

# Impact of dolomite rock waste on soil acidity and absorption of Ca and Mg by barley and wheat

## Impacto dos resíduos de rocha dolomítica na acidez do solo e absorção de Ca e Mg por cevada e trigo

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### ABSTRACT

The dumps of dolomite dropouts from road construction occupy huge arable areas in north-western Russia. Although coarse dolomite particles neglected as a liming material due to its slow solubility, we hypothesise that they can serve as a cheap and long-lasting liming material. The weight loss of dolomite particles of various sizes from the dump applied to *Albic Retisol* and its effect on assimilation of Ca and Mg by barley and wheat were studied. The pot experiment with 300 g soil was conducted for 30 days in a laboratory phytotron. Results showed that coarse particles of dolomite waste had a positive effect on soil acidity already at the initial phases of the experiment. In the process of dissolution of dolomite, all forms of soil acidity decreased. The cultivation of barley had a stronger effect on the dissolution of dolomite particles than the cultivation of wheat. Barley plants accumulated Ca by 1.1-1.4 times higher than wheat, other factors being identical. The relationship between the yield of green biomass and the accumulation of calcium and magnesium in the plants were empirically described using regression analysis. Results of this preliminary study showed that the by-products from dolomite stone processing can be effectively used for reclamation of strongly acidic soil in north-western Russia. This has the dual benefit of reducing the burden on the environment and reclaiming acidic soils. Further studies should include soil microbiological and biological parameters to trace the effect of root activities and dolomite dissolution rate on a field scale.

**Index terms:** Dolomite; dissolution; calcium.

### RESUMO

Os depósitos de dolomita abandonados pela construção de estradas ocupam enormes áreas aráveis no noroeste da Rússia. Embora as partículas grossas de dolomita sejam negligenciadas como material de cal devido à sua baixa solubilidade, hipotetizamos que elas podem servir como um material de cal barato e duradouro. Estudou-se a perda de peso de partículas de dolomita de vários tamanhos do lixão aplicado ao *Retisol Albic* e seu efeito na assimilação de Ca e Mg em cevada e trigo. O experimento em vasos com 300 g de solo foi conduzido por 30 dias em fitotron de laboratório. Os resultados mostraram que partículas grossas de resíduos de dolomita apresentaram um efeito positivo na acidez do solo já nas fases iniciais do experimento. No processo de dissolução da dolomita, todas as formas de acidez do solo diminuíram. O cultivo de cevada teve um efeito mais forte na dissolução de partículas de dolomita do que o cultivo de trigo. As plantas de cevada acumularam 1.1-1.4 vezes mais Ca que o trigo, sendo os demais fatores idênticos. A relação entre o rendimento de biomassa verde e o acúmulo de cálcio e magnésio nas plantas foi descrita empiricamente por meio de análise de regressão. Os resultados deste estudo preliminar mostraram que os subprodutos do processamento da pedra dolomítica podem ser efetivamente usados para recuperação de solo fortemente ácido no noroeste da Rússia. Isso tem o duplo benefício de reduzir a carga sobre o meio ambiente e recuperar solos ácidos. Estudos adicionais devem incluir parâmetros microbiológicos e biológicos do solo para rastrear o efeito das atividades radiculares e a taxa de dissolução da dolomita em escala de campo.

**Termos para indexação:** Dolomita; dissolução; cálcio.

## INTRODUCTION

Over the past 10 years, negative changes in the quality of agricultural land are mainly caused by a significant reduction in the use of all types of fertilizers and liming (Polyakov et al., 2022). Extensive researches are devoted to various aspects of the liming of acidic soils (Danilov; Yakovleva; Nikolaeva, 2020; Islam et al., 2021; Kamprath; Smyth, 2005; Lavrishchev et al., 2020; Litvinovich et al., 2021a, 2021b; Mohammed; Aman; Zewide, 2021; Nebolsin; Nebolsina, 2010; Opala, 2017). One of the problems of reclamation of acid soils is that most liming materials are quickly depleted in this soil due to leaching and fixation of cations (Lavrishchev et al., 2020; Rashid et al., 2021; Xu et al., 2022). Therefore, to control soil pH of acid soils it is necessary to regularly apply lime that is time and resource consuming, or to apply slow release synthesized lime materials that are expensive (Rashid et al., 2021).

