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Comparative Study of Fertilization Value and Neutralizing Power of Lime Materials of Carbonate and Silicate Natures on Plants of the Families *Gramíneae*, *Brassicáceae*, and *Leguminósae*

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Abstract: The dissolution of Ca and Mg in soil and their translocation in plants from different families when using different doses of liming materials of industrial waste origin have not yet been sufficiently studied. In this study, the influence of increasing doses of ameliorants of carbonate (dolomite flour—DF) and silicate (blast furnace slag—BFS) natures on the change in acid–base properties of soddy-podzolic light loamy soil, yield, and chemical composition of plants of the families *Gramíneae* (spring wheat), *Brassicáceae* (spring rapeseed), and *Leguminósae* (vetch and beans) was studied in five-year pot experiments. In the five-year experiments, the ameliorant of a carbonate nature showed greater effect on soil acid–base properties than that of a silicate nature. A return to the initial state of soil pH was not established in any of the treatments. Both ameliorants showed similar effects on wheat straw biomass, but DF had a greater positive effect on wheat grain yield than BFS. Regardless of the dose of DF applied, the accumulation of Ca and Mg by the plants throughout the study period was higher than when BFS was applied. Among the studied plants, those of the family *Brassicáceae* were the most responsive to liming and, at the same time, showed high ecological adaptability. Differences in the effects of the two ameliorants on the soil chemical properties were more significant than differences in their effects on plant productivity.

Keywords: soddy-podzolic soil; liming; carbonate and silicate ameliorants; plants; empirical models

1. Introduction

Liming acidic soil is a never-ending process that often needs to be repeated annually as the applied ameliorants lose their ameliorative properties and/or are washed out, especially in humid climates. Different types and grain sizes of liming material have different H+ neutralizing powers and different reactivity in the soil [1], as their efficiency varies greatly depending on their chemical and mineralogical composition and grain size distribution [1,2]. As a rule, the smaller the lime particle size, the higher the chemical activity [1,3,4]. Hypothetically, by adjusting the fineness through the grinding of ameliorants, it is possible to compensate for differences in their effects on soil and plants caused by the heterogeneity of their chemical composition [3,4]. To date, there are fairly complete ideas about the mechanism and kinetics of dissolution of calcium-containing ameliorants in soil [1,2,5–11].

In general, the interaction of calcareous materials with the soil occurs through the gradual transfer of bases into the soil solution, followed by a reaction with the absorbing soil complex and by the exchange of contact between the surface of the calcareous particles and the soil. During this exchange, the inner layers of the granules are not affected [8]. When limestone powder is dissolved, the calcium contained in the individual polysynthetic twin granules disappears almost completely. Remnants of calcite grains surrounded by fine-grained new formations of $Ca_3(C_6H_5O_7)_3$ slow down further dissolution. However, as the duration of interaction with the soil increases, they also completely dissolve. The dissolution rate and the dynamics of the lime material influence the crop yield more than the Ca/Mg ratio of the lime [5].

Dolomite rock consisting of exceptionally pure dolomite—$Ca,Mg(CO_3)_2$—is very rare. More often, it consists of calcite, magnesite, and dolomite itself. Normally, excess $CaCO_3$ forms a calcium cement that holds the rhombohedral double carbonate crystals together. The dissolution of medium dolomite is the result of two parallel processes: (1) the dissolution of calcite (or magnesite), which holds the crystals of the double salt together; and (2) the dissolution of the grains of the double salt itself. The solubility of pure calcite or pure magnesite is higher than that of the double salt, so that selective dissolution leads to a process with characteristic end products. Dolomite is ground to dolomite powder in the process of chemical weathering [12].

Industrial landfills are a serious environmental problem. The possibility of using blast furnace slag as lime material should be determined after a careful examination for potentially toxic elements and their effectiveness for the reclamation of acidic soils. The results of petrographic studies of blast furnace slag have shown that the dominant mineral in its composition is melinite ($(2CaO\cdot MgO\cdot 2SiO_2)\cdot(2CaO\cdot Al_2O_3\cdot SiO_2)$), consisting of 10% okermanite ($2CaO\cdot MgO\cdot 2SiO_2$) and 90% gelenite ($2CaO\cdot Al_2O_3\cdot SiO_2$). There is a gradual, uniform dissolution of melinite along cracks on the entire surface of its contact with the soil [13]. According to the degree of solubility, all forms of lime fertilizers can be arranged in the following descending order: calcium oxide > calcium carbonate > calcium silicate.

Despite the impressive research on the mechanisms of dissolution of calcareous materials introduced into the soil, questions still remain about the possibility and effectiveness of using blast furnace slag waste and its effects on the growth and quality of crops from different families. This work is devoted to a comparative study of the fertilizing value and neutralizing capacity of finely ground calcareous materials of carbonate and silicate natures obtained from industrial waste. The experiments were conducted under controlled conditions in two pot experiments over five years. The objectives of the study were to assess:

- Changes in the acid–base properties of soddy-podzolic light loam soils limed with calcified dolomite flour (DF) and blast furnace slag (BFS) in a wide dose range over the entire study period;
- Effects of the lime materials used on the yield and chemical composition of the plants investigated;
- Translocation of calcium and magnesium cations in plants from different biological families in the process of interaction of the ameliorants with the soil.

2. Materials and Methods

2.1. Study Design

Two parallel pot experiments using dolomite flour (DF, experiment no. 1) comprised four treatments and blast furnace slag (BFS, experiment no. 2) comprised six treatments. In both experiments, complex azofoska fertilizer (NPK 16:16:16) was applied in equal doses in each treatment. The treatment with NPK alone was used as a control treatment (Table 1). The cultivation of plants was carried out in pots containing 5 kg of soil. Before sowing, the soil was fertilized with azofoska in the amount of 0.2 g per 1 kg of soil weight. The crop rotation was: 1st year—spring wheat (*Triticum*, *Gramíneae* L.); 2nd and 3rd years—rapeseed (*Brássica nápus*, *Brassicáceae* L.); 4th and 5th years—vetch (*Vicia* L.) and beans (*Vicia faba* L., *Leguminósae* L.). Wheat in the experiment was brought to full ripeness; the harvest of the remaining crops was carried out in the flowering phase. Experimental images of the plants grown are given in Supplementary Figures S1–S4.

