Dynamics of weight loss of dolomite dropouts at different stages of dissolution in *Albic Retisol*

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Abstract

In a laboratory experiment in 2020, the dynamics of the decrease in mass of large particles of dolomite dropouts in acidic *Albic Retisol* was established. Dolomite dropouts were collected from the landfill of a road construction factory. The results of the laboratory experiment showed that after 114 days of composting, the loss of dolomite mass ranged from 8.7 to 34.2 % of its initial content. The loss of mass of particles during composting from 114 to 224 days slowed down and fluctuated, depending on the variant, from 2.2 to 5.1 % of the initial mass of dolomite. The mechanism of weathering was considered and the factors enhancing the rate of dissolution of dolomite dropouts in the soil were revealed. Linear empirical dependencies of the rate of dissolution of dolomite in soil at different stages of the experiment were developed. Clustering of the developed models was carried out according to the absolute values of the rate of decrease in the mass of particles in the vessels. When selecting the dose of application of large particles of dolomite for reclamation of acidic soils and duration of their action, it is recommended to take into account the duration of time the dolomite spent in the landfill.

**Keywords:** dolomite, particle size, dissolution rate, weathering, dump, clustering

Introduction

Many research projects have shown that the effectiveness of liming materials primarily depends on its neutralizing capacity and its fineness (particle size) (Musil and Pavliček, 2002; Edmeades and Ridley, 2003; Álvarez, Viadé and Fernández-Marcos, 2009; Wu et al., 2021). When producing crushed stone from carbonate rocks used for road construction, dolomite particles less than 10 mm in size are deposited in waste dumps. Dolomite is less soluble than limestone and therefore needs to be finely ground for a quick neutralizing effect on soil acidity (Kamp-rath and Smyth, 2005). It is thought that the coarse particles of dolomite have a negligible effect on soil due to their slow solubility (Kamprath and Smyth, 2005; Olego et al., 2016). Finer liming particles provide more reactive surface area for neutralizing excess H ions in soil solution. Musil and Pavliček (2002) revealed that the dolomite particles of size > 1 mm did not show any neutralizing effect on soil acidity in acidic soils in Poland.

The main agents for abiotic destruction of carbonate rocks are water, solar energy, and carbon dioxide. Important biotic factors of the dissolution of carbonates are root growth (Wen et al., 2021) and root exudates (Litvinovich, Kovleva and Pavlova, 2021).
Pavlova, 2015), bacterial microflora (Aristovskaya, 1980; Maurice, Lee and Hersman, 2000; Maurice et al., 2001a, 2001b; Zvyagintsev, Babeva and Zenova, 2005; Salih et al., 2019), products of microflora metabolism (Paris, Botton and Lapeyrie, 1996; Wallander and Wickman, 1999; Ehrlich, 2002; Wang et al., 2016), organic acids formed during the decomposition of organic residues (Ponomareva, 1964; Sokolova and Nyuzhenovskaya, 1973; Schnitzer and Kodama, 1976; Kodama, Schnitzer and Jaakkimainen, 1983; Marcia-Benitez et al., 2020). Despite the well-defined theoretical concepts of the mechanism of weathering of carbonate rocks in soils, the question of the rate of dissolution of large particles of dolomite remains unclear.

To date, Leningrad Region (Russia) has accumulated about 70 million tons of dropouts in landfills occupying huge land areas (Fig. 1). Their use 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. In addition, dolomite limestone can also be effective for chemical immobilization of potentially toxic elements in soil, particularly in metal-contaminated soils (Trakal et al., 2011; Palansooriya et al., 2020; Tangviroon et al., 2020) and can improve the quality of the soil (Wu et al., 2021) and cultivated crops (Serrano et al., 2020).

Since 2011, the Laboratory of Soil Reclamation of the Agrophysical Research Institute (St Petersburg, Russia) has been studying the reclamation properties and fertilizing value of large fractions of dolomite dropouts applied to soil in deliberately high doses (Litvinovich et al., 2016, 2017, 2018a, 2018b, 2019; Salaev and Litvinovich, 2018). The theoretical prerequisite for conducting this research was the well-known fact that with an increase in the dose of large particles of liming material, the effect of the fineness of grinding is leveled.

