

VARIABILITY OF THE pH AND OF THE CONTENT OF IRON ASSIMILABLE FROM THE SOIL IN THE CONTEXT OF THE PRESENCE OF BICARBONATES

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Abstract

In order to study the effect of various species of bicarbonates on the pH and on the content of DTPA-extractable iron, an experiment was organized, showing the effect of 7 progressive concentrations (from 0 to 3%) of ammonium, sodium and potassium bicarbonates. The results show the progressive increase of the pH proportionally to the concentration of bicarbonate ion, as well as an initial decrease and then an increase of the extractable iron content. The pH of the soil in the experiment is 5.44 and its DTPA-extractable iron content is 158 mg/kg; following the addition of the bicarbonates, the pH increases up to about 10 in the case of the sodium and potassium bicarbonates and up to 8.5 in the case of the ammonium, while the extractable iron decreases to about 100 mg/kg and then it increases to about 680 mg/kg in case to the sodium, 176 mg/kg in case of the potassium and 130 mg/kg in case of the ammonium.

Key words: iron chlorosis, iron, bicarbonate, pH

Iron chlorosis is a physiological phenomenon with a negative impact on the quality and quantity of grape crops in the vineyards of Romania. The bicarbonates are considered to be the main group of compounds responsible for the immobilization of iron in the soil in forms non-assimilable by the plants and their study is of an outstanding interest in defining the process of iron chlorosis onset.

Wide-ranging research conducted by Răuță et al. (1975, 1977 and 1980) and by Lyndsay and Thorne (1954) show that increased humidity and poor aeration favour the occurrence on limey soils of carbon dioxide which, in its turn, positively influences the formation of mainly calcium bicarbonate. Mengel (1979 and 1984) shows that increase humidity in the absence of aeration, on limey soils, leads to the formation of the bicarbonate ion which, in its turn, is the direct cause for blocking the iron in the soil and plant. In 1980, Morlat and Courbe specified the influence of the fine limestone in the Bca horizon and in water, on the onset of chlorosis, as these are the source of large quantities of bicarbonate ions.

In order to know the issues of irrigation as a technological link in the conditions of certain areas prone to chlorosis, Kivadze (1959), Răuță et al. (1977) and other researchers showed that, in the conditions of a brown carbonatic soil, irrigation increase the incidence of chlorosis even threefold, from a field capacity of 60% to 80%. On the other hand, there are indications that clayey soils can also have a stronger chlorosing effect than the more sandy-skeletal ones. In this case there is the argumentation according to which the phenomena

of excessive humidity, soil compaction and poor aeration occur more frequently on clayey soils and all of these factors, as shown above, favour the onset of chlorosis. Mengel (1983) showed that poor aeration due to excessive carbon dioxide in the soil favour the formation of calcium bicarbonate, directly resulting in the onset of chlorosis. Calcium carbonate has many forms in the soil, it may occur in various sizes, from large boulders to the finest particles, in a crystalline or amorphous state. Hence the great differences between the chlorosing power of the soils pending on the clay forms they contain. Nicolier (1961) shows a lime sensitive rootstock (3390) which has good results on a soil containing 80% lime, the decisive reason being the very low solubility of certain rocks with hard lime and large size of the particles. At the opposite pole, Drouineau (1951) shows the high chlorosing power of the soil when the lime is in soft forms and/or fine particles. Boisshot and Herber (1947) show the inverse proportionality between the size of the lime particles and their solubility. They also show the clay dissolution coefficient as being twice the coefficient of fine sand. The crystallization system is very important in lime solubility. Rod (1974) shows the great difference between some natural rocks as far as the percentage of active limestone is concerned: 4% in dolomite, 9% in aragonite, 15% in calcite and 53% in the Champagne chalk. Rod, like Drouineau, notices the higher solubility of limestone pending on the size of the particles, showing that it increased from light soils (11%) to heavier soils (33%). An important effect of calcium carbonate on the soil is the pH increase,