Table 1. Experimental design of the application of dolomite flour and blast furnace slag.

Experiment no. 1 with dolomite flour (DF)	
1. control (NPK)	Nitrogen/Phosphorus/Potassium: 16:16:16
2. NPK + DF, 0.375 Hy	NPK − dolomite flour at a dose by 0.375 Hy
3. NPK + DF, 0.75 Hy	NPK − dolomite flour at a dose by 0.75 Hy
4. NPK + DF, 1 Hy	NPK − dolomite flour at a dose by 1 Hy
Experiment no. 2 with blast furnace slag (BFS)	
1. control (NPK)	Nitrogen/Phosphorus/Potassium: 16:16:16
2. NPK + BFS at 0.1 Hy	NPK + blast furnace slag at a dose by 0.1 Hy
3. NPK + BFS at 0.25 Hy	NPK + blast furnace slag at a dose by 0.25 Hy
4. NPK + BFS at 0.375 Hy	NPK + blast furnace slag at a dose by 0.375 Hy
5. NPK + BFS at 0.75 Hy	NPK + blast furnace slag at a dose by 0.75 Hy
6. NPK + BFS at 1 Hy	NPK + blast furnace slag at a dose by 1 Hy

NPK—azofoska (NPK 16:16:16); Hy—hydrolytic acidity; DF—dolomite flour; BFS—blast furnace slag.

2.2. Soil and Ameliorant Characteristics

A strongly acidic soddy-podzolic light loam soil with the following physicochemical parameters was used for the experiments: pH_{KCl}—4.1; hydrolytic acidity (Hy)—4.75; the sum of absorbed bases (S)—1.5 mmol (eq)/100 g of soil; humus—1.75%, soil particles less than 0.01 mm—24.1%. The gross chemical composition of the soil is given in Table 2.

Table 2. Gross chemical composition of soddy-podzolic light loamy soil, % for carbonate-free and humus-free soil.

Ignition Loss	**SiO_2**	**R_2O_3**	**Fe_2O_3**	**Al_2O_3**	**CaO**	**MgO**	**P_2O_5**	**SO_3**	**MnO**	**$\sum$**
4.75	82.27	9.12	1.89	8.38	0.29	0.30	0.09	0.38	1.47	99.82

Dolomite flour (DF) produced from the screening of dolomite used for road construction and blast furnace slag (BFS) from a smelting works were used as ameliorants. Before use, the ameliorants were ground to a finely dispersed (powdery) state and sieved through a 0.25 mm mesh sieve. The neutralizing ability of DF was 93%, and that of BFS was 85%. When applied to the soil, the ameliorants were levelled according to their neutralizing capacity.

The dosage of dolomite fractions was calculated based on the hydrolytic acidity (Hy) of the soil. The full dose by Hy was calculated as: $CaCO_3\ ,\ \frac{t}{ha} = \frac{Ha*10*50*3{,}000{,}000}{10^9} = Ha*1.5$, where Hy is the hydrolytic acidity, mmol(eq.) 100^{-1} g soil; 10 is the conversion into mmol(eq.) kg^{-1}; 50 is the amount of $CaCO_3$ required to neutralize 1 mmol (eq) of H^+, mg; 3,000,000 is the mass of the arable layer, kg; and 10^9 is the conversion to t/ha. So, the full dose (1 Hy) was equal to Hy × 1.5. The dose of DF, calculated for 1 Hy, was 12.6 g/pot, and that of BFS was 13.8 g/pot.

The content of $CaCO_3$ in DF was 48.1% and that of $MgCO_3$ was 36.4%, and in BFS, the content of CaO was 39.73, MgO—19.7, SiO_2—38.43, Al_2O_3—6.7, and MnO –0.32 (in %).

As can be seen from the above data, BFS is a calcium silicate fertilizer and DF is a calcium carbonate fertilizer. According to the content of heavy metals in the ameliorants, they pose no danger to soils and plants (Table 3).

Table 3. The contents of pollutants and heavy metals in blast furnace slag and dolomite flour, mg/kg.

As	Hg	Pb	Cu	Zn	Mn	Cd	Ni
Dolomite flour (DF)							
<1.0	<0.015	9.76	1.46	8.50	n.d.	<0.05	6.20
Blast furnace slag (BFS)							
0.14	0.018	27.2	9.0	4.1	1105	<0.01	11.6

2.3. Analytical Methods

Soil acidity (pH_{KCl}) was determined using a glass electrode potentiometer (Mettler Toledo, Columbus, OH, USA) [14]. The amounts of exchangeable calcium and magnesium were determined by the complexometric method [14]. The gross chemical composition of the soil (Table 2) was determined by the sintering method [14]. Trace elements in soil, plants, and ameliorants were determined using an atomic adsorption spectrophotometer (Perkin-Elmer, New Brunswick, NJ, USA) after extraction by a mixture of concentrated HNO_3 and HCl in a 1:3 ratio [14]. Extraction of the amount of Ca + Mg from soils was carried out with acetate-ammonium buffer (pH 4.8), followed by determination of Ca and Mg using an atomic absorption spectrophotometer. The results obtained were processed statistically [15].

3. Results

3.1. Changes in Soil Properties

The results showed that the use of mineral fertilizers alone did not lead to significant changes in soil acidity during the 4-year study period (Table 4). In the control soil, throughout the study period, the fluctuations in pH_{KCl} were insignificant and the reaction of the soil solution did not go beyond a highly acidic value (4.14–4.40 pH).

