

Changes in Mn availability and soil acidity in *Albic Retisol* limed with dolomite screenings of various sizes and doses: A long-term microfield experiment in the north-western Russia

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Abstract

Liming of acidic soils is associated with various processes in the soil, including the availability of nutrients for plants. The vector and extent of these changes depend, inter alia, on the type of lime material and the doses used. Particularly, excessive liming can trigger a deficiency of manganese for crops. A long-term microfield experiment (13 test years) was carried out on *Albic Retisols* reclaimed with the dolomite particles of various sizes as a by-product of stone processing quarries. Ten treatments including various sized dolomite particles and their combinations, as well as traditional limestone flour on the background of NPK fertilizer were studied for the changes in soil acidity indicators (exchangeable acidity, pH; hydrolytic acidity, Hy; total acidity, H_{tot}) and manganese availability. The amount of acidic components passing into the extract of 1N KCl was insufficient to reveal a dependency between the exchangeable acidity and the content of mobile manganese in the soil of most treatments limed with dolomite particles of various sizes. However, the relationship between the content of mobile Mn in soils and the value of hydrolytic acidity was proved by paired linear regressions. Regardless of the dose and size of dolomite particles added, the soil was highly and moderately supplied with plant available manganese during the entire study period.

Keywords: Retisol, dolomite screenings, manganese, hydrolytic acidity, dependency.

Introduction

Manganese (Mn) is an important micronutrient for plant growth and development in metabolic processes in a plant cell. Mn is one of the most abundant metals in soil and comprises about 0.1% of the Earth's crust (Emsley, 2003; Alloway, 2008). In *Albic Retisols* (IUSS, 2014), the concentration of mobile manganese ranges from 0.008 to 0.4 mmol (eq)/100 g of soil. Its amount depends on many factors, including total reserves of Mn in soil, soil acidity, concentration of exchangeable hydrogen, water and air regime of soil (Behera and Shukla, 2014; Rengel, 2015), as well as particle size distribution (Nebolsin and Nebolsina, 2010; Alejandro, Höller, Meier, and Peiter, 2020).

The mobility of manganese increases from soils with an alkaline reaction to neutral and further to acidic soils (Lukin, Avramenko, and Melentsova, 2006; Behera and

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Shukla, 2014; Rengel, 2015; Alejandro, Höller, Meier, and Peiter, 2020; Jatav et al., 2020). Its solubility depends on soil redox condition, pH, organic matter, clay fraction etc. Diatta et al. (2014) found that among studied four microelements the Mn was the least available to crops in the following order: $Zn < Cu < Fe < Mn$. The correlation coefficient between pH_{KCl} and $\log Mn$ for soils of different particle size distribution ranges from 0.10 to 0.35. In the specific conditions of an individual experiment, the closeness of the correlation between pH_{KCl} and $\log Mn$ is much more significant: $R = -0.74 - 0.80$ (Nebolsin and Nebolsina, 2002). Solubility of Mn in soils generally decreases with the increasing pH due to adsorption-precipitation, i.e., oxidation-reduction reactions (Haynes and Swift, 1985; Sparks, 2003; Rengel, 2015). Although Mn belongs to the class of low toxicity for soil living organisms (Pronko et al., 2022), an excess of available manganese in the soil can lead to its actual and potential toxicity to plants, while an increase in soil pH due to liming can lead to Mn unavailability to plants (Alejandro, Höller, Meier, and Peiter, 2020; Jatav et al., 2020).

Albic Retisol is an acid soil formed on unconsolidated glacial till under percolation water regime and therefore with high rates of cation leaching (Meng et al., 2019). In particular, after liming, arable *Albic Retisols* quickly lose their basic cations (Litvinovich et al., 2022) and after two years there is a gradual return to the initial pH level (Shilnikov, 1991). To characterize soil acidity, a different set of intensive and extensive indicators is used. Hydrolytic (pH-dependent) acidity is the sum of exchangeable acidity and active acidity due to H^+ ions, which are released from the pH-dependent positions of the soil absorbing complex. This acidity appears at lower pH values and characterizes the entire possible spectrum of acids present in the soil. It is also determined in the extracts of hydrolytically alkaline salts (Chesworth, 2008).

