and high pH values (pH > 8) were also observed in Bulgaria. In Ukraine, approximately 24% of the soils are acidic. Acidic soils are predominantly found in the Polissya zone, while alkaline soils (18.4%) are more prevalent in the steppe zone. Neutral soils occur in Spain, France, Germany and the countries of the Mediterranean basin [1].

The acceptable pH range for productive agricultural land is about 5.5 to 7.5, with a pH of 6.0 to 6.5 preferred by most crops. The authors of the report “The State of Soils in Europe” indicate that soils with a relatively low pH (below 5.5) constitute 10% of agricultural land

in Europe. Studies of topsoil samples taken from across Europe indicate that their pH value both increases and decreases [1]. For example, in the United Kingdom, reduced sulfate deposition has facilitated the recovery of topsoil from acidification. Monitoring schemes have reported an increase in soil pH across all UK habitats, with national-level data showing a mean increase in pH from 5.4 to 5.9. In Switzerland, soil acidification remains a significant concern in forests in terms of both the extent and ongoing progression [1].

Soil acidification in Poland is one of the most important factors limiting agricultural and horticultural production, adversely affecting the food security of the country. Soil pH depends on both climatic and soil conditions as well as on anthropogenic pressure [2,3]. Over 90% of Poland's land area contains soils made from acidic sedimentary rocks, and the progressing acidification of this land is the result of alkaline cation leaching, which is a process stimulated by precipitation, especially at low temperatures that prevail in the temperate climate of the autumn and winter periods [4]. Microbiological processes taking place in the soil are also important in increasing soil acidification [4,5].

According to research, 35% of Polish soils have an acidic or very acidic pH (below 5.5), 37% of soils have a slightly acidic pH (5.6–6.5), and 28% soils have a neutral or alkaline pH (>6.5) [6].

Therefore, there is a need to improve the acidification of soils because the pH value has a fundamental impact on the bioavailability of nutrients and the presence of potentially toxic trace metals; thus, it is of great importance in the remediation of soils contaminated by anthropogenic sources [7]. Furthermore, numerous studies suggest that under low-soil-pH conditions, free trace element ions can be toxic to plant root systems, resulting in physiological changes. Trace element toxicity leads to the disintegration of cell membranes and the intensive uptake of metal cations and reactive oxygen species [8]. A previous study on soil management using carbonate-clay flour from a deposit in Raciszyn confirms that this material is suitable for soil deacidification. On average, flour contains 93% CaCO_3 , as well as clay minerals such as kaolinite and kainite, both of which play an important role in determining soil fertility [9,10].

As regards soils with low organic carbon contents, enrichment with carbonate-clay flour in organic matter may contribute to an improvement in their physicochemical properties. Adding organic matter increases soil sorption capacity, water retention and nutrient retention in the rhizosphere, as well as improving soil microbial activity and structure [11]. The management of various waste materials that are rich in organic carbon represents an important way to sequester carbon in soil and reduce the concentration of CO_2 in the air, thus mitigating the greenhouse effect [12,13].

Given the above, it is justified to increase the content of organic matter in soil via the addition of humus-forming materials. The sources of organic matter may include, among others, municipal sewage sludge, digestates from biogas production, waste from the agri-food industry and biochar produced from various biological materials. Using organic fertilizers made from the aforementioned materials increases the stability of aggregates and the amount of humic and fulvic substances in soil, thus increasing humification and the biodegradability of organic matter [11].

The addition of sulfate sulfur from waste calcium sulfate may increase the content of available sulfur, the deficit of which in Polish soils is deepening due to reduced SO_2 emissions into the atmosphere, the reduction in the use of phosphorus fertilizers containing this element and the lower consumption of natural fertilizers [14]. In the period from 2000 to 2019, the emissions of sulfur dioxide in Poland decreased by 68%, while the proportion of soils with naturally low sulfur content increased to over 95% [6,15].

Combining these three types of waste produces a new fertilizer containing the nutrients needed by plants. Moreover, the use of waste organic matter (municipal sewage sludge)

and waste sulfate sulfur (calcium sulfate) fits into the concept of the circular economy (CE), which is one of the priorities in the modern world [16].

The aim of this study was to develop formulas and produce innovative test products based on carbonate-clay flour from the Raciszyn deposit, with the addition of organic matter (municipal sewage sludge), sulfate sulfur or organic matter combined with sulfate sulfur. In the incubation experiment, the basic physicochemical properties of the soil were assessed on the day of the introduction of waste materials and after the 3-month incubation period. This study assessed the bioavailability of nutrients and trace elements, including those that are potentially toxic to plants and that can be released from waste materials applied to arable soil. The implementation of the study objectives allowed us to choose the optimal fertilizer products that were the most environmentally safe.

2. Materials and Methods

2.1. Characteristics of the Materials Used in the Incubation Experiment

The soil used in the experiment was taken from an arable layer (0–20 cm), with a texture of loam, belonging to medium soils [17]. We used the proposed fertilizer formulations based on carbonate-clay flour from the Raciszyn deposit on the tested soil.

Carbonate-clay flour came from the processing of carbonate-clay minerals from a deposit in Raciszyn, in the area of the WKG Raciszyn mine. This flour contains large amounts of calcium carbonate, reaching nearly 50% per CaO, which can be used in agriculture, reclamation, and remediation as a liming and stabilizing agent for contaminants [7,10]. Analysis of the content of the following macroelements (Ca, Mg, K, S, P and Na) showed that the carbonate-clay flour contained the most calcium (351.6 g Ca per kg of dry matter in the flour). In terms of calcium oxide, the content was 49.2% CaO, and in terms of calcium carbonate, the content was 87.9% CaCO₃ [10].

The municipal sewage sludge used in the incubation experiment came from a mechanical–biological sewage treatment plant in the municipality of Działoszyń; it is hereinafter referred to as sewage sludge, with the adopted symbol ‘MSS’. The sewage sludge was organic waste (other than hazardous waste), with the catalog number 19 08 05—sludges from the treatment of urban wastewater [18]. Before use, it was stabilized through a process of aerobic stabilization (aeration). The pH of the municipal sewage sludge was alkaline, with a pH_{H2O} value of 9.8, indicating that the municipal sewage sludge was hygienized with lime.

In the incubation experiment, sulfate sulfur from the flue gas treatment plant at the Guardian Czeszowska Sp. z o.o. glassworks was used. The sulfur was a form of solid waste, with the catalog number 10 11 16 (10—waste from thermal processes; 11—glassworks waste; 16—solid waste from flue gas treatment other than those mentioned in 10 11 15) [18].

2.2. Scheme and Conditions for Conducting the Incubation Experiment

The laboratory incubation experiment included 14 combinations each in triplicate, according to the scheme shown in Table 1.

The results of the soil analysis before setting up the experiment are provided in Tables 2–10 in combination 1 in column BI.

The amount of waste used was determined based on the crops’ nutritional requirements. The carbonate-clay flour dose was calculated based on soil extractable acidity, as determined by the Kappen method, and was set at 3 g per container. The soil with the addition of carbonate-clay flour, sewage sludge, sulfate sulfur and these materials together was thoroughly mixed before being placed in polyethylene containers. In each combination, 700 g of dry matter of the tested materials was prepared, of which 500 g was placed in polyethylene containers holding 500 g of soil (air dry matter), while the rest was intended

for analysis immediately after mixing the components. At the time of incubation, the moisture content of the soil and the resulting substrates was initially maintained at 50% MWC, and, after a week at 40% MWC, the losses were systematically replenished with distilled water until a constant weight was reached. The incubation was carried out at room temperature, in the range of 20 ± 2 °C, in the dark, for 3 months. The incubation period was deemed long enough to evaluate changes in the soil's physicochemical properties. After the experiment, laboratory analyses were performed on the incubated material and, on that basis, physicochemical changes and the bioavailability of the components were assessed in terms of their natural use.

Table 1. Incubation experiment design.