Previously, in the long-term field experiments carried out on Albic Retisols (WRB 2015) of different acidity levels, after six experimental years, the presence of undecomposed dolomite particles of sizes 3–5, 5–7 and 7–10 mm was visually established in the soil. At the same time, the effect of their use in an amount calculated by three and five doses of hydrolytic acidity was not inferior to dolomite flour applied in a scientifically based amount (1 Hy) (Litvinovich et al., 2016, 2021).

The aim of this research was to establish the weight loss of the large-size particles of dolomite dropouts during dissolution under long-term composting with strongly acidic Albic Retisols sandy loam soil. The tasks included:

- to develop linear empirical relationships (models) describing the processes of decomposition of large-size dolomite particles in the soil;
- to determine the rate of dissolution of dolomite at different stages of the experiment;
- to cluster the developed dependencies according to the absolute values of the rate of decrease in the mass of particles in the vessels.

![Fig. 1. Dumps of dolomite dropouts from stone processing factory, in St Petersburg region, Russia.](image-url)
Materials and methods

Description of studied soil and dolomite

The experiment was initiated in 2020 in the laboratory of the Agrophysical Research Institute, St Petersburg, Russia, and continues to date. The objects of research were acidic soddy-podzolic sandy loam soil sampled from natural grassland (Albic Retisol, WRB 2015) and large particles of dolomite, which had been in landfills for various years.

The total chemical composition and particle size distribution of the upper humic horizon is presented in Table 1 and Table 2. The soil selected for the study was sandy loamy silty-sandy according to Kachinsky classification and contained insignificant amounts of calcium and magnesium cations. The total chemical composition of the soil was determined by the sintering method (Novitsky, Donskikh and Chernov, 2009). The particle size distribution of the soil was determined by the Kachinsky method (Novitsky, Donskikh and Chernov, 2009).

The content of CaCO$_3$ in the dolomite was 46.1%; MgCO$_3$ — 38.4%. Since dolomite is supposed to be widely used for reclamation of acidic soils, its ecological safety was checked. In terms of the content of potentially toxic elements (heavy metals), the investigated dolomite did not pose a threat to soil and plant pollution (Table 3). The chemical composition of the dolomite was determined by atomic absorption spectroscopy on an AAS-9000 (Shimadzu, Japan).

Experimental design

The experimental procedure was as follows: 200 g of air-dry soil, previously passed through a sieve with 1 mm mesh, was poured into a glass beaker. A granule of dry dolomite of a strictly defined mass of around 3 g was placed in each vessel (Table 4). The soil was moistened to a value corresponding to 60% of the total field moisture capacity. Composting was carried out in a thermostat at a temperature of 24 °C. The five vessels (no. 1, 2, 3, 4 and 5) were weighed daily, the amount of evaporated moisture was added, and the soil was thoroughly mixed. The difference between the vessels was in the mass of the granule placed in the soil and the degree of its weathering.

The decrease in the mass of dolomite particles in each vessel was established 22, 61, 81, 114, 144, 174, 204, 224 days after the experiment was set up. To do so, dolomite granules were removed from the soil, and the soil adhered to the surface of the particles was removed with a brush. Before weighing, dolomite granules were dried at 105 °C for two hours. Next, composting was carried out again by returning the dolomite to the soil. The entire period of the experiment was conventionally divided by approximately 100 days to compare the rate of dissolution of dolomite at these stages: from 1 to 114 and from 114 to 224 days.

The dynamics of mass loss of dolomite particles were statistically processed and the appropriate models were constructed (Bure and Parilina, 2013).

Results and discussion

The data in Table 4 indicate that over 22 days, the decrease in the mass of dolomite particles in most cases could not be established. On the 61$^{st}$ day, the losses ranged from 4.1 to 8.2% of the applied amount. In the interval between 61 and 114 days, the loss of particle mass in individual vessels increased to 34.2, 8.7, 11.8, 17.6 and 14.5% of the initial mass of applied dolomite, depending on the variant (Vessel no.) (Table 4).

Unequal rates of decomposition of the dolomite particles in the soil occurred because the dolomite par-
particles were partially weathered during open-air storage in the landfill. The intensity of weathering depends on the time and placement of the particles in the landfill (on the surface of the dump or buried under a layer of dolomite particles), the size of the dolomite particles, the rate of moisture infiltration, as well as the intensity of precipitation and other weather conditions during this period. Consequently, when entering the soil, the dissolution rate of dolomite particles of various degrees of weathering is different.

