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BICARBONATE AS THE MOST IMPORTANT SOIL FACTOR IN LIME-INDUCED CHLOROSIS IN THE NETHERLANDS

by R. BOXMA

Institute for Soil Fertility, Haren (Gr.), the Netherlands

SUMMARY

Pot experiments and field trials were conducted to determine the direct cause of lime-induced chlorosis in the Netherlands.

The findings may be summarized as follows:

(1) High bicarbonate content in the soil was the main cause of lime-induced chlorosis.

(2) There was a significant correlation between lime-induced chlorosis and the bicarbonate content of the soil in the spring under field conditions.

(3) The effect of high soil moisture content on chlorosis was an indirect one; a high soil moisture content favoured the formation of bicarbonate.

(4) In neutral to weakly acid soils of high soil moisture content some relationship was found between the incidence of iron chlorosis and pH.

(5) In calcareous soils, however, this interaction was not found.

In connection with these results defects in water management and their relation to bicarbonate and lime-induced chlorosis have been discussed.

INTRODUCTION

In the Netherlands the most widespread occurrence of iron deficiency in plants is found on calcareous soils. This disorder, the so-called lime-induced chlorosis, has been the subject of numerous investigations in recent years.

With regard to the exact cause of lime-induced chlorosis, however, there is much diversity of opinion. It is a well-known fact, that plant species vary in their susceptibility to lime-induced chlorosis [2]. Besides the inability of the plant to take up iron from the soil, iron deficiency may also be due to inactivation of the iron within the plant [1]. In their review Wallace and Lunt [8] stress the following causal soil factors:

(a) low iron availability as a result of high pH,
(b) high soil moisture content and poor aeration,
(c) high bicarbonate content in the soil,
(d) extreme temperatures,
(e) high phosphate, and
(f) incorporation of organic matter.

The multiplicity of factors makes it difficult to evaluate each one for its contribution to lime-induced chlorosis. The purpose of this work was to differentiate the effect of pH, bicarbonate and high soil moisture and to estimate their part in causing lime-induced chlorosis under Dutch soil and weather conditions.

EXPERIMENTAL

Pot experiment I

Roses (var. Roselandia) were planted on a soil/peat potting mixture (10:1 by volume) in earthenware pots with drainage holes. The soil/peat mixture was brought to pH 7.5 by liming with $CaCO_3$ and dressed with adequate amounts of N, P and K.

Five weeks after planting the following treatments were carried out in triplicate:

(a) Low soil moisture state.
The plants received just sufficient water as needed for a healthy growth.
(b) High soil moisture state.
The pots were placed into drip-cups. A constant high soil moisture state was maintained by keeping these drip-cups filled with water.
(c) High soil moisture state plus low supply of $Mg(HCO_3)_2$.
A solution of $Mg(HCO_3)_2$ was added to the soil at a rate of 200 ppm HCO_3^-.
(d) High soil moisture state plus high supply of $Mg(HCO_3)_2$ at a rate of 2000 ppm HCO_3^-.

Six weeks after the treatments soil samples were taken from the pots and analyzed for bicarbonate. At the same time the youngest fully developed leaves were washed with 0.2 per cent detergent, dried and used for iron analysis.

Pot experiment II

The same compost soil and pots as in the previous experiment were used, but now the pH was adjusted to 7.5 in two different ways. Half of the pots were limed with $CaCO_3$ and the other half were treated with $Ba(OH)_2$. After fertilization with adequate amounts of N, P and K the roses (var. Roselandia) were planted.

The experiment was replicated three times as follows:

(a) $CaCO_3$ plus low soil moisture state;
(b) $CaCO_3$ plus high soil moisture state;
(c) $Ba(OH)_2$ plus low soil moisture state;
(d) $Ba(OH)_2$ plus high soil moisture state.

The moisture conditions were established in the same way as in Experiment I. Again soil samples from the pots were analyzed for bicarbonate and leaf samples were collected and washed for the determination of iron.

Field trials in 1963, 1964 and 1965

In the province of Zeeland many orchards are subject to lime-induced chlorosis.

Two experiments were conducted in pear orchards on calcareous clay soils at Tholen and Yerseke. A number of pear trees (Beurré Alexander Lucas on quince and Conférence on quince) in these orchards showed severe iron chlorosis. It was striking that the degree of chlorosis in one orchard decreased in the drain line direction towards the ditch whereas in the other orchard the chlorosis increased towards the drainage ditch.

In one row of each orchard parallel to the drainline direction periodic soil samples of the layer 0–20 cm were taken around the stem of the trees and analyzed for bicarbonate and pH. The locations of the trees were indicated by the numbers 1 up to and including 10 with the understanding that number 1 was the farthest from the ditch and 10 the nearest to the ditch. On June of the experimental years the degree of iron chlorosis in the trees was expressed in chlorosis ratings (0 = no chlorosis; 5 = severe iron chlorosis).