Table 4. Changes in acid–base properties of the soil under the influence of increasing doses of dolomite flour (DF) and blast furnace slag (BFS).

Treatment	**pH_{KCl}**				**Al^{3+}**				**Ca^{2+} + Mg^{2+}**			
					mmol(eq)/100 g							
	Years				**Years**				**Years**			
	1st	**2nd**	**3rd**	**4th**	**1st**	**2nd**	**3rd**	**4th**	**1st**	**2nd**	**3rd**	**4th**
Experiment no. 1 Dolomite flour (DF)												
1. control (NPK)	4.14	4.38	4.39	4.40	1.39	0.98	0.97	0.74	1.45	2.01	2.58	2.10
2. NPK + DF at 0.375 Hy	4.52	4.60	4.79	4.49	0.55	0.38	0.88	0.67	3.71	4.24	4.29	3.48
3. NPK + DF at 0.75 Hy	4.97	5.04	5.98	4.81	0.12	0.14	0.55	0.50	5.36	5.39	5.99	5.86
4. NPK + DF at 1 Hy	5.38	5.42	6.58	5.17	0.04	0.02	0.14	0.27	6.63	5.76	6.56	6.27
Experiment no. 2, Blast furnace slag (BFS)												
1. control (NPK)	4.14	4.38	4.39	4.40	1.39	0.98	0.97	0.74	1.45	2.01	2.58	2.10
2. NPK + BFS at 0.1 Hy	4.30	4.44	4.38	4.58	1.18	0.64	0.76	0.92	2.06	2.46	2.63	2.67
3. NPK + BFS at 0.25 Hy	4.39	4.62	4.39	4.49	0.91	0.45	0.49	1.03	2.54	2.24	3.53	3.44
4. NPK + BFS at 0.375 Hy	4.42	4.69	4.40	4.47	0.81	0.53	0.57	1.01	3.05	3.56	3.44	3.79
5. NPK + BFS at 0.75 Hy	4.69	4.78	4.44	4.76	0.51	0.25	0.32	0.62	3.84	4.31	5.40	5.31
6. NPK + BFS at 1 Hy	4.83	5.23	4.56	5.05	0.28	0.09	0.31	0.33	4.71	5.04	6.15	5.29
LSD_{05}	-	-	-	-	0.076	0.103	0.297	0.015	0.545	0.481	0.555	0.445

Note: DF—dolomite flour, BFS—blast furnace slag; 1st year—wheat; 2nd year—rapeseed 1; 3rd year—rapeseed 2; 4th year—vetch; NPK—mineral fertilizer.

As expected, increasing doses of ameliorants led to a regular increase in pH_{KCl} already in the year of application. In terms of dose, the soil treated with a full dose of dolomite flour (DF) showed the highest pH value. In terms of the effect of duration, fertilization with DF increased the soil pH in the first three years regardless of the dose, whilst in the 4th year, the pH_{KCl} value decreased in all treatments.

In the treatments with BFS, an increase in the pH_{KCl} value was observed up to the end of the 2nd year. From the 3rd year onward, the pH of the limed soil decreased. However, the pH value of the soil did not return to the initial value in any of the experiments. The carbonate-containing agent (DF) reduced the acidity of the soil more than the silicate-containing agent (BFS). The concentration of Al^{3+} was influenced both by the time elapsed after lime application and by the dose of the two materials applied, DF and BFS (Tables 4 and 5). The maximum reduction in the aluminum content in most of the studied treatments was achieved after harvesting the rapeseed (2nd year), followed by an increase in its content. The use of DF was more effective. However, complete precipitation of aluminum with the use of either DF or BFS could not be achieved.

Table 5. Pairwise comparisons (Fisher LSD; 95% confidence).

	pH	**Ca + Mg**	**Al**
Experiment no. 1 Dolomite flour (DF)			
control (NPK)	4.33 b	2.03 c	1.020 a
NPK + DF at 0.375 Hy	4.60 b	3.93 b	0.620 ab
NPK + DF at 0.75 Hy	5.20 a	5.65 a	0.327 bc
NPK + DF at 1 Hy	5.64 a	6.31 a	0.117 c
Experiment no. 2, Blast furnace slag (BFS)			
	pH	Ca + Mg	Al
control (NPK)	4.33 c	2.03 e	1.020 a
NPK + DS at 0.1 Hy	4.42 c	2.45 e	0.875 ab
NPK + DS at 0.25 Hy	4.47 c	2.94 d	0.720 b
NPK + DS at 0.375 Hy	4.50 bc	3.46 c	0.730 b
NPK + DS at 0.75 Hy	4.67 b	4.71 b	0.425 c
NPK + DS at 1 Hy	4.92 a	5.30 a	0.252 c

Note: DF—dolomite flour; BFS—blast furnace slag; Means that do not share a letter are significantly different.

The concentrations of calcium and magnesium were influenced more by the dose of lime material applied than by the time elapsed since application (Table 4). The maximum content of Ca + Mg in the soil was established in the treatment with a full dose (1 Hy) of DF. In the pots reclaimed by DF, the sum of the absorbed bases increased until the 3rd year and there was a decrease in the 4th year. There was no return to the initial content of Ca + Mg in the soil.

3.2. Changes in Plant Composition and Yield

In the DF treatments, the straw yield was 2.3–2.5 times higher than in the control for all three doses (Table 6). The effect of BFS was similar to that of DF. The effect of DF on the grain yield was more significant than that of BFS. Yield increases with DF at doses of 0.75 and 1 Hy were higher than in the corresponding treatments with BFS.