No.	Combination	Symbol
1	Soil–Control	C
2	Soil + flour according to extractable acidity 2.0 EA	M
3	Soil + 5% sewage sludge	5%MSS
4	Soil + 10% sewage sludge	10%MSS
5	Soil + 0.2% sulfate sulfur	0.2%S
6	Soil + 0.4% sulfate sulfur	0.4%S
7	Soil + flour + 5% sewage sludge	M5%MSS
8	Soil + flour + 10% sewage sludge	M10%MSS
9	Flour + 0.2% sulfate sulfur	M0.2%S
10	Flour + 0.4% sulfate sulfur	M0.4%S
11	Soil + flour + 5% sewage sludge + 0.2 sulfate sulfur	M5MSS0.2%S
12	Soil + flour + 5% sewage sludge + 0.4 sulfate sulfur	M5MSS0.4%S
13	Soil + flour + 10% sewage sludge + 0.2 sulfate sulfur	M10MSS0.2%S
14	Soil + flour + 10% sewage sludge + 0.4 sulfate sulfur	M10MSS0.4%S

2.3. Methodology of Chemical Analyses

In the collected soil samples and obtained substrates, before and after incubation, basic determinations of physicochemical properties were carried out using generally accepted methods used in accredited laboratories: dry mass was determined by the weight method [19], soil pH in H₂O and 1 mol·dm^{−3} KCl (soil: solution = 1:2.5) were determined potentiometrically [20], extractable acidity (EA) was determined by the Kappen method, electrical conductivity (EC) was determined with a conductometer [21], and organic carbon was determined by the Tiurin method [22]. The content of available forms of macroelements and trace elements, including those potentially toxic to plants, was determined by the Mehlich 3 method [23].

The content of elements in the obtained soil filtrates was determined using the ICP-OES Optima 7300 DV atomic emission spectrometer by PerkinElmer (Tempe, AZ, USA) [24]. Chemical analyses used spectrally pure reagents and Aldrich standard solutions.

2.4. Quality Control of Analyses

The determinations in each of the analyzed samples were performed in triplicate. The accuracy of the analytical methods was verified based on certified reference materials and standard solutions: CRM IAEA/V—10 Hay (International Atomic Energy Agency, Vienna, Austria), CRM—CD281—Rey Grass (Institute for Reference Materials and Measurements, Geel, Belgium), CRM023-050—Trace Metals—Sandy Loam 7 (RT Corporation, Tokyo, Japan).

2.5. Statistical Analysis

Statistical analysis of the study results was conducted using a Microsoft Office Excel 2013 spreadsheet and Statistica package version 13 PL. The data followed the normal distri-

bution according to the Kolmogorov–Smirnov normality test. The statistical evaluation of particular sources of result variability was carried out using two-factor analysis of variance. The significance of differences between mean values was verified using the t-Tukey test at a significance level of $p \leq 0.01$. For selected (parameters) ratios, the value of Pearson’s linear correlation coefficient (r) was computed at a significance level of $p \leq 0.01$. Hierarchical clustering was performed for waste combinations for two data sets: before incubation and after incubation. Ward’s minimum variance method with Euclidean distance was used. Analyses were performed with the statistical software package R [25].

3. Results and Discussion

3.1. Soil pH

The pH of the soil used in the incubation experiment indicated that the soil was very acidic ($\text{pH}_{\text{KCl}} = 4.2$), which indicated the need for the proposed fertilizing formulations based on carbonate-clay flour (Tables 1 and 2). When used alone, at a dose calculated according to an extractable acidity of 2.0 EA, carbonate-clay flour increased soil pH_{KCl} to 6.3, which indicated that liming with this material was effective (Table 2). The pH of the soil used, after applying the flour, was optimal for most plants, in the range of 6.0–7.5 [26]. Successively, the use of only carbonate-clay flour, sewage sludge hygienized with lime, calcium sulfate and their mixtures in the soil had an effect on the alkalization of the soil environment, which resulted primarily from the action of the lime supplied in these materials. Therefore, it was important to dose calcium-containing materials correctly to prevent the soil from becoming too alkaline [26].

Table 2. Soil pH before and after incubation.

No.	Combination *	pH KCl			pH H ₂ O		
		BI **	AI	Mean	BI	AI	Mean
1	C	4.2	4.0	4.1	5.9	5.2	5.6
2	M	6.3	7.1	6.7	6.5	7.6	7.1
3	5%MSS	10.0	7.6	8.8	9.8	7.9	8.8
4	10%MSS	11.3	7.9	9.6	11.5	8.2	9.9
5	0.2%S	7.3	7.1	7.2	7.1	7.1	7.1
6	0.4%S	8.4	7.3	7.8	7.8	7.7	7.8
7	M5%MSS	9.9	7.5	8.7	10.1	7.9	9.0
8	M10%MSS	10.9	7.7	9.3	11.6	8.5	10.0
9	M0.2%S	6.5	7.2	6.9	7.2	7.6	7.4
10	M0.4%S	7.7	7.4	7.6	7.9	7.7	7.8
11	M5MSS0.2%S	10.2	7.6	8.9	10.2	7.8	9.0
12	M5MSS0.4%S	10.1	7.5	8.8	10.5	7.9	9.2
13	M10MSS0.2%S	11.7	7.9	9.8	11.6	8.1	9.9
14	M10MSS0.4%S	11.2	7.3	9.2	11.3	8.3	9.8
	Mean for date	9.0	7.2	8.1	9.2	7.7	8.4
NIR $_{\alpha \leq 0.01}$ for date			0.1			0.1	
NIR $_{\alpha \leq 0.01}$ for combination			0.3			0.2	
NIR $_{\alpha \leq 0.01}$ for interaction			0.5			0.3	

* Combination symbols are explained in Table 1. ** BI—before incubation; AI—after 3 months of incubation.

Formulations in which larger amounts of sewage sludge were used alkalized the soil to as high as $\text{pH} \approx 11$. Such a strong alkalization of soil is not advisable because most agricultural plants develop well and provide a good yield with a soil pH ranging from weakly acidic to neutral. In addition, most nutrients are readily available to plants with a soil pH ranging from weakly acidic to neutral [27].

After the three-month incubation period, it was established that the soil to which only carbonate-clay flour had been introduced (combination 2) had a higher pH value measured in potassium chloride compared to the value determined on the day of setting up the experiment, which pointed to a release of calcium ions responsible for alkalization and the high chemical reactivity of this material [10]. The addition of sulfate sulfur to the flour (combination 9) had a positive effect on the soil pH value. Calcium sulfate does not deacidify soil, but provides, apart from sulfur, large amounts of calcium. Therefore, even after applying large doses of calcium sulfate, there is no change in pH, but the harmful effects of mobile aluminum in the soil are neutralized [28,29]. The appearance of mobile (exchangeable) aluminum in the soil is the result of the disintegration of clay minerals as a result of excessive soil acidification [29]. In addition, under conditions of strong soil acidity, the concentration of free aluminum ions increases. These ions are toxic to plants [30]. In other fertilizer treatments, the incubation period reduced the pH value of these materials compared to the value determined on the day of setting up the experiment. This may have been a result of the exchange of calcium cations from the used materials, occurring between the soil solution and the sorption complex, and a release of hydrogen cations in their place into the solution [31]. The decrease in the pH value in these fertilizing formulations may also have resulted from the release of calcium ions and the transition into insoluble forms that did not enter into chemical reactions [31]. Similar relationships between fertilizer combinations (components) were found after the pH value in distilled water was determined. When the pH of the control soil (object 1) was measured in distilled water after three months of incubation, a decrease in this parameter was registered. This decrease may have been due to the increased activity of microorganisms under conditions of adequate soil moisture.

3.2. Soil Salinity

The value of electrolytic conductivity (EC) of soil is an indicator of the amount of solutes in a soil solution and is the basis for inferring soil salinity [21]. In the control soil, without waste additives, an increase in salinity was recorded. This was most likely due to the optimal moisture content and room temperature conditions promoting greater microbial activity [32].

The application of sewage sludge to the soil, which could contain significant amounts of soluble salts (including salts containing sodium, phosphates and sulfate sulfur), resulted in a large increase in the value of electrolytic conductivity (Table 3).

Table 3. Salinity and organic carbon content in soil before and after incubation.