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which has a significant influence on the availability of the iron in the soil and consequently on the phenomenon of iron chlorosis. Glaue and Jeny (1960) showed for the first time the concentration decrease of a Fe^{2+} and Fe^{3+} solution when its pH comes in the range of 7 – 7.5. Brady (1984) shows that in limey soils, under the influence of an increased pH, iron passes in insoluble oxides and hydroxides. Along with the environmental factors, there are also technological factors which can be instrumental in the onset or evolution of chlorosis. Pouget (1974), Hidalgo (1982), Murisier (1988), Bartolini (1996) show the major importance of the root system in the

absorption of iron and consequently in the onset and evolution of chlorosis. The research conducted by Hidalgo (1958) shows that clay, whose particles are smaller than those of fine limestone, incorporate iron and prevent its dissolution. At the opposite pole, sandy soils have a higher chlorosing influence. The same researchers also bring the argument of differentiated humidity of the two types of soil, showing the fact that the water reserve in the clayey soils is much larger than the one in the sandy soils and a certain quantity of dissolved limestone would result in a higher concentration in the sandy soils and a lower concentration in the clayey soil.

MATERIAL AND METHOD

The research aims at following up the influence of certain progressive concentrations of ammonium, potassium and sodium bicarbonate concentrations on the pH and on the immobilization of the iron in the soil. The soil sample used in the experiment was taken from horizon A of a typical Luvisol (10 – 20 cm), from Ghermănești, Ilfov district, North of Bucharest. The physico-chemical characteristics of the soil are

presented in *table 1*. The samples were kept for 14 days, in order for the pH and the iron bicarbonate to stabilize and then the tests were run. In the autumn of 2011, a trifactorial experiment was organized with 7 degrees of liberty, in 3 repetitions, as follows: three bicarbonate species (ammonium, sodium and potassium) in concentrations of 0.25 g/50 g soil (0.5%), 0.50 g/50 g soil (1%), 0.75 g/50 g soil (1.5%), 1.00 g/50 g soil (2%), 1.25 g/50 g soil (1.5%) and 1.50g/50 g soil (3%), each experimental variant in 3 repetitions.

Table 1

Physico-chemical characteristics of the soil used in the experiment

No.	Tested parameter	Method of determination	Value obtained
1	Total nitrogen	Kjeldahl	0.28%
2	Organic carbon	Wet oxidation	2.54%
3	C/N ratio	Calculation	9.07
4	Pal	Molybdenum blue	9.12 ppm
5	Kal	Flame photometric	133.33 ppm
6	pH	Electrometric	5.44
7	Complexometric Fe extraction in EDTA	Atomic absorption	123.18 ppm
8	Complexometric Fe extraction in DTPA	Atomic absorption	158.52 ppm
9	Total Fe (mineralization in hard acids)	Atomic absorption	2.30%

The soil, dried, ground and screened through a 500 micron sieve, was transferred into 54 100 ml Berzelius beakers: 50.00 grams of soil weighed by the technical balance (Kern EG-2200-2NM) in each beaker, then we added the bicarbonate quantity corresponding to each beaker code – weighed by the Metler-Toledo analytical precision balance and 21 ml of bidistilled water and homogenized the contents with a glass stick. The beakers were covered with watch glasses and kept at a constant laboratory temperature ($20 \pm 2^\circ C$) for 14 days. After 14 days, the soil was dried in the drying oven with forced convection, at the temperature of 40 degrees Celsius, until the sample was brought to constant mass, by checking the loss of water on an hourly basis; the drying process was considered completed when the mass

variation from one weighing to the other was less than 1%, which took place about 8 hours of drying.

The dry soil was ground in the grinding bowl and screened through a 500 micron sieve. Then each separate code was tested for its pH and its DTPA-extractable iron. The pH was determined in aqueous suspension 1:2.5 with bidistilled water. The samples were left to rest for 1 hour in order to balance with carbon dioxide from the atmosphere, then the value was read electrometrically by means of the Crison Basic 20 pH meter and a 20 10T electrode calibrated in 3 points (4.01; 7.00 and 9.21) before starting the measurements. The extractable iron was determined by the Lindsay method, DTPA extraction 0.005M at pH 7.3 in a 1:2 soil:extractant ratio (m/V).