Field trials in 1969 and 1970

Iron deficiency is also found in the orchards of the Betuwe. In contrast with the calcareous clay soil in Zeeland the soil of this river clay region has a very low calcium carbonate content. Experimental plots with different degrees of sensitivity to iron chlorosis were selected in eight orchards and during the years 1969 and 1970 periodic soil samples of the layer 0–20 cm were collected. The soil samples were analyzed for bicarbonate, pH and calcium carbonate.

Iron chlorosis of the apple trees (Jonathan) on these plots was rated in June of the experimental years. In each orchard two plots were chosen.

Chemical methods

A modified o-phenanthroline method according to Van Driel [4] was used for the determination of iron in the leaves.

The bicarbonate analysis in the soil occurred as follows. A 10-g moist soil sample was shaken with 100 ml of CO_2-free water for 15 minutes. After filtration 50 ml of the filtrate was titrated with 0.1 N H_2SO_4 from a microburet using methyl red as indicator. Beforehand it was ascertained that all filtrates were free from OH^- and CO_3^{2-} ions by adding two drops of a phenolphthalein solution. Although other ions like phoshates, silicates and humates were also

TABLE 1

Effect of the soil treatments on the bicarbonate content of the soil and the iron content of the rose leaves in Pot experiment I

	Treatment*	HCO_3^- content of the soil (ppm)	Fe content of the leaves (ppm)	Presence or absence of iron chlorosis
(a)	Low soil moisture state + $CaCO_3$	245	122	no chlorosis
(b)	High soil moisture state + $CaCO_3$	540	81	chlorosis
(c)	High soil moisture state + $CaCO_3$ + + 200 ppm HCO_3^-	500	78	chlorosis
(d)	High soil moisture state + $CaCO_3$ + + 2000 ppm HCO_3^-	659	69	chlorosis

* Each value is a mean of three replications of the treatments.

titrated with H_2SO_4, their amounts in the filtrates were so small to be negligible.

RESULTS

The data of the first pot experiment (Table 1) demonstrate that a high soil moisture content caused a sharp rise of the bicarbonate content in the soil. However, the additions of $Mg(HCO_3)_2$ had little influence on the HCO_3^- content of the soil. Apparently the added bicarbonate was fixed as $CaCO_3$, involving the following reaction:

$$Ca^{2+} + HCO_3^- \rightleftarrows CaCO_3 + H^+$$

Indeed at the highest HCO_3^--level the pH of the soil decreased from 7.5 to 6.7.

It also appears, that the iron uptake was affected by the bicarbonate content of the soil and that no iron deficiency was induced at high pH in combination with a low HCO_3^- content of the soil. Thus a low soil moisture condition prevented the hydrolysis of $CaCO_3$.

Table 2 gives similar data of the second experiment. Both $CaCO_3$ and $Ba(OH)_2$ treatments at low soil moisture state resulted in a low HCO_3^- content in the soil. Under high moisture regime the treatments show a remarkable difference in their action on the HCO_3^- content. In contrast with $CaCO_3$ the addition of $Ba(OH)_2$ gave a low HCO_3^- content in the soil. A possible explanation for this may be given by the fact, that $CaCO_3$ has a higher solubility product than

TABLE 2

Effect of the soil treatments on the bicarbonate content of the soil and the iron content of the rose leaves in Pot experiment II

Treatment*	HCO_3^- content of the soil (ppm)	Fe content of the leaves (ppm)	Presence or absence of iron chlorosis
(a) Low soil moisture state + $CaCO_3$	296	96	no chlorosis
(b) High soil moisture state + $CaCO_3$	506	69	chlorosis
(c) Low soil moisture state + $Ba(OH)_2$	176	100	no chlorosis
(d) High soil moisture state + $Ba(OH)_2$	212	105	no chlorosis

* Each value is a mean of three replications of the treatments.

the formed $BaCO_3$ and that $CaCO_3$ is more hydrolyzed than $BaCO_3$.

The inverse relationship between the iron uptake of the plant and HCO_3^- content of the soil is also clear in this experiment. High soil moisture associated with a poor aeration is often considered as a direct factor of lime-induced chlorosis, but its real effect is an indirect one, namely, the causing of a high bicarbonate content in calcareous soils.

Fig. 1 demonstrates that under field conditions no interaction was found between soil pH and lime-induced chlorosis on the calcareous soils of Tholen and Yerseke. This finding is in agreement with the results of other workers [7]. On the same plots the seasonal fluctuations of the bicarbonate content in the soil were examined. Figs. 2 and 3 show the variations of the bicarbonate content during the vegative period of the trees. In the spring the bicarbonate content of the soil reached its maximum value. During the summer season the bicarbonate decreased to a minimum after which it rose again in the autumn. In both figures the degree of iron deficiency in the trees is indicated by chlorosis ratings. These ratings show a close relationship with the bicarbonate contents when they are correlated with the bicarbonate contents in the spring. The figures can also be used to estimate the minimum value of bicarbonate that may induce iron chlorosis in the trees. Contents of between 200 and 300 ppm HCO_3^- in the spring seem to be critical for the occurrence of lime-induced chlorosis in these orchards.