No.	Combination *	EC (mS·cm ^{−1})			C-org (g·kg ^{−1})		
		BI **	AI	Mean	BI	AI	Mean
1	C	0.2	0.6	0.4	8.5	8.0	8.2
2	M	0.7	1.4	1.0	8.8	8.2	8.5
3	5%MSS	2.5	3.2	2.8	12.0	10.0	11.0
4	10%MSS	2.5	3.5	3.0	16.4	12.3	14.4
5	0.2%S	2.7	3.5	3.1	8.8	7.9	8.3
6	0.4%S	3.5	4.4	4.0	8.9	7.7	8.3
7	M5%MSS	1.4	3.2	2.3	13.3	9.2	11.3
8	M10%MSS	2.3	4.1	3.2	18.9	10.9	14.9
9	M0.2%S	3.1	3.3	3.2	8.5	7.8	8.1
10	M0.4%S	3.4	4.2	3.8	10.4	7.8	9.1
11	M5MSS0.2%S	3.0	5.2	4.1	13.6	9.7	11.6
12	M5MSS0.4%S	3.6	5.3	4.5	14.1	10.1	12.1
13	M10MSS0.2%S	3.9	4.7	4.3	17.6	10.2	13.9

Table 3. Cont.

No.	Combination *	EC (mS·cm ^{−1})			C-org (g·kg ^{−1})		
		BI **	AI	Mean	BI	AI	Mean
14	M10MSS0.4%S	4.0	4.8	4.4	19.2	11.7	15.4
	Mean for date	2.6	3.7	3.2	12.8	9.4	11.1
	NIR _{α≤0.01} for date		0.05			0.2	
	NIR _{α≤0.01} for combination		0.13			0.5	
	NIR _{α≤0.01} for interaction		0.18			0.8	

* Combination symbols are explained in Table 1. ** BI—before incubation; AI—after 3 months of incubation.

After incubation, the largest values were recorded in the soil receiving treatments with flour, sewage sludge and sulfate sulfur (combinations 11–14). Our own study indicates that the additives applied to the soil were highly saline and increased the value of this parameter in the soil. The greater electrical conductivity of the substrates was mainly due to the presence of sulfate ions from the waste used [33]. A study by [34] showed significantly lower electrolytic conductivity values, ranging from 0.129 to 0.245 mS·cm^{−1} in soil with the addition of sewage sludge and sulfur, regardless of the liming used. The introduction of various substances containing readily soluble inorganic compounds subject to dissociation in soil may cause an increase in the concentration of the soil solution to values that may interfere with plant development due to the inability to absorb water and nutrients [21].

When assessing the value of electrolytic conductivity of the tested substrates, it was established that the salt content in these materials was much higher compared to soils on arable land [35]. When the electrolytic conductivity of the soil reached a value of 4 mS·cm^{−1}, this was indicative of salinity in the soil [36]. A value exceeding 4 mS·cm^{−1} was recorded in the presented study, especially in treatments with the addition of sewage sludge and sulfate sulfur. According to the salinity-based categories of soil degradation, plants do not react to salinity if the EC value in the soil does not exceed 2 mS/cm³. If the EC value ranges from 2 to 4 mS/cm³, the soil is poorly degraded and some plants, especially those sensitive to salinity, will respond. If the EC value ranges from 4 to 8 mS/cm³, the soil is moderately degraded and most crops will respond. An EC value above 8 mS/cm³ indicates severe degradation, which only some species, including halophytes, can tolerate [37].

3.3. Organic Carbon in Soil

The content of organic carbon in the soil used in the experiment was at a low level compared to the average values for light soils of Central Poland [38,39]. Immediately after the application of the carbonate-clay flour, there was a slight increase in the carbon content in the soil, while sewage sludge rich in organic matter increased its content by 0.4 to over 1.2 times compared to the control (Table 3). This was a consequence of the organic substances contained in it, as some of them were mineralized and some of them were humidified after introduction to the soil [38]. After the application of doses of sulfate sulfur, the level of organic carbon changed to some extent and was close to the content in the soil of the control plot (combinations 4–5). In contrast, the combined use of sewage sludge, carbonate-clay flour and sulfate sulfur significantly increased the organic carbon content in the soil (combinations 11–14).

After 3 months of incubation, the organic carbon content decreased in all soils receiving treatments in the experiment, and the largest loss was recorded in the soils receiving treatments with the highest dose of sewage sludge. The loss of organic carbon in the soil can be explained by the intensive mineralization of organic matter in the sewage sludge

applied to the soil [40]. Additionally, the loss of organic matter in the soil may have resulted from the leaching of dissolved organic matter [11].

In the control soil, where no waste materials were added, the loss of organic matter was less intense. However, maintaining optimal moisture and room temperature conditions promoted the faster mineralization of organic matter [11,32].

Studies by other authors confirm that various additives, as well as land use, can affect the stability of the carbon pool and sequestration capacity by increasing the amount of organic carbon bound to soil minerals [41]. Therefore, it is significant that some of the organic carbon in the soil was highly stable and did not mineralize.

3.4. Content of Available Forms of Macroelements in Soil (P, Ca, Mg, K, Na and S)

The content of nutrients determined by the Mehlich 3 method is considered mobile and potentially available to plants. This method was used for this study because it enabled the simultaneous extraction of many nutrients and toxic substances with a single solution while maintaining uniform extraction conditions [42]. The Mehlich 3 method is widely used to determine the nutrient content of most mineral soils in many European countries.

The source of available forms of P, Ca, Mg and K in the soil was primarily sewage sludge, while the source of S and Na was waste sulfate sulfur (Tables 4–6).

Table 4. Content of available P and Ca in soil before and after incubation.

No.	Combination *	P (mg·kg ^{−1})			Ca (g·kg ^{−1})		
		BI **	AI	Mean	BI	AI	Mean
1	C	153.8	96.5	125.1	1.2	0.9	1.1
2	M	140.7	120.7	130.7	13.6	8.2	10.9
3	5%MSS	364.7	288.2	326.5	14.7	10.2	12.4
4	10%MSS	471.4	452.2	461.8	25.7	18.1	21.9
5	0.2%S	149.2	132.1	140.7	10.5	8.4	9.5
6	0.4%S	130.3	123.5	126.9	15.7	11.9	13.8
7	M5%MSS	287.4	312.8	300.1	13.6	12.3	13.0
8	M10%MSS	418.7	523.8	471.3	19.2	18.2	18.7
9	M0.2%S	125.2	121.7	123.5	11.0	10.1	10.5
10	M0.4%S	114.9	108.5	111.7	12.9	12.4	12.6
11	M5MSS0.2%S	197.6	257.6	227.6	15.8	11.4	13.6
12	M5MSS0.4%S	186.5	257.8	222.2	17.0	12.3	14.7
13	M10MSS0.2%S	233.1	323.5	278.3	16.6	13.4	15.0
14	M10MSS0.4%S	232.9	318.4	275.7	17.5	14.2	15.9
	Mean for date	229.0	245.5	237.3	14.6	11.6	13.1
	NIR _{α≤0.01} for date		3.5			0.2	
	NIR _{α≤0.01} for combination		9.3			0.7	
	NIR _{α≤0.01} for interaction		13.1			0.9	

* Combination symbols are explained in Table 1. ** BI—before incubation; AI—after 3 months of incubation.

Table 5. Content of available Mg and K in soil before and after incubation.

No.	Combination *	Mg (mg·kg ^{−1})			K (mg·kg ^{−1})		
		BI **	AI	Mean	BI	AI	Mean
1	C	90.8	54.5	72.6	136.1	108.4	122.2
2	M	130.6	55.5	93.0	156.0	128.8	142.4
3	5%MSS	182.8	96.9	139.8	200.8	170.1	185.4
4	10%MSS	309.5	154.0	231.7	257.1	224.5	240.8
5	0.2%S	106.6	47.3	77.0	160.5	139.6	150.0
6	0.4%S	122.8	53.0	87.9	173.3	145.4	159.4
7	M5%MSS	160.0	102.2	131.1	168.0	154.4	161.2

Table 5. Cont.

No.	Combination *	Mg (mg·kg ^{−1})			K (mg·kg ^{−1})		
		BI **	AI	Mean	BI	AI	Mean
8	M10%MSS	222.9	175.0	199.0	175.3	168.3	171.8
9	M0.2%S	94.3	56.1	75.2	165.3	134.5	149.9
10	M0.4%S	105.5	64.8	85.1	176.3	158.7	167.5
11	M5MSS0.2%S	121.2	105.1	113.2	187.3	154.5	170.9
12	M5MSS0.4%S	137.2	118.2	127.7	188.6	176.2	182.4
13	M10MSS0.2%S	156.3	130.2	143.2	231.9	209.6	220.8
14	M10MSS0.4%S	169.8	151.3	160.5	241.8	224.9	233.3
	Mean for date	150.7	97.4	124.1	187.0	164.1	175.6
	NIR _{α≤0.01} for date		3.5			2.8	
	NIR _{α≤0.01} for combination		9.3			7.4	
	NIR _{α≤0.01} for interaction		13.1			10.4	

* Combination symbols are explained in Table 1. ** BI—before incubation; AI—after 3 months of incubation.