The empirical dependencies of the weight loss of dolomite particles for the first 114 experimental days are presented in Table 5.

The empirical models are statistically significant at a very high level of significance. The coefficient of determination fluctuated — $R^2 = 0.88 - 0.99$. The dissolution rate at the first stage of the experiment was: $v_{1.1} = -0.0087$, $v_{2.1} = -0.0025$, $v_{3.1} = -0.0035$, $v_{4.1} = -0.005$, $v_{5.1} = -0.0042$.

Figure 2 shows the linear trends in the decrease in the mass of particles in individual vessels of the experiment. Taking into account the average values of the absolute values of the rate of decrease in the mass of dolomite particles in individual variants and the type (slope) of trends, the following clustering of variants can be proposed. Group 1 includes vessel No. 1, since the average rate of decrease in the mass of dolomite for 114 days was much higher than the other average rates in their groups (Table 5). Group 2 includes vessel No. 2, since the average rate of decrease in the dolomite mass in 114 days was significantly less than in all other variants of the experiment. Group 3 includes vessels No. 3, 4 and 5. The average rates of decrease in the mass of dolomite for 114 days in these variants differed little from each other and they were significantly less than in vessel No. 1 and much more than in the vessel No. 2.

The process of dissolution of dolomite particles continued in the second stage of the experiment (the inter-

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Table 4. Weight loss of dolomite dropouts (g) during composting with soil and the proportion of dissolved dolomite from its initial content, % (in brackets)

<table>
<thead>
<tr>
<th>Vessel no.</th>
<th>Composting period, days</th>
<th>Empirical dependences</th>
<th>$R^2$</th>
<th>$p$-value</th>
<th>Dissolution rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0–22</td>
<td>$y_{1.1} = 3.3 - 0.0087 \cdot t$</td>
<td>$R^2 = 0.77$</td>
<td>0.048</td>
<td>$v_{1.1} = -0.0087$</td>
</tr>
<tr>
<td>2</td>
<td>0–22</td>
<td>$y_{1.2} = 3.16 - 0.006 \cdot t$</td>
<td>$R^2 = 0.84$</td>
<td>0.0004</td>
<td>$v_{1.2} = -0.006$</td>
</tr>
<tr>
<td>3</td>
<td>0–114</td>
<td>$y_{1.3} = 2.14 - 0.0006 \cdot t$</td>
<td>$R^2 = 0.85$</td>
<td>0.02</td>
<td>$v_{1.3} = -0.0006$</td>
</tr>
<tr>
<td>4</td>
<td>0–22</td>
<td>$y_{1.4} = 3.09 - 0.0035 \cdot t$</td>
<td>$R^2 = 0.96$</td>
<td>0.0037</td>
<td>$v_{1.4} = -0.0035$</td>
</tr>
<tr>
<td>5</td>
<td>0–22</td>
<td>$y_{1.5} = 3.03 - 0.0022 \cdot t$</td>
<td>$R^2 = 0.99$</td>
<td>6.10^{-45}</td>
<td>$v_{1.5} = -0.0022$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vessel no.</th>
<th>Period, days</th>
<th>Empirical dependences</th>
<th>$R^2$</th>
<th>$p$-value</th>
<th>Dissolution rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>114–224</td>
<td>$y_{2.1} = 2.9 - 0.0007 \cdot t$</td>
<td>$R^2 = 0.98$</td>
<td>0.0008</td>
<td>$v_{2.1} = -0.0025$</td>
</tr>
<tr>
<td>2</td>
<td>114–224</td>
<td>$y_{2.2} = 3.1 - 0.0017 \cdot t$</td>
<td>$R^2 = 0.94$</td>
<td>0.0007</td>
<td>$v_{2.2} = -0.0007$</td>
</tr>
<tr>
<td>3</td>
<td>114–224</td>
<td>$y_{3.1} = 3.09 - 0.0035 \cdot t$</td>
<td>$R^2 = 0.96$</td>
<td>0.0037</td>
<td>$v_{3.1} = -0.0035$</td>
</tr>
<tr>
<td>4</td>
<td>114–224</td>
<td>$y_{3.2} = 3.03 - 0.0022 \cdot t$</td>
<td>$R^2 = 0.99$</td>
<td>6.10^{-45}</td>
<td>$v_{3.2} = -0.0022$</td>
</tr>
<tr>
<td>5</td>
<td>114–224</td>
<td>$y_{4.1} = 3 - 0.005 \cdot t$</td>
<td>$R^2 = 0.94$</td>
<td>0.005</td>
<td>$v_{4.1} = -0.005$</td>
</tr>
<tr>
<td>6</td>
<td>114–224</td>
<td>$y_{4.2} = 2.94 - 0.003 \cdot t$</td>
<td>$R^2 = 0.89$</td>
<td>0.0001</td>
<td>$v_{4.2} = -0.003$</td>
</tr>
<tr>
<td>7</td>
<td>114–224</td>
<td>$y_{5.1} = 3.07 - 0.0042 \cdot t$</td>
<td>$R^2 = 0.97$</td>
<td>0.0013</td>
<td>$v_{5.1} = -0.0042$</td>
</tr>
<tr>
<td>8</td>
<td>114–224</td>
<td>$y_{5.2} = 3.07 - 0.0042 \cdot t$</td>
<td>$R^2 = 0.93$</td>
<td>0.0007</td>
<td>$v_{5.2} = -0.0001$</td>
</tr>
<tr>
<td>9</td>
<td>114–224</td>
<td>$y_{5.3} = 3 - 0.0026 \cdot t$</td>
<td>$R^2 = 0.91$</td>
<td>0.00005</td>
<td>$v_{5.3} = -0.0026$</td>
</tr>
</tbody>
</table>
val between 114–224 days). The weight loss of dolomite in the second stage was recorded in all variants of the experiment. However, the rate of dissolution decreased significantly. During the first 114 days, the weight loss, depending on the variant, ranged from 8.7 to 34.2%, but over the next 110 days, the losses in some variants varied from 2.2 to 5.1%. Thus, as the experiment proceeded, regardless of the variant, the dissolution of large particles of dolomite in the soil slowed down.