The concentration of Mg in straw in all studied treatments with DF was higher than that in similar treatments with BFS. So, when using DF at a dose of 0.375 Hy, the Mg content in straw was 0.181% of the absolutely dry weight of plants. In the experiment with an equivalent dose of BFS, the Mg content in straw was 0.091%, i.e., two times less. Fluctuations in the Mg content in the treatments with DF were 0.056–0.190% (3.4-fold difference), and with BFS, they were from 0.056 to 0.172% (3-fold difference), according to the dose of lime applied. The significance of the effect of the dose of ameliorant on the transition of Mg to straw was low with DF and high with BFS (models (1) and (2) in Table 7; Figure S5). The fluctuations in the Mg content in wheat grain were 0.165–0.170% and 0.125–147% for DF and BFS, respectively. The significance of the effect of the dose of ameliorant on the transition of Mg to wheat grain in experiment No. 1 was not high, and in experiment No. 2, it was low (models (3) and (4) in Table 7; Figure S6). The expected changes in the concentration of Mg in wheat grain and straw from the dose of ameliorant were: in grain (exp. No. 1 v_3 = 0.043, exp. No. 2 v_4 = 0.0048) and in straw (exp. No. 1 v_1 = 0.126, exp. No. 2 v_2 = 0.111%). The inequalities v_3 = 0.043 > v_4 = 0.0048 and v_1 = 0.126 > v_2 = 0.111 allowed us to conclude that the use of DF contributed to greater Mg enrichment of both generative and vegetative organs of wheat than the use of BFS.

Table 6. Yields and chemical compositions of spring wheat as affected by dolomite flour and blast furnace slag.

Treatment	**Grain**		**Straw**		**Yield, g/pot**	
	Ca	**Mg**	**Ca**	**Mg**	**Grain**	**Yield**
Experiment no. 1, Dolomite flour (DF)						
1. control (NPK)	0.066 a	0.125 a	0.418 a	0.056 a	2.2	4.7
2. NPK + DF at 0.375 Hy	0.053 a	0.162 b	0.425 a	0.181 b	9.7	10.8
3. NPK + DF at 0.75 Hy	0.047 ba	0.167 b	0.488 a	0.190 b	11.9	11.4
4. NPK + DF at 1 Hy	0.049 ba	0.170 b	0.470 a	0.190 b	12.5	11.6
p	0.1	0.1	0.138	0.15	N/A	N/A
R^2	0.80	0.79	0.74	0.71	N/A	N/A
Experiment no. 2, Blast furnace slag (BFS)						
1. control (NPK)	0.066 a	0.125 a	0.418 a	0.056 a	0.79	0.37
2. NPK + BFS at 0.1 Hy	0.047 a	0.145 a	0.403 a	0.092 b	0.75	0.43
3. NPK + BFS at 0.25 Hy	0.058 a	0.130 a	0.407 a	0.078 ba	0.92	0.49
4. NPK + BFS at 0.375 Hy	0.048 a	0.147 a	0.433 a	0.091 b	0.81	0.53
5. NPK + BFS at 0.75 Hy	0.051 a	0.140 a	0.435 a	0.150 b	1.11	0.62
6. NPK + BFS at 1 Hy	0.048 a	0.136 a	0.460 a	0.172 b	1.24	0.70
p	0.28	0.67	0.019	0.0019	N/A	N/A
R^2	0.278	0.04	0.78	0.92	N/A	N/A

Note: DF—dolomite flour, BFS—blast furnace slag. Means that do not share a letter are significantly different.

Table 7. Empirical models of Ca and Mg translocation into plants.

	Model	**Model**	***p*-Value**	**v***	**R^2**
Exp. 1 (Mg, straw)	1	$y_1 = 0.087 + 0.126 \cdot x$	0.15	0.126	0.71
Exp. 2 (Mg, straw)	2	$y_2 = 0.061 + 0.111 \cdot x$	0.0019	0.111	0.92
Exp. 1 (Mg, grain)	3	$y_3 = 0.133 + 0.043 \cdot x$	0.1	0.043	0.79
Exp. 2 (Mg, grain)	4	$y_4 = 0.135 + 0.0048 \cdot x$	0.67	0.0048	0.04
Exp. 1 (Ma, straw)	5	$y_5 = 0.415 + 0.067 \cdot x$	0.138	0.067	0.74
Exp. 2 (Ma, straw)	6	$y_6 = 0.406 + 0.048 \cdot x$	0.019	0.048	0.78
Exp. 1 (Ma, grain)	7	$y_7 = 0.063 - 0.018 \cdot x$	0.1	−0.018	0.8
Exp. 2 (Ma, grain)	8	$y_8 = 0.057 - 0.01 \cdot x$	0.28	−0.01	0.278
Exp. 1 (Ma, rapeseed 1st year)	9	$y_9 = 0.713 + 0.569 \cdot x$	0.067	0.569	0.86
Exp. 2 (Ma, rapeseed 1st year)	10	$y_{10} = 0.738 + 0.481 \cdot x$	0.004	0.481	0.896
Exp. 1 (Ma, rapeseed 2nd year)	11	$y_{11} = 0.649 + 0.915 \cdot x$	0.009	0.915	0.98
Exp. 2 (Ma, rapeseed 2nd year)	12	$y_{12} = 0.682 + 0.468 \cdot x$	0.01	0.468	0.828
Exp. 1 (Mg, rapeseed 1st year)	13	$y_{15} = 0.413 + 0.456 \cdot x$	0.04	0.456	0.91
Exp. 2 (Mg, rapeseed 1st year)	14	$y_{16} = 0.395 + 0.31 \cdot x$	0.0001	0.31	0.98
Exp. 1 (Mg, rapeseed 2nd year)	15	$y_{17} = 0.481 + 0.491 \cdot x$	0.096	0.491	0.81
Exp. 2 (Mg, rapeseed 2nd year)	16	$y_{18} = 0.434 + 0.011 \cdot x$	0.8	0.011	0.005
Exp. 1 (Ca, vetch)	17	$y_{19} = 0.637 + 1.06 \cdot x$	0.014	1.06	0.97
Exp. 2 (Ca, vetch)	18	$y_{20} = 0.827 + 0.77 \cdot x$	0.012	0.77	0.82
Exp. 1 (Mg, vetch)	19	$y_{21} = 0.191 + 0.747 \cdot x$	0.007	0.747	0.98
Exp. 2 (Mg, vetch)	20	$y_{22} = 0.228 + 0.22 \cdot x$	0.02	0.22	0.78
Exp. 1 (Ca, beans)	21	$y_{23} = 0.712 + 0.716 \cdot x$	0.0023	0.716	0.995
Exp. 2 (Ca, beans)	22	$y_{24} = 0.791 + 0.572 \cdot x$	0.0039	0.572	0.899
Exp. 1 (Mg, beans)	23	$y_{25} = 0.146 + 0.623 \cdot x$	0.0006	0.623	0.998
Exp. 2 (Mg, beans)	24	$y_{26} = 0.164 + 0.285 \cdot x$	0.001	0.285	0.94