RESULTS AND DISCUSSIONS

In the case of the ammonium bicarbonate, we notice a progressive pH increase up to 8.4 units at a content of 0.75 g/50 g soil (1.5%), where the curve flattens and the values remain relatively constant if the bicarbonate content still increases (*fig. 1*). As for the iron, the bicarbonate content influences it initially downward and then, starting from the value of 0.75 g/50 g soil (1.5%), a slight

increase can be noticed up to the value of 130 ppm (*fig. 2*).

In the case of the sodium bicarbonate, a progressive pH increase can be noticed up to a relatively high value, i.e. 10.12 units at a content of 1.5 g/50 g soil (3%) and the function seems to be still ascending (*fig. 3*). As for the influence on the extractable iron (*fig. 4*), it is initially decreasing, and then it is increasing to a value much above the one initially available, reaching almost 690 ppm.

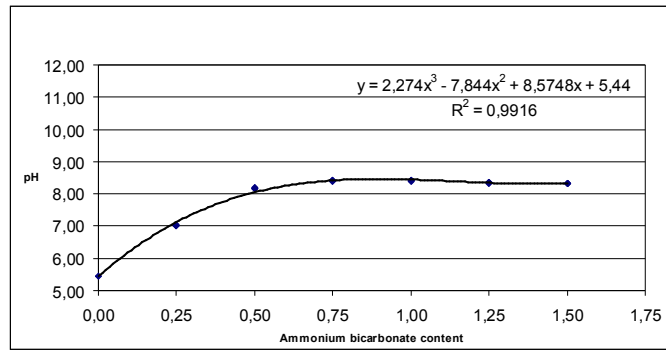


Figure 1 Influence of the (NH₄) HCO₃ content on the pH

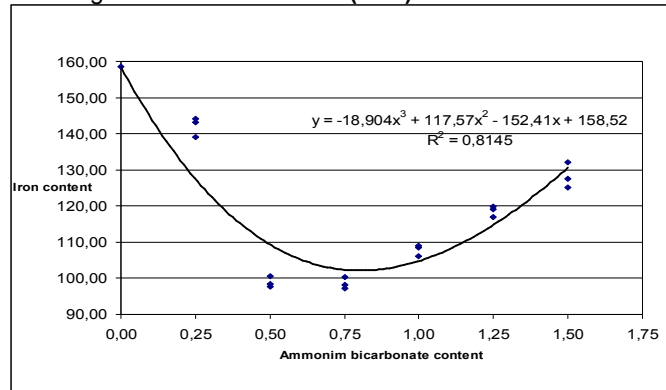


Figure 2 Influence of the (NH₄) HCO₃ content on the iron

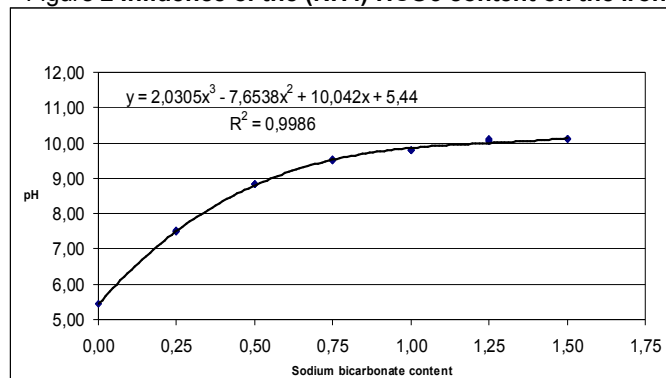


Figure 3 Influence of the NaHCO₃ content on the pH

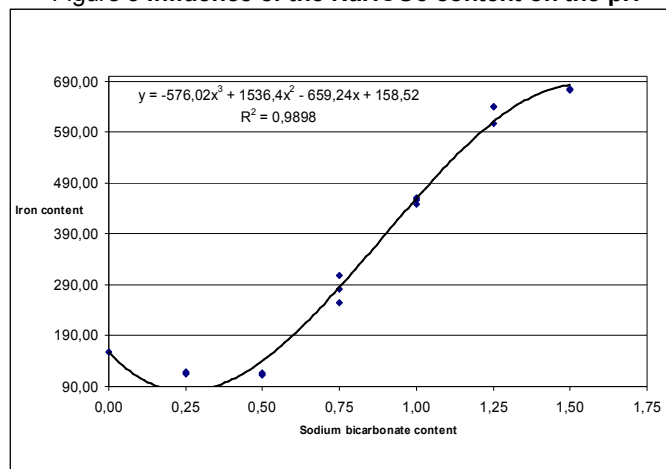
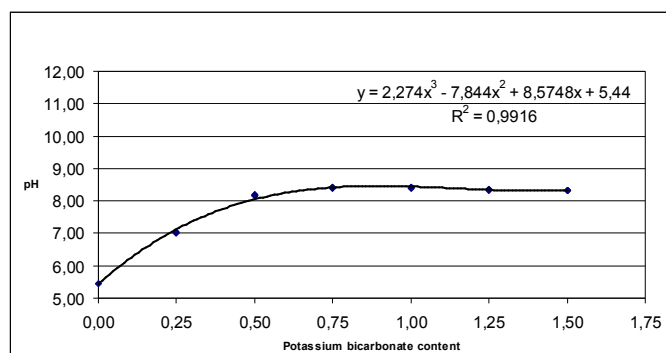
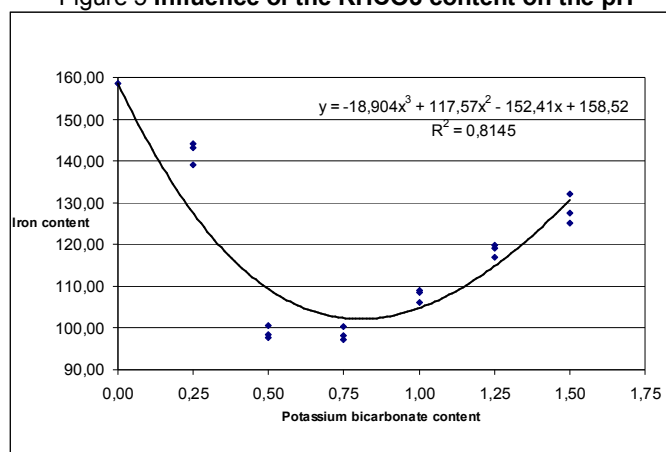


Figure 4 Influence of the NaHCO₃ content on the iron

In the case of the potassium bicarbonate, a progressive increase of the pH value can be noticed up to the value of 9.89 units at a content of 1.5 g/50 g soil (3%) and the function seems to be still

ascending (fig. 5). As for the extractable iron (fig. 6), initially it drops to 100 mg/kg, and then it increases up to 176 mg/kg.