The dumps of dolomite screenings from stone processing, accumulated near former and existing quarries in Leningrad region, are considered unsuitable for use in agriculture, since the size of these screenings is large and therefore considered to be of low activity. These dolomite particles have different chemical composition, density and porosity, so their dissolution rate and duration of action will vary. The dissolution rate of large dolomite particles during prolonged composting with strongly acidic *Albic Retisols* was studied in (Litvinovich et al., 2021). They showed that the process of dissolution of large particles of dolomite in the soil affects only the outer layers of the particles. As a result, the particles gradually decrease in volume, and the duration of the ameliorant action increases. The working hypothesis of the study was based on the fact that the fineness of grinding affects the dissolution rate of the ameliorant, and liming in general leads to a deficiency of manganese available to plants (Gupta, Macleod, and Macleod, 1973; Nebolsin and Nebolsina, 2002, 2010; Diatta et al., 2014; Ijaz et al., 2021). The tasks of this work were: 1) to reveal the

relationship between soil acidity indicators (pH_{KCl} and Hy) and the content of mobile Mn in *Albic Retisol* in a long-term field experiment; and 2) to assess the ability of soil limed with dolomite particles of various sizes to meet the needs of plants for manganese in a long aftereffect.

Materials and methods

Experimental design and study site

In the microfield experiment, the effect of dolomite screening fractions from the Elizavetino deposit (Gatchinsky District of the Leningrad Region, Fig. 1; N 59°29'33", E 29°45'51") less than 0.25 mm in size (dolomite flour — DF); 0.25–1 mm in size (D); 1–3 mm (D) and 3–5 mm (D) and their combinations (Fig. 2) was studied on *Albic Retisol* (IUSS, 2014). Plots without the use of ameliorant and with the use of standard limestone flour (LF) added at a dose equivalent to the dolomite screenings served as controls. The doses of dolomite were calculated based on the hydrolytic acidity (Hy). The inclusion of treatments with a mixture of dolomite particles of different sizes in a deliberately overestimated doses (3, 4, and 6 Hy, plots No. 7, 8 and 9) was based on the known fact that the fineness of grinding affects the dissolution rate of the ameliorant. It was assumed that the fraction <0.25 mm, added at a dose of 0.5 Hy, would dissolve immediately after application. The rate of dissolution of 0.25–1 mm fraction will be lower and the fraction 1–3 mm in size will have a reclamation effect at later stages of the experiment (Litvinovich et al., 2022) since particles of lime larger than 1 mm are inert and have a weak reclamation effect (Musil and Pavliček, 2002).

The inclusion of the treatment using an overestimated dose of dolomite particles with a size of 3–5 mm (treatment No. 10) was based on the fact that with an increase in the dose of ameliorant, the effect of the fineness of grinding is levelled. The experiment was initiated in 2011 and included the following treatments:

1. Control (NPK)
2. NPK + LF (<0.25 mm, 1 Hy)
3. NPK + D (<0.25 mm, 1 Hy)
4. NPK + D (0.25–1 mm, 1 Hy)
5. NPK + D (1–3 mm, 1 Hy)
6. NPK + D (3–5 mm, 1 Hy)
7. NPK + D (<0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 2 Hy)
8. NPK + D (<0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 3 Hy)
9. NPK + D (<0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 5 Hy)
10. NPK + D (3–5 mm, 5 Hy),

Where, NPK fertilizer is $NH_4H_2PO_4 + NH_4NO_3 + KCl$; LF is a limestone flour; 1Hy is a full dose of lime determined by the hydrolytic acidity; D is dolomite.



Fig. 1. Dolomite screening dump site.