Carbonate rocks are the most unstable components in the soil of humid and cool climate of north-west Russia. The main agents of abiotic destruction of carbonate rocks are water, solar thermal energy and carbon dioxide. Root exudates of plants, bacterial microflora, metabolic products of microflora, organic acids formed during the decomposition of organic residues and humic substances are important biotic factors in the dissolution process (Aye; Sale; Tang, 2016; Liang et al., 2021; Wang et al., 2016). At the same time assimilation of cations from the dissolved liming material is controlled by many factors, including plant physiology and soil properties that regulate antagonism/synergism effect during plant uptake (Bibi et al., 2022; Farina et al., 2008; Gaj et al., 2018; Gransee; Fühns, 2013).

Beside of neutralizing soil acidity, some positive effects of dolomite materials are their ability to remove some potentially toxic metals (Cu (2+) and Pb (2+)) from aqueous solution (Palansooriya et al., 2020; Pehlivan et al., 2009; Tangviroon et al., 2020; Trakal et al., 2011), to increase stability of soil aggregates (Zhan et al., 2022), to improve agrochemical properties of soil (Wu et al., 2021) and nutrition of crops (Serrano et al., 2020).

It is considered that the coarse particles of dolomite have a negligible neutralizing effect on soil acidity due to their slow solubility (Kamprath; Smith, 2005; Olego et al., 2016). Musil and Pavliček (2002) revealed that the dolomite particles of size > 1mm did not show any neutralizing effect on soil acidity in acidic soils in Poland. Similarly, Conyers, Scott and Whitten (2020), studied the effects of limestone particles of different sizes and suggested that the use of finer in size liming materials should remain a viable practice for

growers. However, the question of the rate of dissolution of large particles of dolomite remains unclear, especially in the profile of soddy-podzolic light soil against the background of various mineral fertilizers has not been fully studied and, in particular, the mechanisms of soil-lime-plant interaction have not been elucidated.

To date, in Leningrad region, Russia, about 70 million tons of dolomite screenings has been accumulated from rock processing. The use of dolomite by-products as an ameliorant could significantly reduce the severity of the problem of liming acidic soils in the region and at the same time solve the important environmental problem of reducing the areas occupied by dumps. Since 2011, the Soil Reclamation Laboratory of the Agrophysical Research Institute in St. Petersburg, has been conducting experiments aimed at establishing the rate of decomposition of dolomite particles of various sizes used as lime fertilizer.

It is well-known fact that the dissolution of large particles of lime in the soil occurs due to the contact exchange of the surface of the ameliorant with a soil, without affecting the inner layers of dolomite particle (Nebolsin; Nebolsina, 2010). Based on our previous studies (Litvinovich et al., 2021a; Pavlova et al., 2020), we assume that large particles of dolomite can have a prolonged liming and aftereffect on acidic soils and contribute to the assimilation of Ca and Mg ions by plants, since they are partially weathered while in the dumps.

The aim of the research was studying the dissolution of large particles of dolomite at the initial stage of growing spring grain crops in a pot experiments on acidic soddy-podzolic sandy loam soil. The research tasks included: (i) effect of local introduction of dolomite on soil acidic properties under growing crops; (ii) influence of liming and fertilization on accumulation of Ca and Mg by wheat and barley plants; (iii) dependences of plant productivity on the content of calcium and magnesium in their tissues.