Figure 5 Influence of the KHCO₃ content on the pHFigure 6 Influence of the KHCO₃ content on the iron

CONCLUSIONS

All of the bicarbonate species influence both the soil pH and its extractable iron content. As far as the changes in the pH are concerned, the sodium bicarbonate has the greatest influence, namely it causes an increase from 5.44 (at 0% bicarbonate) to 10.12 units (at 3% bicarbonate).

In terms of its influence on pH, the values caused by the potassium bicarbonate are similar to those of the sodium bicarbonate, namely an increase from 5.44 (at 0% bicarbonate) to 9.89 units (at 3% bicarbonate). The ammonium bicarbonate has the weakest influence, namely the pH increased from 5.44 (at 0% bicarbonate) to 8.37 (at 3% bicarbonate). As for the DTPA-extractable iron content, again the greatest influence was recorded with the sodium bicarbonate which, against all odds and in spite of the fact that it increases the pH, it makes DTPA-extractable iron available, causing an increase from 158 mg/kg to 676 mg/kg, which suggests some exchange phenomena at the level of the soil matrix.

On the other hand, the potassium bicarbonate and the ammonium bicarbonate have similar influences, initially a drop of the DTPA-extractable iron content from 158 mg/kg to about 99 mg/kg (at 1.5% potassium bicarbonate and ammonium bicarbonate) and then a slight increase up to 176 mg/kg for the potassium bicarbonate (at 3% bicarbonate), and 127 mg/kg for the ammonium bicarbonate (at 3% bicarbonate).

This variation also suggests some exchange phenomena at the level of the soil matrix or its absorptive complex.

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