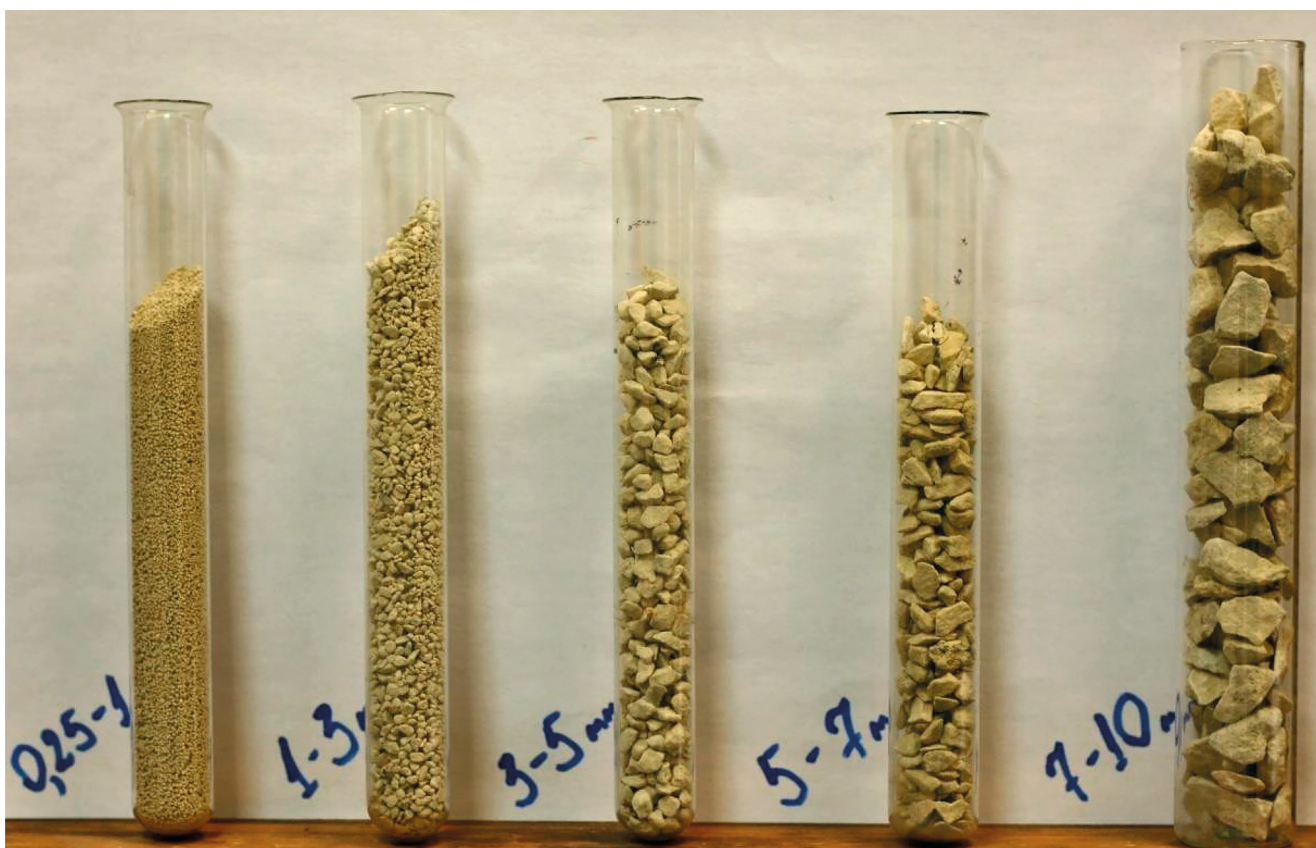


Fig. 2. Size partitioning of dolomite screenings form the dump.

Analytical and crop growing approaches

The methodology of the microfield experiment was as follows: vessels of 40 litres capacity without a bottom were buried into the soil to the depth of 50 cm (Fig. 3). 40 kg of soil, calcified with various fractions of dolomite screening at a full dose of Hy (8.4 t/ha), were placed in the vessels. Crops responsive for liming and with high demand for calcium and magnesium have been grown throughout the experimental years. In 2011 — rapeseed (*Brassica napus*, L.), in 2012 — vetch and mustard (*Vicia* and *Sinapis alba*, L.), in 2013 and 2014 — beans and mustard (*Vicia faba* and *Sinapis alba*, L.). Since 2015, acid-tolerant timothy (*Phleum pratense*, L) has been included in the range of cultivated crops. In 2015, barley (*Hordeum vulgare*, L) with over-sowing of timothy. In 2016 and 2017, timothy was harvested twice each year, and in 2018 one harvest was carried out. Altogether, 13 experimental phases were performed and analysed. Plants were harvested in the flowering phase. The concentration of plant available manganese in the soil was established after harvesting each crop (13 determinations).