v*—the expected change in the nutrient content in plants with an increase in the dose of ameliorant; R^2 is the coefficient of determination.

Calcium predominantly accumulated in the vegetative organs of wheat (Table 6). Its content in straw ranged from 0.418 to 0.488% for DF depending on the treatment. The maximum accumulation was with 0.75 Hy. The dose of DF at 1 Hy resulted in less Ca content (0.47%). The empirical significance of models (5) and (6) describing the effect of DF dose on the concentration of Ca in wheat straw was low (Table 7, Figure S7).

There was no statistically significant relationship in some variants between the dose of ameliorant applied and the translocation of alkaline earth metals into plants. This may have been due to various mechanisms: different rates of dissolution of carbonate and silicate ameliorants, differences in the removal of Ca and Mg by plants from different biological families, different composition of root secretions of plants, etc.

Use of BFS showed a gradual increase in the Ca content in wheat straw. In most treatments using BFS, the Ca content was lower than in similar treatments using DF, ranging from 0.403 to 0.460%. The dose of BFS significantly influenced Ca accumulation in straw tissues (Table 7). The concentration of Ca in the grain was an order of magnitude lower than in straw, ranging from 0.047 to 0.053% and 0.047 to 0.058% for DF and BFS, respectively. It was not possible to identify any regularities associated with the effect of the dose of ameliorant on the accumulation of Ca in the grain (models (7) and (8), Figure S8). The reaction of plants to the accumulation of Ca in the tissues with DF was more pronounced than with BFS:

Grain

$$\mathrm{abs}(v_7) = 0.018 > \mathrm{abs}(v_8) = 0.01$$

Straw

$$v_5 = 0.067 > v_6 = 0.048$$

where v_7 and v_8 are the expected changes (absolute (abs) values of these rates) in the Ca content of the grain with an increase in the dose of ameliorant (the penultimate column of Table 7) for the corresponding number of the model (7 and 8). Respectively, v_5 and v_6 are the expected changes in the Ca content of the straw.

Liming had a positive effect on rapeseed productivity (Table 8). In the treatments with DF, the productivity of rapeseed was 1.8–2.5 times higher than in the control, and the highest biomass (12.8 g/pot) was in the treatment with the highest dose of DF.

Table 8. Effect of increasing doses of dolomite flour and blast furnace slag on yields of rapeseed, vetch, and beans, g/pot.

Treatment	Rapeseed		Vetch	Beans	Total Biomass	% of Control
	1st Year	2nd Year				
		Experiment no. 1				
1. control (NPK)	5.1 a	7.0 ab	5.1 a	4.8 a	22.0 c	100.0
2. NPK + DF at 0.375 Hy	9.3 b	8.7 b	6.3 a	5.6 a	29.9 c	135.9
3. NPK + DF at 0.75 Hy	10.3 b	7.2 ba	7.2 ba	5.3 a	30.0 c	136.4
4. NPK + DF at 1 Hy	12.8 bc	10.4 b	6.3 a	7.1 ba	36.6 dc	166.4
p	<0.001	<0.001	<0.001	<0.001	<0.001	
		Experiment no. 2				
1. control (NPK)	5.1 a	7.0 a	5.1 a	4.8 a	22.0 a	100
2. NPK + BFS at 0.1 Hy	8.2 a	7.2 a	4.5 c	5.1 c	25.0 d	113.6
3. NPK + BFS at 0.25 Hy	10.1 ba	8.4 a	5.8 c	6.7 a	31.0 e	140.9
4. NPK + BFS at 0.375 Hy	10.3 ba	9.5 ab	5.1 c	6.9 a	31.8 e	144.5
5. NPK + BFS at 0.75 Hy	10.6 ba	7.0 a	6.5 c	7.3 a	31.4 e	142.7
6. NPK + BFS at 1 Hy	9.5 ba	8.0 a	7.0 a	7.1 a	31.6 e	143.6
p	<0.001	<0.001	<0.001	<0.001	<0.001	

Note: DF—dolomite flour, BFS—blast furnace slag. Means that do not share a letter are significantly different

The use of BFS also contributed to an increase in the yield of crops. The maximum biomass of rapeseed was with the use of BFS in doses of 0.25–0.75 Hy: 10.1–10.6 g/pot, which was 198–208% of the control. At the full dose (1 Hy), the biomass was 9.5 g/pot or 186% of the control.

The positive effect of liming on rapeseed productivity was also observed 3 years after land reclamation, although the reclamation effect was weaker. The productivity of plants both with DF and BFS was lower than in similar treatments of the 2nd year. It was not possible to identify clear patterns of the influence of the dose of lime on the productivity of rapeseed. The increases in yield ranged from 1.02 to 1.48 and 1.02–1.36 times for DF and BFS, respectively, compared to the control.