These dynamics are explained as follows: Dolomite in the landfill undergoes physical destruction (weathering of the granule surface). In the process of weathering of the outer layer, it acquires a certain friability (Baqués et al., 2020) and, when it enters soil, the loose particles quickly dissolve. Further, the dissolution rate slows down, since the inner layers are more durable.

In Litvinovich et al. (2021), we showed that the dynamics of pH_KCl change in the treatments using particles of 5–7 and 7–10 mm size, regardless of the dose of application, had a similar pattern. It followed the regularity: a sharp increase in the pH value after the first year of the experiment; then after the second year, the pH_KCl decreased; in the third year, the pH increased again, and then in the fourth, fifth and sixth years, the fluctuations of soil pH in individual treatments were insignificant.

The average rates of decrease in the mass of dolomite particles in the interval from 114 to 224 days differed little from each other: \( v_{1,3} = -0.0006, v_{2,3} = -0.0007, v_{3,3} = -0.001, v_{4,3} = -0.001, v_{5,3} = -0.001 \).

The graphs of the models built for this time interval are almost parallel to each other (Fig. 3).

The empirical dependencies of the rate of dissolution of dolomite particles for the entire period of the experiment (224 days) are given in Table 5. All constructed empirical dependencies are statistically significant at a high level of significance. Therefore, all average rates for 224 days are also statistically significant at a high level of significance. This implies that the conclusions about the variants clustered based on the values of the average rates and on the constructed empirical dependencies are quite reasonable. Figure 4 shows the graphs of the models for the entire study period (224 days).

According to Figure 4 and the numerical values of the average rates of loss of the mass of dolomite, the three groups are identified for the entire duration of the experiment (224 days) — Group 1 includes vessel No. 1 with a much higher rate of decrease; Group 2 includes vessel No. 2 with the lowest rate of decrease; and Group 3 includes vessels No. 3, 4 and 5, which differed little from each other and fell between the rates of Group 1 and 2.
Fig. 3. Dependencies of the dissolution of dolomite particles for the interval 114–224 days of the experiment.