When setting up the experiment, the soil was fertilized with NPK in an amount of 48 g per vessel. In addition, before sowing the plants, NPK was used annually at a rate of 6 g per vessel. The soil exchangeable acidity (pH) in a 1 M KCl solution was determined potentiometrically, and hydrolytic acidity (Hy) was determined with the Kappen method (Kappen, 1929): 0.5 M dm^{-3} Ca-acetate solution adjusted to pH 8.2 was added to the soil in the ratio of 1:2.5. After 1 hour of shaking the suspension was filtrated and followed by titration with 0.1 M dm^{-3} NaOH solution. The H_{total} values were calculated from the amount of alkali consumed (0.1 M dm^{-3} NaOH cm^3 for 50 g soil). Manganese was extracted from the soil and the pHKCl of the solution was brought to 5.6 units with an ammonium acetate buffer (AAB pH 4.8). Determination of Mn was carried out on a Varian “Spectr AA 240 FS” atomic adsorption spectrophotometer by flame atomization. Hydrolytic acidity (Hy) was determined by the Kappen method using CH_3COONa with pH 8.2 (Novitsky et al., 2021). The statistical differences between the treatments were described using the standard deviation, *t*-test and regression analyses. Empirical processing of the data was carried out according to Bure (2007).



Fig. 3. General view of the microfield experiment.

Results

The gross chemical composition of the soil was given earlier in Litvinovich et al. (2022). The physicochemical characteristics of the soil were: pH_{KCl} — 4.2; Hy — 5.6 mmol (eq)/100 g soil; humus — 1.76%; particles < 1 mm — 21.2%; content of exchangeable Ca and Mg — 1.54 and 0.34 mmol (eq)/100 g soil, respectively. Content of plant available manganese — 32 mg/kg soil. The high acidity of the studied soils is a hereditary property, mainly associated with the state of waterlogging and the history of fertilization.

The data on the dynamics of pH_{KCl} and Hy for 13 experimental phases are given in Tables 1 and 2. The results show that the effect of dolomite particles < 0.25 mm on soil pH_{KCl} and Hy was recorded over 8 experimental years. The return to the initial value of pH_{KCl} and Hy upon liming with dolomite particles 0.25–1 and 1–3 mm in size was established after 8 experimental years, while the effect of 3–5 mm fractions at a dose of 1 Hy on soil acidity indicators was traced for 7 experimental years. Table 3 shows the dynamics of plant available manganese in the soil. In the treatments using only mineral fertilizers, the concentration of mobile Mn changes in an increasing amplitude with a statistically insignificant rate.

Regardless of the treatment with liming, the maximum change in the concentration of Mn was achieved in the year of aftereffect and depended on the size of particles and the dose of dolomite application. Further, an increase in its concentration began. The effect of using particles less than 0.25; 0.25–1 mm; 1–3 and 3–5 mm at a dose of 1 Hy lasted for at least 6–7 experimental phases, and the effect of using mixtures of fractions in an amount corresponding to 3, 4 and 6 Hy doses, lasted for the entire observation period.

Linear models of the content of mobile manganese depending on pH_{KCl} are presented in Table 4. A statistically significant change in the content of mobile manganese with a change in pH_{KCl} value over the entire study period was established for the treatments with LF (limestone flour), dolomite particles of < 0.25; 0.25–1 and 1–3 mm in size, as well as a mixture of these fractions at a dose of 3 Hy.

The linear dependences of the mobile manganese on the pH_{KCl} value in the treatments 1, 5, 6, 8, 9, and 10 imply that for these treatments a statistically significant change in the manganese content with a change in the pH_{KCl} value on average was not observed over the entire interval of the experimental years.

On the contrary, paired linear regressions of the dependence of the mobile Mn on hydrolytic acidity (Hy) revealed a different trend. In this case, only in the treatment using NPK only, a significant statistical relationship between these indicators was not found, while in

all other treatments, the dependency of Mn and Hy was significant (Table 5).