## MATERIAL AND METHODS

### Characteristics of soil, plants and dolomite studied

In 2021, the experiment was carried out in a laboratory with a very strongly acidic soddy-podzolic sandy loam soil (*Albic Retisol* according to the World Reference Base for Soil Resources classification (Food and agriculture organization of the United Nations - FAO, 2014). The soil was taken under a natural perennial meadow in the Leningrad region (Russia) from a depth of 0-15 cm. The soil was air dried, ground and passed through a sieve with 1 mm mesh. The soil studied has  $pH_{KCl}$  3.75;

hydrolytic acidity (Hy) - 11.75 mmol<sub>c</sub>; content of humus - 3.02%; content of particles < 0.01 mm - 18.6%. The soil was sandy loam, silty-sandy variety and contained Ca<sup>2+</sup> and Mg<sup>2+</sup>: 0.44% and 0.47%, respectively.

### Design of the experiment

Two factor experiment was carried out in a laboratory. The first factor was type of grain crops: spring wheat (*Triticum aestivum* (L.)) and spring barley (*Hordeum vulgare* (L.)). The second factor included three types of mineral fertilizers: 1. Control; 2. NPK (16:16:16); 3. Chemically pure NH<sub>4</sub>NO<sub>3</sub> and 4. Chemically pure KCl. Fertilization doses were: NPK 0.360, NH<sub>4</sub>NO<sub>3</sub> 0.18 and KCl 0.90 g per pot, i.e., 300 g soil. The studying variable was large-size dolomite particles from the dump. The experiment was performed in four replications as follows: 300 g of air-dry soil passed through 1 mm mesh was placed on tray pots. The soil in the pots was conventionally divided into four equal segments. In each segment (except for the control plot), a large dolomite particles of a certain weight (from 1.5 to 2.8 g) were placed. CaCO<sub>3</sub> content in dolomite was 46.1%, MgCO<sub>3</sub> - 38.4%. Sowing of wheat and barley was carried out with sprouted seeds. The seeding rate was 100 plants per vessel. Sowing of plants was carried out with seeds that had hatched to a depth of 1 cm. The growing was carried out in a phytolapm installation with blue and red ranges: FAR (photosynthetic active radiation) sub-ranges of blue (400-500 nm) and red (600-700 nm). During the experiment, the soil moisture was maintained at 60% of the field moisture capacity. The experiment lasted 30 days.

Immediately after harvesting of wheat and barley, dolomite particles were taken out from the soil, and the adhered soil was removed from the surface with a brush. Then, the collected dolomite particles were dried at a of 105° C for 2 hours followed by weighing. The particle weight loss was determined by the difference. The soil from each pot was dried, mixed thoroughly, passed through a 1 mm sieve and used for the further analyses.

### Analytical methods

Physicochemical parameters of the soil were determined by conventional methods: humus by wet combustion according to the Tyurin method (Novitsky et al., 2021), hydrolytic acidity according to the Kappen method (Novitsky et al., 2021), pH<sub>KCl</sub> was determined on a glass electrode potentiometer (Mettler Toledo) in 1:4 solution. Amount of exchangeable calcium and magnesium were determined by complexometric method (Novitsky et al., 2021). The barley and wheat plants were dried, weighed,

crushed and ashed in a muffle stove at a temperature of 550°C. The ash was dissolved in the concentrated nitric acid followed by determination of Ca and Mg on the Perkin-Elmer atomic absorption spectrophotometer.

### Data processing

For data analysis, the regression analysis method was used. The empirical dependence was determined using the regression analysis method. The statistical significance of the empirical model (dependence) is given by the p-value coefficients (according to the F-criterion) and the coefficient of determination. The development of empirical dependences (models) of the yield of the vegetative mass of barley and wheat on the content of Ca and Mg in plant tissues was determined using the regression analysis method (Bure, 2007).