Table 6. Content of available Na and S in soil before and after incubation.

No.	Combination *	Na (mg·kg ^{−1})			S (mg·kg ^{−1})		
		BI **	AI	Mean	BI	AI	Mean
1	C	91.6	82.5	87.0	25.2	24.0	24.6
2	M	72.8	97.3	85.1	27.5	35.6	31.5
3	5%MSS	254.8	313.2	284.0	75.2	95.4	85.3
4	10%MSS	470.4	505.8	488.1	125.6	157.7	141.7
5	0.2%S	445.8	355.8	400.8	709.7	730.9	720.3
6	0.4%S	754.4	587.7	671.0	943.3	982.8	963.1
7	M5%MSS	524.6	277.2	400.9	89.9	112.0	101.0
8	M10%MSS	724.3	434.8	579.5	122.7	186.0	154.3
9	M0.2%S	450.8	312.7	381.8	443.5	721.5	582.5
10	M0.4%S	727.0	482.8	604.9	749.5	1141.1	945.3
11	M5MSS0.2%S	466.8	414.0	440.4	450.6	754.7	602.6
12	M5MSS0.4%S	563.7	514.3	539.0	677.3	1107.3	892.3
13	M10MSS0.2%S	638.1	524.5	581.3	545.2	742.3	643.8
14	M10MSS0.4%S	724.9	675.6	700.2	737.8	852.3	795.1
	Mean for date	493.6	398.4	446.0	408.8	546.0	477.4
	NIR _{α≤0.01} for date		3.5			4.2	
	NIR _{α≤0.01} for combination		9.3			11.2	
	NIR _{α≤0.01} for interaction		13.1			15.8	

* Combination symbols are explained in Table 1. ** BI—before incubation; AI—after 3 months of incubation.

The addition of only carbonate-clay flour and sulfate sulfur, as well as a combination of both products, and combinations including all three components, significantly increased the Ca and Mg content (except for combination 9) in the soil immediately after application. The increase in the content of available Ca in the soil confirms the suitability of using carbonate-clay flour on light, acidic, poorly buffered soils [10,31]. Among the studied macronutrients, a slight increase in the content of available K under the influence of the materials used (flour, sewage sludge, and sulfate sulfur) was found compared to the control. In the case of P, it was established that sulfate sulfur, used alone and together with flour, reduced the amount of available forms of this nutrient compared to the control. The application of only sulfate sulfur to the soil as well as in combination with carbonate-clay or flour and sewage sludge increased the available S content compared to the control. With regard to the content of sodium available for plants, only the exclusive use of carbonate-clay flour resulted in a significant reduction in this value (combination 2). For the other combinations, a significant increase in sodium content was recorded.

Incubation of the control soil resulted in a decrease in the bioavailability of P, Ca, Mg and K, which was probably due to these nutrients being permanently retained in the soil sorption complex [27].

The 3-month incubation period resulted in a reduction in the content of available Ca, Mg, K and, as a rule, Na in the soil with waste compared to the content of these elements on the day of setting up the experiment. A reduction in bioavailable forms of macronutrients can be explained by their possible precipitation into insoluble forms or permanent retention in the soil sorption complex [27,43]. In the case of S, it was established that during incubation, the content of this element in the form available to plants increased (except the control), which substantiates the possibility of using this material for enriching soils low in sulfur [14,15,34]. The process of the incubation of soil with the addition of sewage sludge and carbonate flour, as well as flour, sewage sludge and sulfate sulfur, also increased the bioavailable forms of P in the soil, which is beneficial from the point of view of the nutritional needs of plants [34,44].

The content of all the studied macroelements increased significantly after the application of the tested additives in relation to the soil of the control plot, both immediately after application and after 3 months of incubation. On the one hand, this is a positive phenomenon because these materials provide nutrients. On the other hand, given the increased electrolytic conductivity, it may prove unfavorable when using fertilizers in agricultural practice [34]. The most beneficial practice in this respect is the use of carbonate-clay flour, which, while causing a positive change in soil pH, did not cause excessive salinity in the soil or a release of excessive amounts of nutrients in a short time frame. Nutrients are released into the soil through sorption and desorption processes, which are regulated by the pH level and changes in the soil's physicochemical properties [27,44,45]. Therefore, adding the studied waste alters the pH and properties of the soil.

The optimal dose of the tested waste materials do not cause excessive salinity and can promote the leaching of nutrients and the subsequent contamination of soils and groundwater [34]. Combining alkaline carbonate–lime meal with sewage sludge probably increases nitrogen losses in the form of ammonia, which is harmful to crops and the environment [41].

The assessment of the macroelement content in soil before and after incubation, according to the limit values for the Mehlich 3 method, pointed to a high content of P and K and a very high content of Mg recognized for most crops [42].

The introduction of deficit elements—magnesium and sodium—into the soil can be considered a beneficial feature of sewage sludge. At the same time, a large load of sodium and phosphorus introduced with sewage sludge may have an adverse effect on soil and plant properties [45]. A large load of sodium may cause salinity in the soil, and a large load of phosphorus may lead to the eutrophication of the environment if fertilizer is applied to soils exposed to erosion, causing a washout of the topsoil [21,45]. This is dangerous, especially when, immediately after their application, there is a cloudburst because, then, large amounts of the solid phase of the soil may be washed away with freshly applied soluble phosphates contained within it [46]. Moreover, in soils with a content of more than 200 mg P·kg^{−1}, increases in yields of crops under the influence of phosphorus fertilization are rarely observed, and, therefore, this content was considered a good indicator for the preliminary assessment of the risk associated with excess phosphorus in the soil [42].

3.5. Content of Available Microelements in Soil (Fe, Mn, Zn, Cu, Ni, Cr)

The highest content of available Fe was recorded in the control (Table 7). The use of the prepared formulations resulted in a reduction in the content of this microelement compared to the control. The content of available Mn in the soil of the control plot and

after the use of carbonate-clay flour was at a similar level, and the greatest amount of this microelement was found in the soil receiving combinations with the addition of 0.4% sulfate sulfur (Table 7). As in the case of Fe, the combined application of carbonate-clay flour with sewage sludge and sulfate sulfur reduced the Mn content compared to the control.

The largest quantities of available Zn, Cu, Ni and Cr were observed in the soil to which municipal sewage sludge had been added, and the addition of sulfate sulfur to the soil decreased the content of these micronutrients compared to the control (Tables 8 and 9). The carbonate-clay flour, used alone and together with other additives, reduced the content of available Zn, Cu and Ni in the soil. The reduction in the content of these microelements resulted primarily from their possible precipitation into carbonate forms, which are insoluble and therefore inaccessible to plants [45].

Table 7. Content of available Fe and Mn in soil before and after incubation.

No.	Combination *	Fe (mg·kg ⁻¹)			Mn (mg·kg ⁻¹)		
		BI **	AI	Mean	BI	AI	Mean
1	C	1036.3	664.4	850.3	231.9	140.0	186.0
2	M	864.8	452.9	658.9	224.8	115.0	169.9
3	5%MSS	812.7	427.0	619.9	207.9	125.2	166.6
4	10%MSS	712.5	360.3	536.4	223.6	137.4	180.5
5	0.2%S	855.1	573.6	714.4	235.3	132.6	183.9
6	0.4%S	752.4	482.3	617.3	238.8	172.3	205.5
7	M5%MSS	652.8	462.9	557.9	168.7	148.8	158.8
8	M10%MSS	665.8	495.6	580.7	182.9	168.6	175.8
9	M0.2%S	613.9	575.7	594.8	203.8	133.5	168.7
10	M0.4%S	574.9	545.4	560.1	218.2	196.2	207.2
11	M5MSS0.2%S	543.8	427.6	485.7	129.1	110.1	119.6
12	M5MSS0.4%S	480.1	393.8	436.9	141.8	123.3	132.5
13	M10MSS0.2%S	412.0	327.1	369.5	164.5	159.4	162.0
14	M10MSS0.4%S	386.3	311.6	348.9	204.2	188.6	196.4
	Mean for date	668.8	464.3	566.6	198.3	146.5	172.4
	NIR _{α≤0.01} for date		3.5			4.7	
	NIR _{α≤0.01} for combination		9.3			12.5	
	NIR _{α≤0.01} for interaction		13.1			17.7	

* Combination symbols are explained in Table 1. ** BI—before incubation; AI—after 3 months of incubation.