Discussion

There are numerous studies showing that liming, in general, leads to a decrease in the mobility of manganese in soils (Gupta, Macleod, and Macleod, 1973; Nebolsin and Nebolsina, 2002, 2010; Litvinovich, Kovleva, and Pavlova, 2015; Litvinovich et al., 2021; Ijaz et al., 2021). The variation in the content of manganese can be associated with the level of soil acidity, where 92.4% of the change in the content of manganese available to plants in soils occurs due to the changes in soil pH (Nebolsin and Nebolsina, 2010). In our study, the maximum decrease in the mobility of Mn was observed at pH_{KCl} value of 6.5–7.2. This level of reaction corresponds to the formation of oxides Mn_2O_3 and MnO in soils with normal moisture, which have low solubility. When moist soils are limed excessively, precipitation occurs at pH_{KCl} value of 8–9 units due to the formation of $\text{Mn}(\text{OH})_2$ and MnCO_3 (Nebolsin and Nebolsina, 2010). Moreover, Kessick and Morgan (1975) found that at $\text{pH} > 8$, manganese is able to start auto-oxidation which leads to a reduction in mobility. As mentioned earlier, among three oxidation states (Mn(II), Mn(III), and Mn(IV)) crops uptake only the divalent Mn (Mn^{2+}) (Fageria, Stone, and Moreira, 2008; Dabkowska-Naskret and Jaworska, 2013; Ijaz et al., 2021). At about neutral pH, oxidation of soluble Mn(II) to hardly soluble Mn(IV) occurs. At the lower pH values the insoluble MnO_2 is reduced to the plant-available Mn^{2+} form through biological or chemical processes due to the presence of protons and electron-carrying reducing agents produced by plant roots, microorganisms, or through organic matter decomposition (Uren, 1981; Di-Ruggiero and Gounot, 1990; Rusin and Ehrlich, 1995).

Vondráčková et al. (2013) found no effect of dolomite and lime application on plant available concentrations of Mn. However, concentrations of acid extractable Mn slightly decreased under dolomite application and greatly decreased under lime application in the studied alluvial soils with the initial soil pH ranging from 6.5 to 7.3 which is substantially higher than the soil studied in our experiment. Under addition of CaCO_3 a chemical sorption of Mn followed by precipitation of MnCO_3 occurs (Bradl, 2004; Otero et al., 2009). Although the study of Vondráčková et al. (2013) lasted for 42 days of incubation experiment, this indicates once more that Mn transformations due to liming are highly sensitive in acid and very acid soils, and at a high soil pH the mobility of Mn is generally low (Adriano, 2001).

One of the objectives of this study was to establish an average (calculated) value of the change in the concentration of mobile Mn in the soil that corresponds to a decrease in pH_{KCl} and an increase in Hy over the entire study interval. Data analysis showed that the dynamics

Table 1. Dynamics of pHKCl over 13 experimental phases

	Treatment	Test-year												
		1	2	3	4	5	6	7	8	9	10	11	12	13
1	Control (NPK)*	3.95a	3.85a	4.10a	4.00a	3.83a	3.60a	3.92a	3.40a	3.76a	3.58a	3.70a	3.70a	3.40a
2	NPK + LF (< 0.25 mm, 1 Hy)	5.32b	4.95b	4.90b	4.70b	4.34b	4.10b	4.44b	4.00b	4.13b	3.95b	4.20b	4.03ab	3.80b
3	NPK + D (< 0.25 mm, 1 Hy)	5.45b	5.12c	5.15c	4.95c	4.58c	4.22c	4.74c	4.10bc	4.19b	3.95b	4.30bc	3.93a	4.10b
4	NPK + D (0.25–1 mm, 1 Hy)	5.13c	5.05bc	5.32d	5.10d	4.80d	4.33d	4.90d	4.00b	4.16b	3.90b	4.40bc	4.10ab	3.80b
5	NPK + D (1–3 mm, 1 Hy)	4.62d	4.42d	5.00bc	4.85bc	4.40bc	4.15bc	4.58bc	3.90b	4.13b	3.98b	4.30b	4.10ab	3.90b
6	NPK + D (3–5 mm, 1 Hy)	4.60d	4.05e	4.40e	4.45e	4.38e	3.95e	4.26b	3.80cb	4.11b	3.95b	4.10d	3.90ac	3.80b
7	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 2 Hy)	5.82e	5.75f	6.10f	6.00f	5.63f	5.60f	6.10f	5.0d	5.23c	5.08c	5.70e	5.50d	5.50c
8	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 3 Hy)	5.95e	5.85f	6.30g	6.30g	5.93g	5.80g	6.40f	5.50e	5.80d	5.63d	6.20f	6.00d	5.90cd
9	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 5 Hy)	6.10ef	6.00fg	6.40g	6.40h	6.20h	6.10h	6.63f	5.85f	6.00d	6.08e	6.40g	6.30e	6.10cd
10	NPK + D (3–5 mm, 5 Hy)	5.35b	4.85b	5.70h	5.65i	5.12i	5.20i	5.71f	4.80d	5.00c	5.23c	5.70e	5.40ac	5.40cd

* The letters within a column signify a statistically significant difference as confirmed by t-test at $P < 0.05$ level; LF — limestone flour; NPK — mineral fertilizer; Hy — hydrolytic acidity; D — dolomite fraction.