## RESULTS AND DISCUSSION

### Dolomite weight loss under wheat and barley

After harvesting of wheat and barley in 30 days, the weight loss of dolomite particles was established in all treatments of the experiment (Table 1). In the pots with wheat weight loss ranged between 0.025 to 0.031 g in 30 days and in pot with barley the weight loss ranged between 0.047-0.077 g in 30 days in absolute weight, depending on the treatment. In relative terms, when treated with the NPK, the weight loss in the pot with wheat was 1.58% of the applied amount, in the pot with barley - 2.67%, in the soil fertilized with NH<sub>4</sub>NO<sub>3</sub> - 1.45% and 2.89 % for wheat and barley, respectively. In the soil with addition of KCl it was 1.23% and 4.56 % for wheat and barley, respectively. This result imply that the surface of dolomite particles, already at the initial stage of interaction with the soil, undergoes dissolution, as a result of which Ca and Mg cations pass into a plant available forms.

In our experiment, taking into account the identity of all factors, except for the type of crop, the rhizospheric activity of barley and its effect on the rate of dissolution of dolomite turned out to be higher than that of wheat. This assumption is supported by earlier findings, where 22 days of composting large particles of dolomite with soil without growing plants, did not result in the dissolution of dolomite in most cases (Pavlova et al., 2020). In their study, the decrease in the weight of dolomite depended on the composting time and the period of their storage in dumps. On the other hand, the physiological and biological activity of the rhizosphere and soil microorganisms, as well as the products of their metabolic activity, have a strong influence on the rate of dissolution of calcareous materials (Aye; Sale; Tang, 2016; Liang et al., 2021; Wang et al., 2016).

**Table 1:** Weight loss of dolomite particles when growing wheat and barley for 30 days.

Treatment	Particle weight at start point, g <sup>†</sup>	Particle weight after dissolution, g	Particle weight loss, g	Weight loss, % of the initial weight
Wheat				
Control	-	-	-	-
NPK	1.838	1.809	0.029	1.58
NH <sub>4</sub> NO <sub>3</sub>	2.127	2.096	0.031	1.45
KCl	2.024	1.999	0.025	1.23
Barley				
Control	-	-	-	-
NPK	1.946	1.894	0.052	2.67
NH <sub>4</sub> NO <sub>3</sub>	1.628	1.581	0.047	2.89
KCl	1.700	1.623	0.077	4.53

<sup>†</sup> dolomite particle weight, average of 4 replicates for each treatment.

Moreover, the study of Lavrishchev et al. (2022) showed that the rate of dissolution of liming materials in the soil is influenced both by the species of plants, and also by the varietal characteristics of plants. The later research found that the residual amount of carbonates after harvesting of 6 varieties of spring wheat ranged from 9.3 to 25% of the applied amount (Litvinovich et al., 2015) given all other factors identical. Unlike plant species, the role of mineral fertilizers used in the experiment could not be identified.

#### Effect of treatments on soil acidity

The natural soil was very strongly acidic ( $\text{pH}_{\text{KCl}}$  3.75 and Hy -11.75  $\text{mmol}_c$ ). After 30 days of the experiment, the soil from the category of “very strongly acidic” moved to the category of “strongly acidic” in all treatments regardless of the cultivated crop (Table 2). Cultivation of barley had a more significant effect on the hydrolytic acidity (Hy). At the start of the experiment, it was equal to 11.75  $\text{mmol}_c$ , then after harvesting plants, the fluctuations between the treatments ranged from 8.92 to 9.7  $\text{mmol}_c$ , i.e., decreased by 2.85-1.05  $\text{mmol}_c$ .

The value of hydrolytic acidity (Hy) allows determining the entire possible spectrum of acids present in the soil and as thus should be a mandatory analysis on acidic soils with application of lime. Throughout the data set, an average negative relationship was established between the weight loss of dolomite particles and the Hy ( $r = -0.68$ ). Consequently, the more the mass of dolomite particles in the soil decreases over 30 days of growing crops, the lower the value of Hy. This suggests that the large particles of dolomite already at the initial stage of dissolution have a positive effect on soil acidity.