Two years after liming, the fluctuations in Ca concentrations ranged from 0.79 to 1.37% and 0.79 to 1.24% for DF and BFS, respectively. In most treatments, the concentration of Ca with DF was slightly higher than that with BFS. The maximum level of accumulation was observed in the treatments using a full dose (1 Hy). Empirical models (9) and (10) describing the effect of ameliorant dose on the transition of Ca to rapeseed are given in Table 7. Graphs of empirical dependencies describing the effect of increasing dose of ameliorant on the transition of Ca to rapeseed are shown in Figure S9. The statistical significance of the models was high. The ratio $v9 = 0.569 > v10 = 0.481$ allowed us to conclude that two years after liming, the reaction of rapeseed to DF was stronger than to BFS.

The increase in the concentration of Ca in the tissues of spring rapeseed continued three years after liming. In the limed plots, the concentration of Ca was higher than in similar treatments of the 2nd year. In the experiment with BFS, a similar pattern was established only for the 0.75 Hy dose of BFS. In other limed plots, the concentration of Ca in rapeseed was lower than in similar plots of the 2nd year. The fluctuations in the calcium content in rapeseed tissues three years after liming with DM were 0.68–1.55% and with BFS, they were 0.68–1.08%.

Empirical models (11) and (12) describing the effect of increasing dose of ameliorant on the transition of calcium to rapeseed plants three years after liming are given in Table 8 and Supplementary Figure S10. The statistical significance of the models was high. The ratio $v11 = 0.915 > v12 = 0.468$ indicated that the reaction of spring rapeseed to the accumulation of Ca when DF was applied to the soil three years after liming was stronger than when BFS was applied. Generally, statistically significant changes in the concentration of Ca occurred both in the 2nd and 3rd years after land reclamation.

Liming with increasing dose of ameliorant containing Mg significantly affected the concentration of this element in rapeseed and vetch (Table 9). Fluctuations in Mg content in rapeseed in the DF experiment ranged from 0.37 to 0.81% and from 0.41 to 0.87% in the 2nd and 3rd years after application, respectively. The higher the dose of DF, the greater the Mg content in plants. Rapeseed of the 2nd year accumulated a higher Mg content than the 1st year rapeseed, regardless of the dose of DF applied.

In the experiment with BFS, the Mg content in rapeseed ranged from 0.37 to 0.70% and 0.41–0.52% for the 2nd and 3rd years after application, respectively. Increased dose of BFS resulted in increased content of Mg in rapeseed in the 1st year but not in the 2nd year. The use of 0.1–0.25 Hy of BFS did not make a difference in the Mg content in the tissues of rapeseed in both years, while doses of 0.375–1.0 Hy led to a decrease in the concentration of Mg in the 2nd year rapeseed by 1.6–1.5 times compared with the 1st year.

Empirical models (13) and (14) describing the effect of increasing dose of ameliorant on the transition of Mg to rapeseed plants are given in Table 7 and Figure S11. In the plots with DF (2nd and 3rd years) and in the plots with BFS (2nd year), the increase in the Mg content in rapeseed tissues was statistically significant. In the plot with BFS (3rd year), there was no statistically significant change in the Mg content (Figure S12).

Statistically significant changes in the calcium content in rapeseed under the influence of increasing doses of ameliorants occurred both two and three years after land reclamation. In the fourth year after liming, DF continued to have a positive effect on the productivity of vetch plants (Table 8). The minimum biomass of vetch was in the treatment without liming (5.1 g/pot). In the pots reclaimed with increasing doses of DF, the yield increase of vetch was 127.5–141.2% of the control (Table 8). A low dose of BFS (0.1 Hy) did not lead to an increase in the yield.

Table 9. The contents of Ca and Mg in rapeseed, vetch, and beans, %.

Treatment	**Rapeseed 1st Year**		**Rapeseed 2nd Year**		**Vetch**		**Beans**	
	Ca	**Mg**	**Ca**	**Mg**	**Ca**	**Mg**	**Ca**	**Mg**
				Experiment no. 1				
1. control (NPK)	0.79 a	0.37 a	0.68 a	0.41 a	0.63 a	0.17 a	0.72 a	0.15 a
2. NPK + DF at 0.375 Hy	0.83 a	0.63 b	0.92 b	0.74 b	1.09 b	0.52 b	0.98 a	0.38 b
3. NPK + DF at 0.75 Hy	1.07 ab	0.81 c	1.39 c	0.95 b	1.32 b	0.71 c	1.22 ab	0.60 c
4. NPK + DF at 1 Hy	1.37 b	0.81 c	1.55 c	0.87 b	1.76 bc	0.95 c	1.45 b	0.78 c
				Experiment no. 2				
1. control (NPK)	0.79 a	0.37 a	0.68 a	0.41 a	0.63 a	0.17 a	0.72	0.15 a
2. NPK + BFS at 0.1 Hy	0.75 a	0.43 a	0.76 a	0.46 a	0.98 b	0.24 a	0.80	0.16 a
3. NPK + BFS at 0.25 Hy	0.92 ab	0.49 a	0.80 a	0.52 a	1.24 b	0.36 ab	1.04	0.26 b
4. NPK + BFS at 0.375 Hy	0.81 a	0.53 a	0.76 a	0.34 a	1.08 b	0.32 ab	1.04	0.31 b
5. NPK + BFS at 0.75 Hy	1.11 b	0.62 ab	1.17 ab	0.44 a	1.35 b	0.40 b	1.27	0.38 b
6. NPK + BFS at 1 Hy	1.24 b	0.70 b	1.08 ab	0.46 a	1.59 bc	0.42 b	1.29	0.43 bc
p	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Note: DF—dolomite flour, BFS—blast furnace slag. Means that do not share a letter are significantly different within a column.