Table 2. Dynamics of hydrolytic acidity (Hy) over 13 experimental phases, mmol (eq) 100⁻¹ g of soil

	Treatments	Test-year												
		1	2	3	4	5	6	7	8	9	10	11	12	13
1	Control (NPK)*	5.42a	5.58a	5.04a	4.52a	5.01a	5.86a	6.48a	7.52a	6.79a	6.77a	6.97a	5.35a	9.91a
2	NPK + LF (< 0.25 mm, 1 Hy)	2.65b	3.23b	3.08b	2.92b	4.35b	4.16b	4.68b	5.32bc	5.31b	5.85bc	5.10b	4.51b	7.37bc
3	NPK + D (< 0.25 mm, 1 Hy)	2.54bc	2.86c	2.76b	2.68bc	3.54c	4.14b	4.10b	5.23b	5.37b	5.32b	5.03bc	5.17a	5.82c
4	NPK + D (0.25–1 mm, 1 Hy)	3.41d	3.09b	2.66b	2.58bc	2.94d	4.70b	4.11b	5.97bc	5.06b	5.80bc	4.74c	4.50b	4.83bc
5	NPK + D (1–3 mm, 1 Hy)	4.45e	4.25d	3.00b	3.03b	3.79c	4.40b	4.81b	5.93bc	5.26b	5.58bc	5.01bc	4.54b	4.59bc
6	NPK + D (3–5 mm, 1 Hy)	5.35a	5.34e	4.72a	3.82d	5.01a	4.70a	6.29a	7.28a	5.88cb	6.07c	5.93d	5.26a	4.63c
7	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 2 Hy)	2.16bc	2.05f	1.71c	1.30e	1.45e	1.78c	2.03c	3.39d	2.39d	3.11d	2.24e	2.43c	1.85d
8	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 3 Hy)	2.02bc	1.90f	1.50c	1.16e	1.31e	1.55cd	1.63cd	2.56e	1.43e	2.40e	1.49f	1.32d	1.33d
9	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 5 Hy)	1.80c	1.64g	1.28c	1.01e	0.99e	1.28cd	1.54cd	1.86e	1.46e	2.06e	1.26f	1.09d	1.23d
10	NPK + D (3–5 mm, 5 Hy)	4.17e	3.72h	3.08b	2.41cd	3.26cd	2.75e	3.04e	3.95d	3.55f	2.84d	2.62g	2.36c	2.00d

* The letters within a column signify a statistically significant difference as confirmed by t-test at $P < 0.05$ level; LF — limestone flour; NPK — mineral fertilizer; Hy — hydrolytic acidity; D — dolomite fraction.

Table 3. Dynamics of changes in plant available Mn throughout the experiment, mg/kg