**Table 2:** Acidic properties of soddy-podzolic loamy soil after harvesting plants.

Treatment	$\text{pH}_{\text{KCl}}$	Hy	Ca
		$\text{mmol}_c$	
Wheat			
Control	4.04a	10.95a	2.06a
NPK	4.14b	10.40a	2.06a
NH <sub>4</sub> NO <sub>3</sub>	4.19ba	11.33b	1.94a
KCl	4.09a	11.88b	1.81ba
LSD <sub>05</sub>	0.06	0.54	0.54
Barley			
Control	4.07a	9.63a	2.06a
NPK	4.12a	9.40a	1.95a
NH <sub>4</sub> NO <sub>3</sub>	4.18ba	8.92b	1.85ba
KCl	4.09a	9.70a	1.81b
LSD <sub>05</sub>	0.05	0.32	0.51

#### Effect of the treatments on green biomass and Ca and Mg content in plants

The use of mineral fertilizers and liming had a positive effect on the productivity of the biomass of barley and wheat. The maximum green biomass was in the treatment with the use of full mineral fertilizer (NPK). The productivity of plants in the treatments with the application of only nitrogen and only potassium fertilizers was lower (Table 3). According to the influence on the green biomass, the studied treatments can be arranged in the following

descending order: NPK > KCl >  $\text{NH}_4\text{NO}_3$  > control. The total yield of dry mass of plants in fertilized treatments with barley, was 1.91, 1.69 and 1.43 times higher compared to the control, respectively. In the treatments with wheat, it was 1.49, 1.22 and 1.3 times, respectively.

**Table 3:** Yield of wheat and barley and accumulation of Ca and Mg (%) by crop tissues.

Treatment	Yield, g vessel <sup>-1</sup>	Ca	Mg	Ca + Mg
Wheat				
Control	0.79a	0.56a	0.352a	0.912
NPK	1.18b	0.46b	0.311b	0.771
$\text{NH}_4\text{NO}_3$	0.96ab	0.49b	0.405c	0.895
KCl	1.06ab	0.52ab	0.310b	0.830
LSD <sub>05</sub>	0.12	0.11	0.120	-
Barley				
Control	0.65a	0.78a	0.374a	1.154
NPK	1.20b	0.61b	0.306b	0.916
$\text{NH}_4\text{NO}_3$	0.90b	0.62b	0.410a	1.03
KCl	1.10b	0.55c	0.306b	0.856
LSD <sub>05</sub>	0.07	0.09	0.095	-

The Ca concentration in wheat plants ranged from 0.46 (in NPK) to 0.56% (in control), while in barley tissues it ranged from 0.55 (in KCl treatment) to 0.78% (in control treatment), i.e., Ca accumulation in plant tissues of barley was for 1.1-1.4 times higher than in wheat. Considering the identical conditions other than crop type we assume that the different effects of the root exudates of wheat and barley on dolomite dissolution, determined the differences in the accumulation of calcium in the tissues of wheat and barley. Differently, assimilation of Mg by both crops showed that the greatest amount was in the treatments with  $\text{NH}_4\text{NO}_3$ , which had the highest pH value. This is probably related to the antagonistic/synergetic effect of Mg uptake, since the uptake of Mg is strongly influenced by the availability of other cations like  $\text{NH}_4$ , Ca and K (Gransee; Fühns, 2013; Fageria, 2001; Römheld; Kirkby, 2007).

A dolomite rock composed exclusively of mineralogically pure dolomite ( $\text{CaMgCO}_3$ )<sub>2</sub> is rare. More often dolomite rock consists of  $\text{CaCO}_3$ ,  $\text{MgCO}_3$  and double salt. In this case, calcite and magnesite form a calcium cement that holds the rhombohedral crystals of double carbonate together (Zhang et al., 2021). According to the degree of dissolution, they can be arranged in the following

descending order: calcite > magnesite > dolomite. The different nature of the accumulation of Ca and Mg by plants when using different fertilizers with and without dolomite is most probably attributed to the level of soil pH changes, and possibly the antagonistic interaction of fertilizer nutrients and Ca and Mg released from dolomite (Gransee; Fühns, 2013; Rietra et al., 2017; Xie et al., 2021). And the difference in the accumulation of calcium and magnesium in barley and wheat plants is probably due to the different compliance of the dissolution of carbonates by root exudates of these plants.