Regardless of the type of ameliorant used, there was an increase in the concentration of Ca in the tissues of vetch from 0.63 in the control to 1.76% at full dose of DF (1 Hy) (Table 9). In the experiment with increasing doses of BFS, the concentration of Ca ranged from 0.63 to 1.59%, i.e., it differed by 2.5 times. Statistically significant changes in calcium concentration, depending on the dose of DM and BFS, occurred at a high level of significance in both experiments (Table 7). Graphs of empirical dependencies are shown in Figure S13. The inequality $v17 = 1.06 > v18 = 0.77$ (Table 7) implied that the vetch response to calcium accumulation when using DF was more pronounced than when using BFS.

An increase in the dose of DF resulted in an increase in the concentration of Mg in the tissues of vetch from 0.17% to 0.95%, i.e., by 5.6 times. Application of BFS resulted in changes in the Mg concentration from 0.17 to 0.42%. Empirical models describing the effect of increasing dose of ameliorant on the transition of Mg to plants are given in Table 7 and Figure S14. The statistical significance of the models was high. The effect of DF on the absorption of Mg by vetch plants was more pronounced than that of BFS: $v19 = 0.747 > v20 = 0.22$.

The positive effect of chemical reclamation on plants of the family *Leguminósae* was also observed 5 years after liming. The biomass of beans increased by 1.10–1.47 and 1.06–1.52 times for DF and BFS, respectively, compared to the control. There were no differences in the productivity of beans in the treatments reclaimed with full doses of DF and BFS (Table 7).

Regardless of the type of ameliorant used in the experiments, there was an increase in the concentration of Ca in the tissues of beans as the dose of lime increased (Table 9) (models (21) and (22) in Table 7, Figure S15). The effect of DF on the accumulation of Ca by bean plants was more pronounced than that of BFS: $v21 = 0.716 > v22 = 0.572$. Similarly, as for Ca, a statistically significant change in the concentration of Mg in beans as the dose of DF and BFS increased occurred in both experiments (models (23) and (24)) (Table 7; Figure S16). The inequality $v23 = 0.623 > v24 = 0.285$ indicated that DF five years after application had a more significant effect on the formation of the chemical composition of beans.

4. Discussion

4.1. Changes in Soil Properties

Generally, a reclamation effect was achieved in both experiments. The higher the dose of application, the greater the reclamation effect. The use of DF over the entire period of study had a more significant effect on the change in the acid–base properties of the soil than the use of BFS. There was no return to the original state of the acid–base properties of the soil as a result of soil reclamation for both DF and BFS.

In the strongly acidic soil of the northwest region, aluminum plays a leading role in the formation of exchange acidity. In the soil, mobile aluminum accounts for 95–96% [8]. According to its effect on plants, aluminum is a typical root poison that leads to mucus of the roots and slows down their growth [16–18]. Differences in the formation of the root system of wheat (1st) and beans (5th year of the experiment) in the treatments without and with liming can be visually seen in Figure 1. The results implied that the higher the dose of ameliorant, the less mobile aluminum was found in the soil.

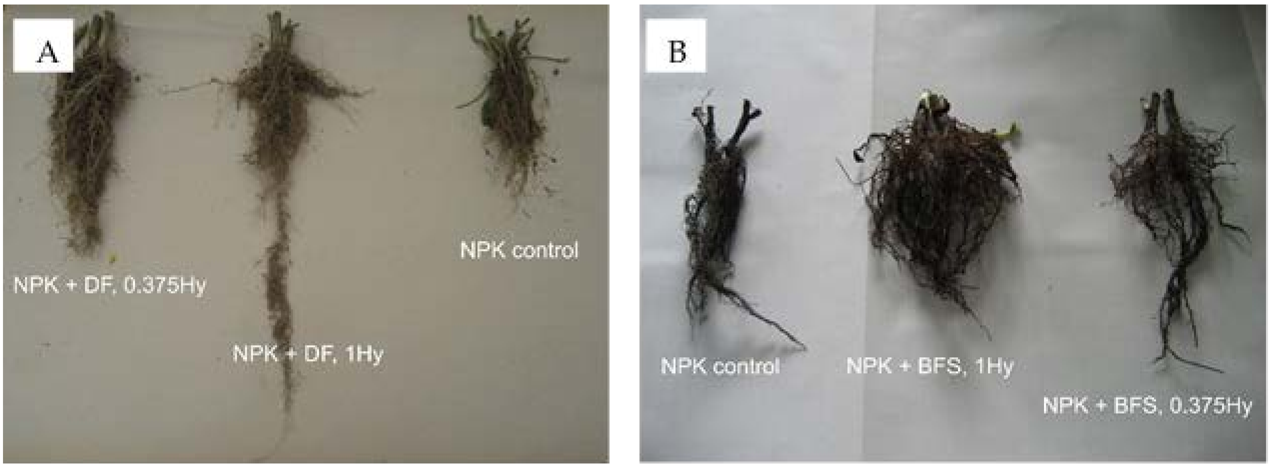

Figure 1. Formation of the root systems of wheat (**A**) and of beans (**B**) at different doses of DF.

The negative effect of aluminum in low-humus soils is eliminated at pH 4.9–5.2 and in soil with a high organic matter content at pH 4.5–4.7 [8]. The use of DF led to a more noticeable increase in the amount of absorbed bases in the year of use than the use of BFS, which was associated with better solubility of calcium and magnesium carbonates compared to silicates. In similar treatments with BFS, this increase was gradual. The exceptions were the treatments with the use of slag in doses of 0.1–0.375 Hy, where the content of Ca + Mg increased in all four years of observation.