Treatment	Test-year												
	1	2	3	4	5	6	7	8	9	10	11	12	13
1 Control (NPK)*	43.08a	22.68a	26.38a	38.55a	32.17a	30.3a	49.97a	38.86a	21.84a	19.72a	17.02a	19.99abc	23.19a
2 NPK + LF (< 0.25 mm, 1 Hy)	20.78b	8.96bc	17.83b	18.00bd	22.18b	25.1b	40.65b	44.07a	31.70bc	26.95b	20.54bc	20.57abc	30.77bc
3 NPK + D (< 0.25 mm, 1 Hy)	21.92b	8.67bc	16.40b	15.65b	16.54c	25.6b	30.95c	49.98cde	36.03b	28.95b	21.31b	25.57b	28.64ac
4 NPK + D (0.25–1 mm, 1 Hy)	29.01c	9.49c	17.13b	12.44c	14.73c	20.7c	29.00c	44.45ac	34.98b	25.76b	17.47a	21.58ab	30.49bc
5 NPK + D (1–3 mm, 1 Hy)	36.81da	12.58d	16.55b	19.78bd	19.05bc	24.8b	31.81c	46.17ad	33.31b	25.57b	18.75ab	17.60ac	27.90ab
6 NPK + D (3–5 mm, 1 Hy)	40.94a	17.85e	23.50c	27.00e	25.10b	29.0a	40.14b	46.15ae	27.30ac	24.84ab	18.46ac	15.65c	24.19ab
7 NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 2 Hy)	14.87e	7.87bf	13.85de	8.06f	7.91d	11.9d	14.81de	31.24abg	21.37a	18.01a	10.48de	16.05ac	20.46ad
8 NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 3 Hy)	15.13e	7.19f	14.53d	9.46f	8.77d	14.0d	15.45de	18.84f	11.51d	17.46a	9.29d	8.87d	13.73d
9 NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 5 Hy)	15.01e	7.23f	12.48e	9.88cf	7.39d	12.5d	13.66d	11.92f	12.17d	14.88a	10.88de	9.37d	15.14d
10 NPK + D (3–5 mm, 5 Hy)	33.08dc	10.66c	14.68d	12.59c	13.58c	14.8d	21.68de	29.41g	19.45a	16.44a	11.88e	9.66d	14.14d
LSD	4.03	1.49	1.63	2.82	4.91	3.1	7.59	8.63	5.97	5.73	2.38	6.09	7.24

* The letters within a column signify a statistically significant difference as confirmed by t-test at $P < 0.05$ level; LF — limestone flour; NPK — mineral fertilizer; Hy — hydrolytic acidity; D — dolomite fraction.

Table 4. Empirical dependence of the manganese concentration in *Albic Retisol* on the pH_{KCl} value

No.	Treatments	Model equation	b	Significance	p-value	Coefficient of determination
1	control (NPK)	$y_{1,1} = -25,6 + 14,7 \cdot x$		Non-significant	0.3	$R^2 = 0.097$
2	NPK + LF (1 Hy)	$y_{2,1} = 74.6 - 11.3 \cdot x$	11.3	Significant	0.056	$R^2 = 0.29$
3	NPK + D (< 0.25 mm, 1 Hy)	$y_{3,1} = 81.2 - 12.4 \cdot x$	12.4	Significant	0.03	$R^2 = 0.36$
4	NPK + D (0.25–1 mm, 1 Hy)	$y_{4,1} = 70.8 - 10.4 \cdot x$	10.4	Significant	0.046	$R^2 = 0.31$
5	NPK + D (1–3 mm, 1 Hy)	$y_{5,1} = 65.7 - 9.35 \cdot x$		Non-significant	0.245	$R^2 = 0.12$
6	NPK + D (3–5 mm, 1 Hy)	$y_{6,1} = 2.28 + 6.15 \cdot x$		Non-significant	0.57	$R^2 = 0.03$
7	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 2 Hy)	$y_{7,1} = 87.7 - 12.9 \cdot x$	12.9	Significant	0.009	$R^2 = 0.48$
8	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 3 Hy)	$y_{8,1} = 40.1 - 4.6 \cdot x$		Non-significant	0.26	$R^2 = 0.113$
9	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 5 Hy)	$y_{9,1} = 13.6 - 0.31 \cdot x$		Non-significant	0.94	$R^2 = 0.0006$
10	NPK + D (3–5 mm, 5 Hy)	$y_{10,1} = 43.4 - 4.95 \cdot x$		Non-significant	0.47	$R^2 = 0.049$

Notes: b = the coefficient of the mean change in pH_{KCl} value; LF — limestone flour; NPK — mineral fertilizer; Hy — hydrolytic acidity; D — dolomite fraction.