Table 8. Content of available Zn and Cu in soil before and after incubation.

No.	Combination *	Zn (mg·kg ⁻¹)			Cu (mg·kg ⁻¹)		
		BI **	AI	Mean	BI	AI	Mean
1	C	36.3	32.5	34.4	8.2	5.5	6.9
2	M	33.0	17.9	25.4	7.3	6.3	6.8
3	5%MSS	48.3	33.4	40.8	11.5	7.7	9.6
4	10%MSS	55.2	48.7	51.9	13.7	9.7	11.7
5	0.2%S	33.3	21.0	27.2	7.3	7.8	7.6
6	0.4%S	28.8	19.7	24.3	6.2	7.2	6.7
7	M5%MSS	37.3	41.5	39.4	7.7	10.3	9.0
8	M10%MSS	44.0	55.4	49.7	8.3	11.5	9.9
9	M0.2%S	26.5	19.2	22.9	5.7	8.0	6.8
10	M0.4%S	23.2	21.3	22.2	5.2	7.5	6.3
11	M5MSS0.2%S	25.3	42.5	33.9	5.3	10.4	7.8
12	M5MSS0.4%S	20.3	37.4	28.8	4.3	9.3	6.8
13	M10MSS0.2%S	36.5	55.3	45.9	7.6	11.2	9.4
14	M10MSS0.4%S	31.7	36.5	34.1	5.8	10.1	7.9
	Mean for date	34.3	34.4	34.4	7.4	8.7	8.1

Table 8. Cont.

No.	Combination *	Zn (mg·kg ⁻¹)			Cu (mg·kg ⁻¹)		
		BI **	AI	Mean	BI	AI	Mean
	NIR _{α≤0.01} for date		3.5			1.2	
	NIR _{α≤0.01} for combination		9.3			3.0	
	NIR _{α≤0.01} for interaction		13.1			4.3	

* Combination symbols are explained in Table 1. ** BI—before incubation; AI—after 3 months of incubation.

Table 9. Content of available Ni and Cr in soil before and after incubation.

No.	Combination *	Ni (mg·kg ⁻¹)			Cr (mg·kg ⁻¹)		
		BI **	AI	Mean	BI	AI	Mean
1	C	3.1	1.8	2.5	1.5	0.5	1.0
2	M	2.3	1.1	1.7	1.0	0.7	0.8
3	5%MSS	3.2	2.2	2.7	1.8	1.5	1.6
4	10%MSS	3.4	2.4	2.9	2.2	1.8	2.0
5	0.2%S	1.8	1.2	1.5	1.6	1.5	1.5
6	0.4%S	1.5	1.1	1.3	1.3	1.0	1.2
7	M5%MSS	1.6	1.4	1.5	1.3	1.2	1.3
8	M10%MSS	1.8	1.6	1.7	1.5	1.4	1.4
9	M0.2%S	1.7	1.5	1.6	0.9	0.9	0.9
10	M0.4%S	1.4	1.3	1.4	0.9	0.7	0.8
11	M5MSS0.2%S	1.9	1.1	1.5	1.6	1.2	1.4
12	M5MSS0.4%S	1.7	1.0	1.3	1.5	1.1	1.3
13	M10MSS0.2%S	2.3	1.7	2.0	2.2	1.4	1.8
14	M10MSS0.4%S	2.1	1.3	1.7	2.1	1.2	1.6
	Mean for date	2.1	1.5	1.8	1.5	1.1	1.3
	NIR _{α≤0.01} for date		3.5			0.04	
	NIR _{α≤0.01} for combination		9.3			0.11	
	NIR _{α≤0.01} for interaction		13.1			0.16	

* Combination symbols are explained in Table 1. ** BI—before incubation; AI—after 3 months of incubation.

After 3 months of incubation, there was a decrease in the content of Fe, Mn, Ni and Cr in the soil compared to the content before incubation. In the case of Zn and Cu, the incubation period in treatments where municipal sewage sludge was used along with flour, or a combination of flour and sulfur, increased the content of the bioavailable forms of Zn and Cu in the soil.

The assessment of microelement content (Fe, Mn, Zn and Cu) according to the limit values for the Mehlich 3 method indicated that their content in the soil, before and after incubation, was well above the values considered low for all crops [42]. From the point of view of plant nutrition, the addition of these deacidifying materials to light, acidic soil increased the content of available microelements, which confirms the need for their use as alternative fertilizing agents [34,45]. Unpolluted soil contains Zn, Cu, Ni and Cr at levels of no more than 70, 20, 25 and 30 mg·kg⁻¹ d.m. of soil, respectively [47]. This study shows that the materials used did not contaminate the soil with heavy metals and that their levels were acceptable for growing all crops.

3.6. Trace Elements in Soil (Pb, Cd)

The content of available forms of Pb and Cd in the control soil was low, and an even lower content of these elements was recorded in the soil with the addition of carbonate-clay flour (Table 10). The addition of sewage sludge or sulfate sulfur increased the content of these elements in the soil. The combined use of carbonate-clay flour with sewage sludge and sulfate sulfur resulted in a reduction in Pb and Cd content, compared to the soils

receiving sludge and sulfur separately. Studies clearly indicate that the addition of sewage sludge, sulfate sulfur and carbonate-clay flour reduces the content of bioavailable forms of Pb and Cd, which limits the possibility of these potentially toxic elements being taken up by plants [48]. The addition of alkaline waste immobilizes heavy metals, leading to their precipitation into insoluble carbonate forms that are inaccessible to plants [33]. Reducing the amount of bioavailable heavy metals in soil decreases the likelihood of ecological and health risks [7].

Table 10. Content of available Pb and Cd in soil before and after incubation.

No.	Combination *	Pb (mg·kg ^{−1})			Cd (mg·kg ^{−1})		
		BI **	AI	Mean	BI	AI	Mean
1	C	8.0	7.0	7.5	0.37	0.32	0.35
2	M	1.6	1.2	1.4	0.27	0.23	0.25
3	5%MSS	7.8	6.5	7.1	0.85	0.78	0.82
4	10%MSS	8.3	7.3	7.8	0.95	0.80	0.88
5	0.2%S	8.3	7.5	7.9	0.97	0.93	0.95
6	0.4%S	8.7	8.0	8.3	1.10	1.06	1.08
7	M5%MSS	2.4	2.1	2.3	0.87	0.83	0.85
8	M10%MSS	3.0	2.4	2.7	0.95	0.91	0.93
9	M0.2%S	1.9	1.7	1.8	0.75	0.70	0.73
10	M0.4%S	2.1	1.9	2.0	0.85	0.81	0.83
11	M5MSS0.2%S	2.6	2.5	2.5	0.59	0.52	0.55
12	M5MSS0.4%S	2.8	2.8	2.8	0.63	0.59	0.61
13	M10MSS0.2%S	2.9	2.9	2.9	0.69	0.64	0.67
14	M10MSS0.4%S	3.0	2.9	3.0	0.91	0.89	0.90
	Mean for date	4.5	4.0	4.3	0.77	0.72	0.74
	NIR _{α≤0.01} for date		3.5			0.1	
	NIR _{α≤0.01} for combination		9.3			0.3	
	NIR _{α≤0.01} for interaction		13.1			0.4	

* Combination symbols are explained in Table 1. ** BI—before incubation; AI—after 3 months of incubation.

The content of Pb and Cd in the used materials after incubation was slightly lower compared to the content in the starting materials, which could have been due to the low amount of bioavailable forms in the soil solution [48]. Previous studies have confirmed that carbonate-clay flour is characterized by a low content of metal (loid)s and does not exceed the permissible content for agricultural limestone and other mineral fertilizers and plant growth enhancers of mineral origin [49]. A low content of potentially toxic elements will not exclude the use of these materials for enriching soil with other elements necessary for plants [50,51].

The repeated application of the materials tested would lead to increased soil salinity and heavy metal content. Excessive heavy metal content would prevent plants from being consumed, and high salinity would hinder their growth and development [35]. Therefore, if the materials are to be applied repeatedly, the chemical composition of the substrate and the plants grown should be monitored [39].