4.2. Effect on Tissues and Yield

The higher level of grain productivity using DF is apparently explained by the higher content of Ca + Mg available to plants in soil reclaimed with DF in the year of application. It is known that the bulk of mineral nutrients enters wheat plants before BBCH 51 (earring phase), the reproductive organs are provided with nutrients due to the outflow from the leaves and stem before anthesis, and then about 60–95% of nutrients are transported to the grain [19–21]. Along with the unequal solubility of ameliorants, it is the redistribution of Mg from the vegetative organs to the grain that should explain the high variability of its content in the vegetative organs and the low variability in the grain of wheat. This statement is supported by the following observations. The concentration of Mg in wheat straw in all DF-limed treatments was higher than in the plant grain. In the experiment with BFS, a similar pattern was established only in the treatments with low doses: 0.1–0.375 Hy. When liming BFS at a dose of 0.75–1 Hy, the amount of Mg in the straw increased sharply and began to exceed the concentration of Mg in the grains. At the same time, fluctuations in the Mg content in wheat grain were observed in the treatments with low doses, and the dose corresponding to 1 Hy was insignificant (0.136–0.145%).

These results indicate that plants of the family *Brassicáceae* are highly responsive to liming, while rapeseed is an ecologically plastic plant species. The formation of the chemical composition of rapeseed depended on both the dose and the type of ameliorant used. Statistically significant changes in the calcium content in rapeseed under the influence of increasing doses of ameliorant occurred both two and three years after land reclamation. Regardless of the type of ameliorant used, liming led to an increase in the Ca content in plant tissues. Similarly, three-year experiments in [8] with radioisotope-labelled ^{45}Ca lime were indicative, showing that plants use both soil Ca and lime Ca.

Magnesium is another indispensable element of plant nutrition. Plants need Mg throughout their lives, but they are most sensitive to its deficiency in the initial period of development. Magnesium deficiency is common in light soddy-podzolic soils, where Mg starvation increases with increasing acidity of the soil. The use of Mg-containing ameliorants and industrial waste is currently the only source of soil enrichment with this element. The different solubility of ameliorants in the studied treatments inevitably affected the amount of Mg absorbed by wheat. The differences were 1.03 and 1.2 times for DF and BFS, respectively. This indicates a certain stability in the concentration of Mg in the generative organs of wheat, compared with the vegetative organs.

It is interesting to note that with an equal yield of beans (*Leguminósae*) in the treatments with DF and BFS at a full dose (1 Hy), the concentration of Mg with DF was 1.81 times higher than that with BFS (0.78% and 0.43%, respectively). In a situation of slight Mg deficiency, optimal plant nutrition can be achieved through economical use of the absorbed element, while in a situation of moderate excess, the plant activates protective mechanisms that limit the flow of excess ions into metabolically important centers. We hypothesize that there is a relatively wide range of favorable magnesium concentrations for bean plants.

According to modern concepts, the formation of the elemental composition of plants proceeds under the influence of genetically determined and environmental factors [20,22–24]. Not all plant organs equally reflect the chemical situation in the soil through their elemental composition [25,26]. There is a significant difference between the elemental compositions of seeds and vegetative organs [20–22]. Wheat grain consists primarily of carbohydrates (70–75%), mainly in the form of starch, followed by protein (10–15%), fats (1–2%), vitamins (such as B-vitamins), minerals (like iron and magnesium), fiber (2–3%), and water (10–15%) [27,28]. Since the contents and ratios of the main nutrients in wheat seeds are more constant, the chemical composition of the grain is considered to a greater extent as a hereditary property. It can be argued that plants exercise more stringent genetic control over the content of nutrients in generative organs. This ensures the normal functioning of plants at the initial stage of their development.

5. Conclusions

- Throughout the entire period of study, DF (dolomite flour, carbonate nature) showed a higher neutralizing efficiency than BFS (furnace blast slag, silicate nature).
- Differences in the effects of the two ameliorants on the soil chemical properties were more significant than differences in their effects on plant productivity.
- Both BFS and DF applied in equal quantities had positive effects on the productivity of wheat straw. Regardless of the dose, the assimilation of Ca and Mg by plants from DF was higher than that from BFS.
- Calcium and magnesium from both ameliorants were involved in the formation of the elemental composition of plants. Due to the better solubility of DF, the contribution of this ameliorant to the formation of the elemental composition of plants was more pronounced.
- Plants of the family *Brassicáceae* were highly responsive to liming and, at the same time, showed high ecological plasticity.

- The chemical nature of the ameliorant was a stronger factor in the fertilization efficiency and neutralizing power than the particle size (fineness of grinding) of the lime material.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su16177717/s1, Figure S1: Effect of increasing doses of DS on wheat productivity; Figure S2: Effect of increasing doses of DS on rapeseed productivity (2nd year of study); Figure S3: Effect of increasing doses of DF and DS on vetch productivity; Figure S4. Effect of increasing doses of DF and DS on the productivity of beans; Figure S5. Changes in the Mg content in wheat straw depending on the dose of ameliorant; Figure S6. Changes in the Mg content in wheat grain depending on the dose of ameliorant; Figure S7. Changes in the Ca content in wheat straw depending on the dose of ameliorant; Figure S8. Changes in the Ca content in wheat grain depending on the dose of ameliorant; Figure S9. Changes in the Ca content in rapeseed (2nd year) depending on the dose of ameliorant; Figure S10. Changes in the Ca content in rapeseed (3rd year) depending on the dose of ameliorant; Figure S11. Changes in the Mg content in rapeseed (2nd year) depending on the dose of ameliorant; Figure S12. Changes in the Mg content in rapeseed (3rd year) depending on the dose of ameliorant; Figure S13. Changes in the Ca content in vetch depending on the dose of ameliorant; Figure S14. Changes in the Mg content in vetch depending on the dose of ameliorant; Figure S15. Changes in the Ca content in beans depending on the dose of ameliorant; Figure S16. Changes in the Mg content in beans depending on the dose of ameliorant.

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