Table 5. Empirical dependence of the manganese concentration in *Albic Retisol* on the value of hydrolytic acidity (Hy)

No.	Treatments	Model equation	b	Significance	p-value	Coefficient of determination
1	control (NPK)	$y_{1,1} = -39,4 - 1,58 \cdot x$		Non-significant	0.47	$R^2 = 0.047$
2	NPK + LF (1 Hy)	$y_{2,1} = 6.4 + 4,19 \cdot x$	4.19	Significant	0.037	$R^2 = 0.338$
3	NPK + D (< 0.25 mm, 1 Hy)	$y_{3,1} = -0.34 + 6.1 \cdot x$	6.1	Significant	0.009	$R^2 = 0.48$
4	NPK + D (0.25–1 mm, 1 Hy)	$y_{4,1} = -2.4 + 6.2 \cdot x$	6.2	Significant	0.005	$R^2 = 0.53$
5	NPK + D (1–3 mm, 1 Hy)	$y_{5,1} = -5.76 + 6.87 \cdot x$	6.87	Significant	0.02	$R^2 = 0.398$
6	NPK + D (3–5 mm, 1 Hy)	$y_{6,1} = 0.83 + 4.97 \cdot x$	4.97	Significant	0.1	$R^2 = 0.225$
7	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 2 Hy)	$y_{7,1} = -3.04 + 8.49 \cdot x$	8.49	Significant	0.0025	$R^2 = 0.58$
8	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 3 Hy)	$y_{8,1} = 3.19 + 5.69 \cdot x$	5.69	Significant	0.013	$R^2 = 0.45$
9	NPK + D (< 0.25 mm, 0.5 Hy) + D (0.25–1 mm, 0.5 Hy) + D (1–3 mm, 5 Hy)	$y_{9,1} = 6.27 - 3.84 \cdot x$	3.84	Significant	0.09	$R^2 = 0.235$
10	NPK + D (3–5 mm, 5 Hy)	$y_{10,1} = -6.39 + 7.68 \cdot x$	7.68	Significant	0.008	$R^2 = 0.49$

Notes: b = the coefficient of the mean change in pH_{KCl} value; LF — limestone flour; NPK — mineral fertilizer; Hy — hydrolytic acidity; D — dolomite fraction.

of changes in the content of Mn and the dynamics of pH and Hy values were significantly nonlinear. But the use of paired linear regressions showed statistically significant outputs and made it possible to correctly assess the average variability of manganese content depending on the increase or decrease of other indicators (pH, Hy) over the entire study period. These results imply that the level of significance of the linear dependences of mobile manganese on the pH_{KCl} among treatments implies that the value of exchangeable acidity, which characterizes the amount of acidic components passing into salt ex-

tracts from the constant positions of the soil-absorbing complex (SAC) is insufficient to reveal its interdependence with the content of mobile manganese in most of the treatments. On the contrary, paired linear regressions of the dependence of the mobile Mn on hydrolytic acidity (Hy) showed that the entire spectrum of acidic components present in the soil allows to reveal a relationship between the content of mobile manganese and Hy in all treatments with liming.

Another important issue that was raised at the start of the experiment is whether soil limed with dolomite

(especially in deliberately large doses) is capable to meet the needs of plants for manganese. According to the gradation given by Nebolsin and Nebolsina (2002), soils are subdivided into: very rich — 0.15 mmol (eq)/100 g of soil (41 mg/kg); rich — 0.08 mmol (eq)/100 g of soil (21.9 mg/kg); moderately supplied — 0.045 mmol (eq)/100 g of soil (12.3 mg/kg); poor — 0.02 mmol (eq)/100 g of soil (5 mg/kg). In the studied soil the content of plant available manganese compounds in all treatments falls within the range from very rich to medium-rich soils. Of the studied crops, mustard was the most sensitive to the content of manganese in the soil. In our study, the concentration of manganese in the limed plots significantly exceeded the lower limit of 1.6–2.2 mg/kg for this crop (Nebolsin and Nebolsina, 2002). Thus, the threat of manganese deficiency for plants from various biological families grown on soil reclaimed with dolomite particles has not been established.

Conclusions

- The amount of the initial soil components passing into the salt extracts (1N KCl) is not enough to reveal the relationship between the exchange acidity and the content of mobile manganese in the majority of the treatments limed with dolomite particles.
- Hydrolytic (pH-dependent) acidity allowed to reveal the relationship between the content of plant available manganese and the value of H_y in the soils of limed treatments.
- Regardless of the dose and size of dolomite particles added, the limed soil belonged to the category of highly and moderately supplied with plant available manganese throughout the entire study period.
- The relationship of Mn available to plants in limed soil requires the closest attention and further study, since due to the very high dynamism of the processes of transformation of manganese and the instability of its compounds of different valence in soils, inept human intervention can create either conditions for the manifestation of the toxicity of Mn, or its sharp deficiency as a nutrient.

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