Based on the results of the incubation experiment, it can tentatively be concluded that carbonate-stabilized flour containing a single dose of sewage sludge and sulfate sulfur can be introduced on a larger scale for agricultural and reclamation management purposes.

3.7. Statistical Analysis

Pearson's linear correlation analysis, using the Statistica package, allowed us to demonstrate the relationship between selected parameters of soil physicochemical properties and selected waste materials before and after incubation. This analysis shows that the carbonate-

clay flour, sewage sludge and calcium sulfate introduced to the soil significantly influenced the change in physicochemical properties of the soil. A significant decrease in soil pH after incubation favored the dissolution of oxides and carbonates from the carbonate-clay flour, which led to the desorption of elements (Ca, Mg, K, Na, Fe, Mn, Ni and Cr) from the soil sorption complex. The higher salinity value in the soils receiving fertilizer formulations also promoted a greater release of macronutrients from the soil sorption complex.

The soil pH value was strictly correlated with salinity, organic carbon content and the available forms of Ca, Mg, K, Na and P in the soil (Figure 1), indicating a strong influence of this parameter on the availability and bioavailability of soil components. A negative correlation was found between the soil pH value and the available forms of Fe and Mn, which indicates the possible precipitation of micronutrients under the influence of the tested waste materials of an alkaline nature. On the other hand, the positive correlation between soil pH and the content of Zn, Cu, Cr and Cd ($0.435 < r < 0.898$) confirms the significant impact of this parameter on increasing the amount of their bioavailable forms. The above correlations point to a significant impact of the materials used on the physicochemical properties of soil, assessed in terms of the possibility of their improvement and the environmental management of nutrients.

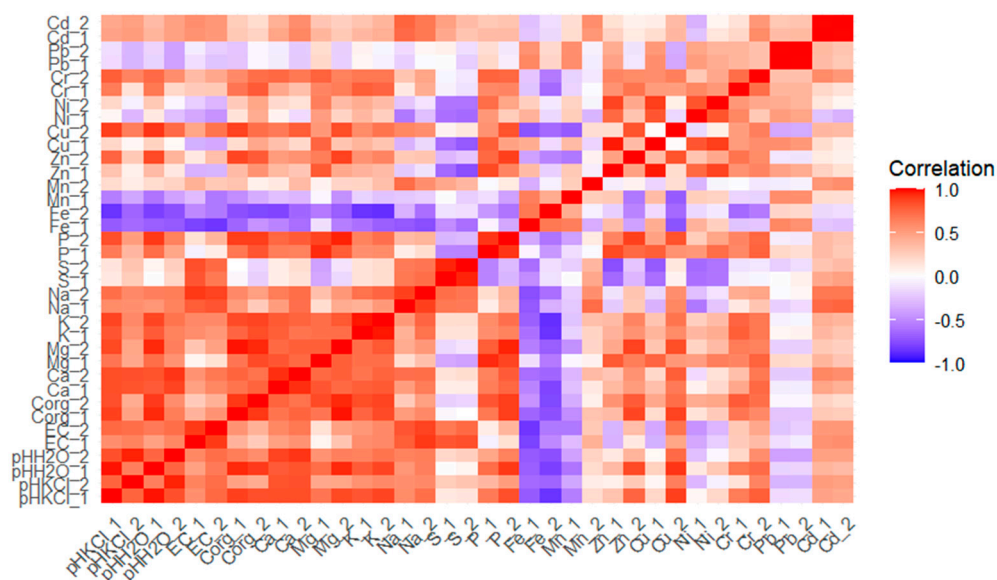


Figure 1. Correlation matrix heatmap of soil parameters. _1—before incubation; _2—after incubation.

Hierarchical cluster analysis allowed us to recognize patterns among the 28 experimental waste combinations (14 before incubation and 14 after incubation). The plots studied were always grouped by incubation date and mostly by combinations. Four clusters were identified (Figure 2). The first one consisted of the pre-incubation combinations in which sewage sludge was applied. These combinations were further grouped with respect to the combination of waste used. The second cluster included controls and combinations after the introduction of carbonate-clay flour, with the same incubation dates that were the basis for forming the groups. The use of sulfate sulfur in both doses alone and in the mixtures with flour resulted in the grouping in the third cluster. It was further divided into groups based on similarities due to the same incubation date and type of components. The fourth cluster comprised the combinations after incubation, following sewage sludge application. The same doses of sewage sludge in flour–sludge–sulfur combinations, and sludge applied alone and in a mixture with flour, showed greater similarity to each other.

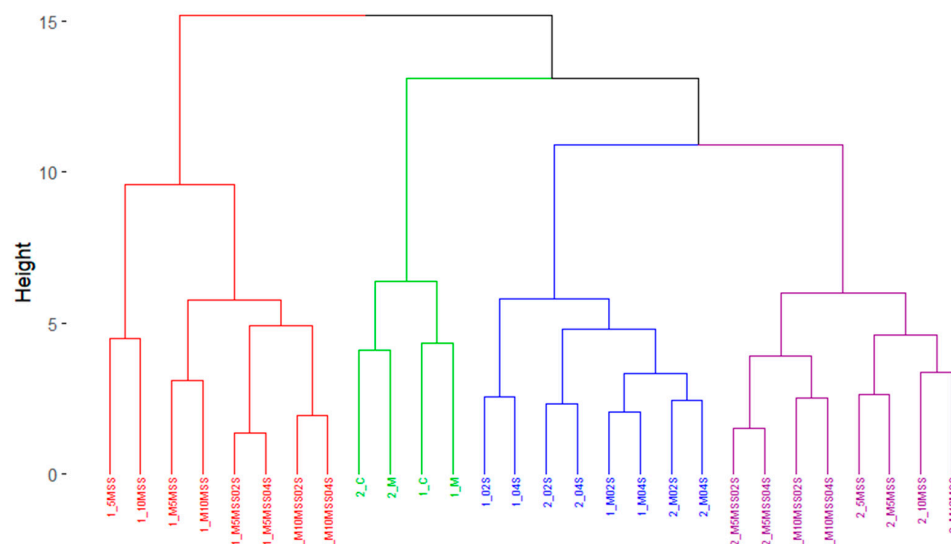


Figure 2. Hierarchical clustering of waste combinations. Combinations: 1_—before incubation; 2_—after incubation; C—control; M—flour; 5MSS—5% sewage sludge; 10MSS—10% sewage sludge; 02S—0.2% sulfate sulfur; 04S—0.4% sulfate sulfur; M5MSS—flour + 5% sewage sludge; M10MSS—flour + 10% sewage sludge; M02S—flour + 0.2% sulfate sulfur; M04S—flour + 0.4% sulfate sulfur; M5MSS02S—flour + 5% sewage sludge + 0.2 sulfate sulfur; M5MSS04S—flour + 5% sewage sludge + 0.4 sulfate sulfur; M10MSS02S—flour + 10% sewage sludge + 0.2 sulfate sulfur; M10MSS04S—flour + 10% sewage sludge + 0.4 sulfate sulfur.

4. Conclusions

The conducted incubation experiment, in which the proposed fertilizer formulations were the object of study, allowed for the following conclusions to be drawn:

1. When carbonate-clay flour is used in an amount balancing the extractable acidity of the soil (1 EA), it is an efficient liming agent that does not excessively alkalize the substrate, instead improving the pH of very acidic soil to a level close to neutral. This indicates the high reactivity of carbonate-clay flour.
2. All fertilizer formulations provide neutralization; however, immediately after application, the formulations with larger amounts of sewage sludge can be used to alkalize soil to a pH as high as ≈ 11 .
3. The use of sulfate sulfur in the form of calcium sulfate favors the maintenance of the deacidifying effect; however, at the same time, it does not lead to the excessive alkalization of soil.
4. All proposed formulations containing sewage sludge have a positive effect on the organic carbon content in soil. However, during incubation, a relatively rapid decomposition of organic matter and a reduction in the content to a level not much higher than the original content take place, which is probably favored by alkaline soil.
5. Carbonate-clay flour increases the electrolytic conductivity of soil and keeps it at about $1.4 \text{ mS} \cdot \text{cm}^{-1}$, which provides optimal conditions for plant development.
6. Formulations with a large share of sewage sludge significantly increase the electrolytic conductivity of soil; this effect persisted throughout the study period. Exceeding a pH of $4 \text{ mS} \cdot \text{cm}^{-1}$ indicates salinity, which may hinder the uptake of water and nutrients by cultivated plants.
7. The quantities of Ca, P, K and Mg released from sewage sludge are partly limited by the use of carbonate-clay flour and sulfate, and sewage sludge and carbonate-clay flour do not limit the release of sulfate in a form that is readily available to plants.
8. Sewage sludge and waste calcium sulfate provide a significant amount of sodium to soil, which can have a positive effect on the nutritional value of plants; however,

at the same time, this can lead to the deterioration of the soil structure, since excess sodium may reduce the stability of soil aggregates.