The insignificance of the dependence of yield on Ca and Mg calculated separately was probably due to impossibility of isolating the effect of calcium and magnesium separately, due to the fact that their effect is of a similar nature, and it is more correct to consider their sum.

One of the objectives of this experiment was the development of empirical dependencies (models) describing the relationship between grain crops and the accumulation of alkaline earth metals in their tissues. Dependences were developed separately for calcium, for magnesium, and for calcium and magnesium considered together (two-factor model), as well as for the sum of Ca + Mg (Table 4). The empirical dependences of the crop yield on the concentration of Ca and Mg in barley tissues were statistically significant. Of all the empirical models describing the yield of barley, the Ca + Mg factor was the best. Empirical models of the dependence of yield on Ca and Mg separately turned out to be significantly worse.

**Table 4:** Dependence of the green biomass of grain crops on the concentration of Ca and Mg in their tissues.

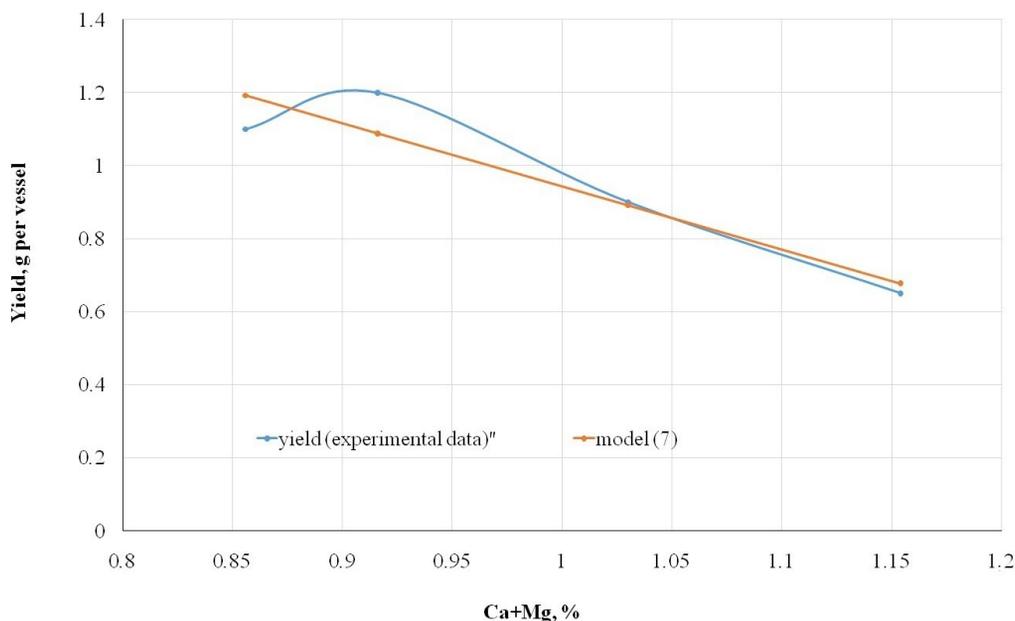
Parameter	Model	p-value	R <sup>2</sup>
Wheat			
Ca		0.15	0.71
Mg		0.47	0.29
Ca+Mg		0.04	0.91
Ca, Mg		0.18	0.97
Barley			
Ca		0.13	0.75
Mg		0.26	0.54
Ca+Mg		0.06	0.88
Ca, Mg		0.35	0.88

$x_1$  - Ca concentration,  $x_2$  - Mg concentration,  $x_3$  - Ca + Mg concentration,  $y$  - yield, g vessel<sup>-1</sup>.