Fig. 4. Dependencies of the dissolution of dolomite particles for the 224 days of the experiment.
The clustering of the average rates of the decrease in the mass of particles in the soil over the entire study period (224 days) exactly corresponded to the clustering of the experimental variants at the first stage of the experiment (114 days). Consequently, the rate of loss of mass of granules during dissolution in soil was largely determined by the degree of weathering (dissolution) of the outer layer of particles in the landfill, while the inner layers of dolomite were protected from weathering. At the second stage of the experiment, their dissolution in the soil significantly slowed down and differed little in individual vessels.

Thus, after 224 days of the experiment, the decrease in the mass of dolomite particles in the soil of individual variants of the experiment ranged from 11.3 to 36.4%. This implies that large particles of dolomite are not “ballast.” They gradually dissolve in the soil, transferring calcium and magnesium cations into solution.

At the same time, the experiment showed how differently dolomite granules dissolve during composting. Obviously, when determining the dose of application of large particles of dolomite for liming, one should take into account the time spent in the landfill. The longer this period, the less time it will take to dissolve.

When carbonate rocks enter the soil, during contact exchange of the surface of particles with the soil, they gradually dissolve. First, the destruction of structural bonds occurs due to the dissolution of the cryptocrystalline carbonate substance located between the carbonate crystals (Gagarina, 1968; Anter, Hilal and El-Damaty, 1973; Makeicheva, 1991; Salih et al., 2019). At this stage, the process of dissolution does not affect the inner layers of the granules. When dolomite screenings have been in waste dumps for a long time, the porosity of large particles of carbonates and their surface roughness increase due to weathering, while their size and density decrease. This increases the access of aggressive solutions to the carbonates of the inner layers and accelerates their dissolution. Ultimately, the weathering of dolomite yields dolomite flour, which is loose accumulations of dolomite crystals accumulated at the site of dissolution of carbonate cement (Yarg, 1974; Morad, 1998).

The experiment was conducted in a pure soil without cultivated crops that would influence the solubility of dolomite particles (Wen et al., 2021) and absorb cations from local soil foci adjacent to the surface of the ameliorant (Nebolsin and Nebolsina, 2010). Nevertheless, the results of the laboratory monitoring of the rates of dissolution of the large particles of dolomite dropouts contributed to a better understanding of the dynamics of dolomite dissolution in soil.

Generally, the study showed that after a long period of composting, a significant amount of undecomposed carbonates remains in the limed soil, suggesting their long-term aftereffect. Consequently, large particles of dolomite applied into the soil in deliberately overestimated doses can be regarded as a long-acting ameliorant. This finding may suggest choosing such a dose of large dolomite particles for liming, at which the annual plant demand for calcium and magnesium as nutrients will be fully satisfied, and unproductive losses due to migration are minimized. In addition, the widespread use of dolomite dropouts will reduce the severity of the liming problem in regions where dolomite screenings are deposited in landfills, and will also free up some land currently occupied by these landfills.

Conclusions

1. In the process of long-term composting of large particles of dolomite (~ 3 g) with a strongly acidic soddy-podzolic sandy loam soil, the decrease in the mass of dolomite particles 114 days after the interaction ranged from 8.7 to 34.2% of the applied amount. After 224 days, the amount of dissolved dolomite increased from 11.3 to 36.4%.

2. The dissolution rate at the first stage of the experiment (0–114 days) was: \( v_{1.1} = -0.0087, \ v_{2.1} = -0.0025, \ v_{3.1} = -0.0035, \ v_{4.1} = -0.005, \ v_{5.1} = -0.0042 \). Average rates of decrease in the mass of dolomite particles in the range from 114 to 224 days were: \( v_{1.3} = -0.0006, \ v_{2.3} = -0.0007, \ v_{3.3} = -0.001, \ v_{4.3} = -0.001, \ v_{5.3} = -0.001 \).

3. Linear empirical dependencies of the rate of dissolution of dolomite in soil at different stages of the experiment have been developed. Clustering of the developed models was carried out according to the absolute values of the rate of decrease in the mass of particles in the vessels.

4. The rate of dissolution of dolomite in soil differs significantly and depends on the time of dolomite storage in landfills. When determining the dose of application of large particles of dolomite for reclamation of acidic soils and the duration of their action, it is proposed to take into account the duration of time the dolomite has been in the landfill.

References