9. The soil used in the experiment provided the greatest amount of Fe and Mn, and the addition of carbonate-clay flour affected their reduction. In contrast, sewage sludge provided the most Zn, Cu, Ni and Cr, while the addition of carbonate-clay flour and sulfate sulfur affected the availability of Zn and Cu as well as the reduction in Ni and Cr content.
10. The combined addition of carbonate-clay flour with sewage sludge and sulfate sulfur keeps the content of heavy metals (Pb and Cd) at a stable level in soil.
11. The use of carbonate-clay flour, sewage sludge and sulfate sulfur brings about a positive fertilizer effect because these materials are a rich source of biogenic nutrients, mainly macronutrients and organic matter, and so they may contribute to carbon sequestration in soil. However, the aim is to maintain a stable chemical composition and avoid exceeding the recommended doses of CaO added in the process of soil deacidification.
12. The most environmentally safe and optimal fertilizing combinations were (a) carbonate-clay flour used alone and (b) carbonate-clay flour used together with a single dose of sewage sludge and sulfate sulfur. Introducing a double dose of sewage sludge and sulfate sulfur leads to the excessive alkalization and salinization of soil. Using higher doses of these materials increases ecological and health risks.

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References

1. The State of Soils in Europe 2024. Available online: <https://publications.jrc.ec.europa.eu/repository/handle/JRC137600> (accessed on 12 March 2025).
2. Filipek-Mazur, B.; Lisowska, A.; Kulig, B. Formation of selected soil properties as an effect of sulfur pulp application with organic materials. *Przem. Chem.* **2024**, *9*, 984–989. (In Polish) [[CrossRef](#)]
3. Kołodziej, B.; Bryk, M.; Antonkiewicz, J. Temporal and spatial variability of physical and chemical properties in reclaimed soil after sulphur borehole mining. *Soil Tillage Res.* **2024**, *237*, 105980. [[CrossRef](#)]
4. Zadrożny, P.; Nicia, P.; Wojewodzic, T.; Dacko, M.; Paluch, Ł.; Płonka, A.; Janus, J.; Pijanowski, J.; Bejger, R.; Ukalska-Jaruga, A.; et al. Cause–Effect Modelling of Soil Liming in Poland. *Sustainability* **2024**, *16*, 10361. [[CrossRef](#)]
5. Rheinheimer, D.S.; Bortoluzzi, E.C.; Moterle, D.F.; Guet, T.L.; Bastos, M.C.; Coelho, L.L.; Meotti, B.L.; Santana, A.S.; Tiecher, T. Kinetics of soil re-acidification under no-tillage system. *Soil Tillage Res.* **2024**, *242*, 106137. [[CrossRef](#)]
6. Statistics Poland. Environment 2024. In *Statistical Analyses*; Statistics Poland: Warsaw, Poland, 2024; p. 193, ISSN 0867-3217. Available online: <https://stat.gov.pl/obszary-tematyczne/srodowisko-energia/srodowisko/ochrona-srodowiska-2024,1,25.html> (accessed on 28 February 2025).
7. Antonkiewicz, J.; Gworek, B. *Remediation of Contaminated Soils and Lands*, 1st ed.; Scientific Publishing PWN: Warszawa, Poland, 2023; p. 204, ISBN 978-83-01-22827-1. [[CrossRef](#)]

8. Li, G.; Wu, J.; Kronzucker, H.J.; Li, B.; Shi, W. Physiological and molecular mechanisms of plant-root responses to iron toxicity. *J. Plant Physiol.* **2024**, *297*, 154257. [CrossRef] [PubMed]
9. Guzik, K.; Figarska-Warchoł, B.; Skuta, I. Jurassic limestones from deposits in the Działoszyn Region—lithology and directions of applications. *Górnictwo Odkryw.* **2023**, *2*, 57–66. (In Polish) [CrossRef]
10. Skuta, I.; Antonkiewicz, J.; Guzik, K.; Kołodziej, B. Possibilities of utilizing jurassic limestones and waste raw materials generated during their processing—A case study from central Poland. *Acta Sci. Polonorum. Form. Circumiectus* **2024**, *23*, 5–18. [CrossRef] [PubMed]
11. Feng, H.; Han, X.; Biswas, A.; Zhang, M.; Zhu, Y.; Ji, Y.; Lu, X.; Chen, X.; Yan, J.; Zou, W. Long-term organic material application enhances black soil productivity by improving aggregate stability and dissolved organic matter dynamics. *Field Crops Res.* **2025**, *328*, 109946. [CrossRef]
12. Ami, I.J.; Nasrin, S.; Akter, F.; Halder, M. Potential agricultural waste management modes to enhance carbon sequestration and aggregation in a clay soil. *Waste Manag. Bull.* **2025**, *3*, 100196. [CrossRef]
13. IPCC Climate Change 2001: Working Group I: The Scientific Basis. Intergovernmental Panel on Climate Change. Available online: https://www.ipcc.ch/site/assets/uploads/2018/02/WG1_TAR-FRONT.pdf (accessed on 28 February 2025).
14. Klikocka, H.; Podleśna, A.; Podleśny, J.; Narolski, B.; Haneklaus, S.; Bloem, E.; Schnug, E. Improvement of the Content and Uptake of Micronutrients in Spring Rye Grain DM Through Nitrogen and Sulfur Supplementation. *Agronomy* **2020**, *10*, 35. [CrossRef]
15. Klikocka, H.; Skwaryło-Bednarz, B.; Podleśna, A.; Narolski, B. The response of spring rye (*Secale cereale* L.) to NPK and S fertilizers. The content and uptake of macroelements and the value of ionic ratios. *J. Elem.* **2022**, *27*, 249–263. [CrossRef]
16. Kettunen, M.; Gionfra, S.; Monteville, M. *EU Circular Economy and Trade: Improving Policy Coherence for Sustainable Development*; IEEP: Brussels, Belgium; London, UK, 2019. Available online: <https://ieep.eu/wp-content/uploads/2022/12/EU-trade-CE-and-sustainable-development-IEEP-2019-FINAL.pdf> (accessed on 28 February 2025).
17. Polish Soil Classification. *Polskie Towarzystwo Gleboznawcze, Komisja Genezy Klasyfikacji i Kartografii Gleb*; Wydawnictwo Uniwersytetu Przyrodniczego we Wrocławiu: Wrocław, Poland, 2019; 292p. (In Polish)
18. Regulation of the Minister of Climate on Catalogue of Waste Dated 2th January 2020. Journal of Laws of Poland, Item 10. 2020. Available online: <http://isap.sejm.gov.pl/isap.nsf/download.xsp/WDU2020000010/O/D20200010.pdf> (accessed on 15 March 2025).
19. ISO 11465:1993; Soil Quality—Determination of Dry Matter and Water Content on a Mass Basis—Gravimetric Method. ISO: Geneva, Switzerland, 1993.
20. PN-EN ISO 10390:2022-09; Soil Quality—Determination of pH. Polish Committee for Standardization: Warszawa, Poland, 2022.
21. USDA—United States Department of Agriculture. *Soil Survey Manual 2018. Soil Survey Manual. Soil Science Division Staff; HANDBOOK No. 18*; United States Department of Agriculture: Washington, DC, USA, 2018; p. 605.
22. PN-ISO 10694:2002; Soil Quality—Determination of Organic and Total Carbon After Dry Combustion (Elementary Analysis). ISO: Geneva, Switzerland, 2002.
23. Mehlich, A. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.* **1984**, *15*, 1409–1416. [CrossRef]
24. Jones, J.B., Jr.; Case, V.W. Sampling, Handling, and Analyzing Plant Tissue Samples. In *Soil Testing and Plant Analysis*, 3rd ed.; Westerman, R.L., Ed.; SSSA Book Series, Chapter 15; Soil Science Society of America: Madison, WI, USA, 1990; pp. 389–427, ISBN 9780891188452. [CrossRef]
25. R Core Team. *A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2025. Available online: <https://www.R-project.org/> (accessed on 4 April 2025).
26. Jadczyzyn, T. Nowe zalecenia w zakresie wapnowania gleb. *Stud. Rap. IUNG-PIB* **2021**, *65*, 99–109. [CrossRef]
27. Barrow, N.J.; Hartemink, A.E. The effects of pH on nutrient availability depend on both soils and plants. *Plant Soil* **2023**, *487*, 21–37. [CrossRef]
28. Łabętowicz, J.; Rutkowska, B.; Szulc, W.; Sosulski, T. Estimation of liming and gypsum application on the content of exchangeable aluminium in sandy soil. *Ann. Univ. Mariae Curie-Skłodowska Sect. E Agric.* **2004**, *59*, 631–637. (In Polish)
29. Soon, Y.K. Fractionation of extractable aluminium in acid soils: A review and a proposed procedure. *Commun. Soil Sci. Plant Anal.* **1993**, *24*, 1683–1708. [CrossRef]
30. Khan, S.; Li, R.; Pan, R.; Zhang, C.; Lv, Y.; Tang, H.; Huang, J.; Yin, L. Aluminium bioavailability and toxicity disrupted chloroplast structure and inhibited inorganic carbon utilization and nutrient uptake in *Vallisneria spiralis* at acidic and alkaline pH. *Environ. Exp. Bot.* **2024**, *228*, 105997. [CrossRef]
31. Świercz, A.; Gandzel, A.; Tomczyk-Wydrych, I. Dynamics of changes in selected traits in the profiles of arable soils anthropogenically alkalisied by the cement and lime industry within the Kielecko-Łagowski Vale (Poland). *Land* **2021**, *10*, 84. [CrossRef]
32. Skowrońska, M.; Bielińska, E.J.; Szymański, K.; Futa, B.; Antonkiewicz, J.; Kołodziej, B. An integrated assessment of the long-term impact of municipal sewage sludge on the chemical and biological properties of soil. *Catena* **2020**, *189*, 104484. [CrossRef]