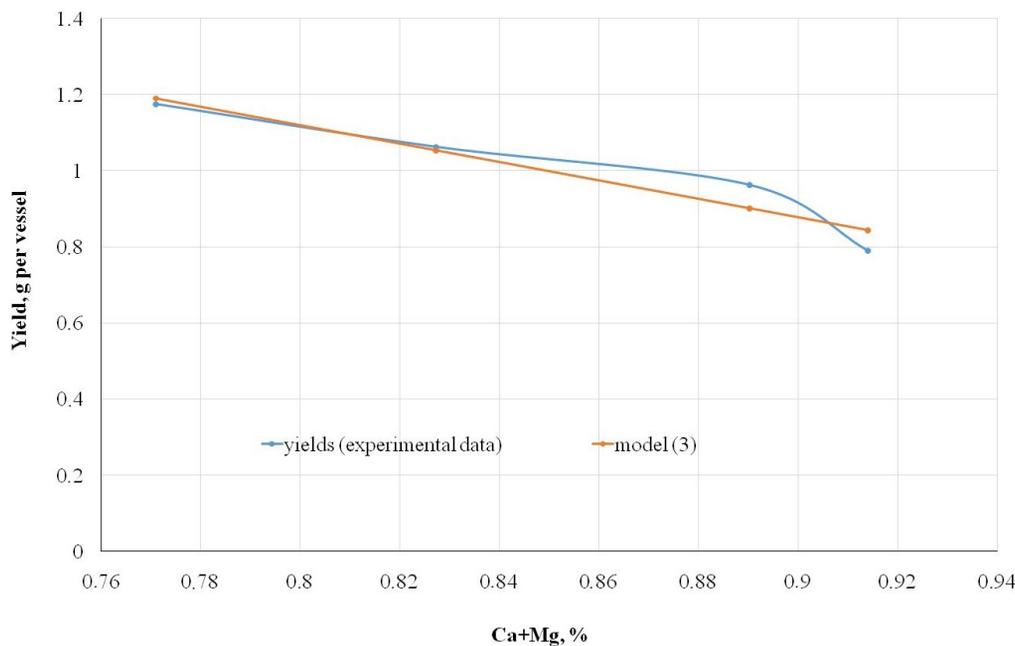
Figure 1 shows that the dependence of barley yield on the Ca + Mg factor is close to linear, which is convincingly confirmed by model No. 7 for barley.

The linear empirical dependence of wheat yield on calcium content, the sum of calcium and magnesium (Ca +

Mg), as well as calcium and magnesium considered together, also was statistically significant. The relationship between wheat yield and magnesium concentration could not be identified. Similarly as for barley, the dependence of wheat yield on the sum of Ca + Mg turned out to be the best (Figure 2).



**Figure 1:** Dependence of the yield of the vegetative mass of barley on the content of Ca + Mg in plant tissues of barley.



**Figure 2:** Dependence of the yield of the vegetative mass of wheat on the content of Ca + Mg in plant tissues.

## CONCLUSIONS

Dolomite by-products can be widely used in the region as an ameliorant of a long-lasting effect, since large particles of dolomite gradually release Ca and Mg cations. Barley and wheat has different effect on the rate of dolomite dissolution. The results obtained can be applied for rational land use, both from the point of view of soil quality and from the point of view of saving resources,

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## AUTHOR CONTRIBUTION

Conceptual idea: Litvinovich, A.; Lavrishchev, A.; Methodology design: Litvinovich, A.; Lavrishchev, A.; Data collection: Lavrishchev, A.; Kekilbayeva, G.; Data analysis and interpretation: Zhapparova, A.; Bure, V.; Saljnikov, E.; Writing and editing: Litvinovich, A.; Saljnikov, E.

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