33. Gałuszka, A.; Migaszewski, Z.M.; Pelc, A.; Trembaczowski, A.; Dołęgowska, S.; Michalik, A. Trace elements and stable sulfur isotopes in plants of acid mine drainage area: Implications for revegetation of degraded land. *J. Environ. Sci.* **2020**, *94*, 128–136. [CrossRef] [PubMed]
34. Lisowska, A.; Filipek-Mazur, B.; Sołtys, J.; Niemiec, M.; Gorczyca, O.; Bar-Michalczyk, D.; Komorowska, M.; Gródek-Szostak, Z.; Szeląg-Sikora, A.; Sikora, J.; et al. Preparation, characterization of granulated sulfur fertilizers and their effects on a sandy soils. *Materials* **2022**, *15*, 612. [CrossRef] [PubMed]
35. Smreczak, B.; Ukalska-Jaruga, A.; Łysiak, M.; Strzelecka, J.; Niedźwiecki, J.; Sobich, D. Funkcje, jakość i usługi ekosystemowe gleb. *Stud. Rap. IUNG-PIB* **2017**, *54*, 9–23. [CrossRef]
36. Cheraghi, S.A.M. Wheat yield response and seasonal salt profile evolution under irrigation with saline waters in a semi-arid region. *J. Water Land Dev.* **2020**, *44*, 26–32. [CrossRef]
37. Elmeknassi, M.; Elghali, A.; de Carvalho, H.W.P.; Laamrani, A.; Benzaazoua, M. A review of organic and inorganic amendments to treat saline-sodic soils: Emphasis on waste valorization for a circular economy approach. *Sci. Total Environ.* **2024**, *921*, 171087. [CrossRef] [PubMed]
38. Siebielec, G.; Łopatka, A.; Smreczak, B.; Kaczyński, R.; Siebielec, S.; Koza, P.; Dach, J. Materia organiczna w glebach mineralnych Polski (Organic matter in the mineral soils of Poland). *Stud. Rap. IUNG-PIB* **2020**, *64*, 9–30. [CrossRef]
39. Monitoring Chemizmu Gleb Ornych Polski. IUNG-PIB, GIOŚ. 2020. Available online: https://www.gios.gov.pl/chemizm_gleb/index.php?mod=monit (accessed on 11 April 2025).
40. Simões-Mota, A.; Barré, P.; Baudin, F.; Poch, R.M.; Bruni, E.; Anton, R.; Enrique, A.; Virto, I. Effects of long-term sewage sludge addition to a calcareous soil on soil organic C fractions and soil functions. *Geoderma* **2024**, *445*, 116868. [CrossRef]
41. Shoumik, B.A.A.; Khan, M.Z.; Błońska, E.; Lasota, J. Dynamics of soil organic carbon and total nitrogen in particulate and mineral-associated organic matter fractions under different continuous land use patterns across Europe. *Agric. Ecosyst. Environ.* **2025**, *381*, 109411. [CrossRef]
42. Kęsik, K. Zastosowanie metody Mehlich 3 w systemie doradztwa nawozowego (Application of the Mehlich 3 method in the fertilizer advisory system). *Stud. Rap. IUNG-PIB* **2016**, *48*, 95–104. [CrossRef]
43. Baran, A.; Tack, F.M.G.; Delemazure, A.; Wiczorek, J.; Boguta, P.; Skic, K. Use of selected amendments for reducing metal mobility and ecotoxicity in contaminated bottom sediments. *J. Environ. Manag.* **2024**, *360*, 121183. [CrossRef] [PubMed]
44. Zohar, I.; Ganem, H.E.; DiSegni, D.M.; Jonas-Levi, A. The impact of alternative recycled and synthetic phosphorus sources on plant growth and responses, soil interactions and sustainable agriculture-lettuce (*Lactuca sativa*) as a case model. *Sci. Total Environ.* **2024**, *948*, 174719. [CrossRef] [PubMed]
45. Zhao, L.; Sun, Z.F.; Pan, X.W.; Tan, J.Y.; Yang, S.S.; Wu, J.T.; Chen, C.; Yuan, Y.; Ren, N.Q. Sewage sludge derived biochar for environmental improvement: Advances, challenges, and solutions. *Water Res. X* **2023**, *18*, 100167. [CrossRef] [PubMed]
46. Huang, Y.Z.; Lee, Y.Y.; Fan, C. Innovative fertilization strategies for in-situ pollution control and carbon negativity enhancement in agriculture. *Agric. Water Manag.* **2025**, *307*, 109270. [CrossRef]
47. Kabata-Pendias, A.; Piotrowska, M.; Motowicka-Terelak, T.; Maliszewska-Kordybach, T.; Filipiak, K.; Krakowiak, A.; Pietruch, C.Z. Basis for the assessment of chemical contamination of soil-heavy metals, sulfur and PAHs. In *State Inspectorate for Environmental Protection; Library of Environmental Monitoring*; Warsaw, Poland, 1995; p. 41.
48. Zhang, C.; Li, J.; Dai, Y.; Gustave, W.; Zhai, W.; Zhong, Z.; Chen, J. Spatial and Temporal Variations of Heavy Metals' Bioavailability in Soils Regulated by a Combined Material of Calcium Sulfate and Ferric Oxide. *Toxics* **2023**, *11*, 296. [CrossRef] [PubMed]
49. Regulation of the Minister of Agricultural and Rural Development Dated 21 August 2024 Concerning the Implementation of Certain Provisions of the Act on Fertilizers and Fertilization. Journal of Laws of Poland, Item 1261. 2024. Available online: <https://isap.sejm.gov.pl/isap.nsf/download.xsp/WDU20240001261/O/D20241261.pdf> (accessed on 15 March 2025).
50. Regulation of the Minister of the Environment on the R10 Recovery Process Dated 20 January 2015. Journal of Laws of Poland, Item 132. 2015. Available online: <https://isap.sejm.gov.pl/isap.nsf/download.xsp/WDU20150000132/O/D20150132.pdf> (accessed on 15 March 2025).
51. Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 Laying Down Rules on the Making Available on the Market of EU Fertilising Products and Amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and Repealing Regulation (EC) No 2003/2003 (Text with EEA Relevance). OJ L 170/1. 25 June 2019. Available online: <http://data.europa.eu/eli/reg/2019/1009/oj> (accessed on 15 March 2025).

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