With regard to the drainage ditch there was a distinct difference between the bicarbonate patterns in the two rows. In the row at

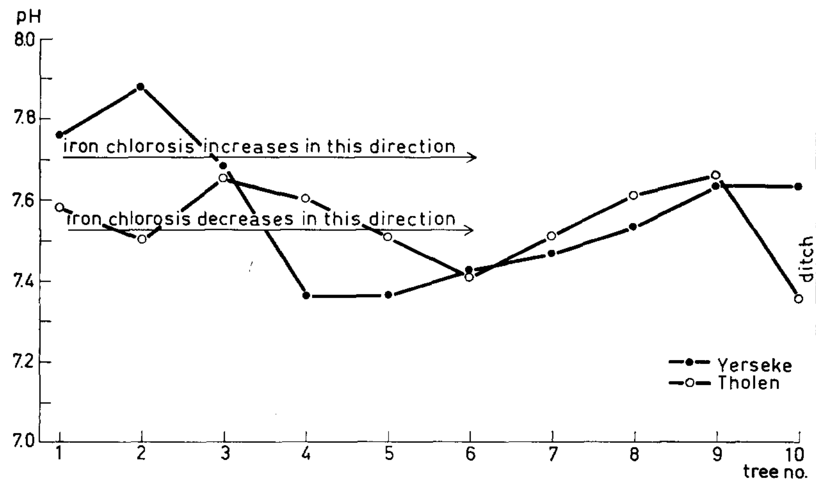

Fig. 1. Pathway of the soil pH in a row of pear trees at Tholen and Yerseke.

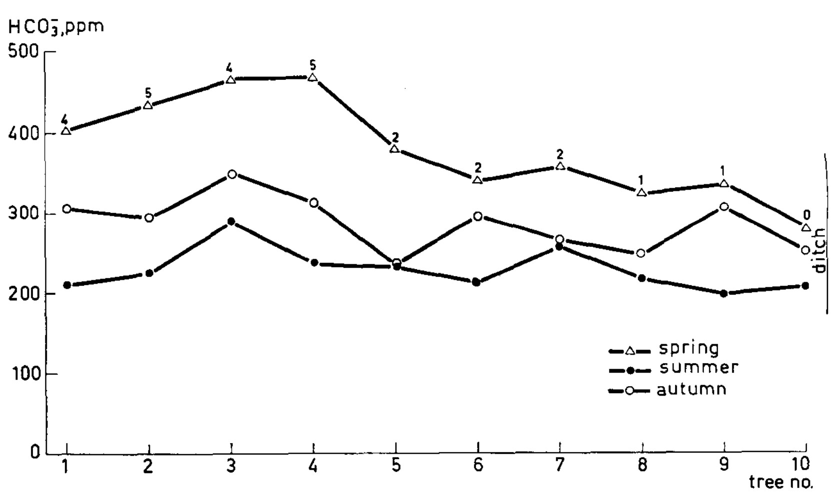

Fig. 2. Local and seasonal variations of the bicarbonate content in the soil and their relation to lime-induced chlorosis in a row of pear trees at Tholen in 1963. Each bicarbonate value is the mean of two replicates.

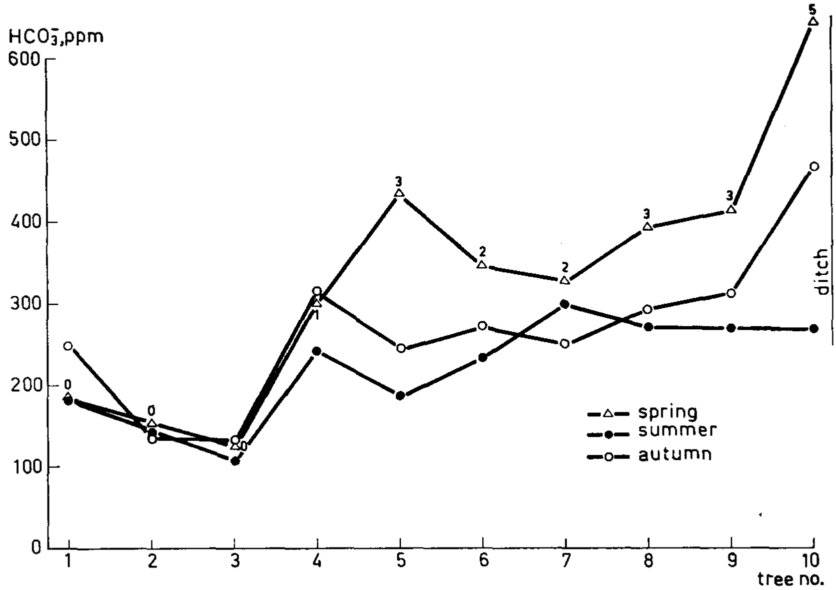

Fig. 3. Local and seasonal variations of the bicarbonate content in the soil and their relation to lime-induced chlorosis in a row of pear trees at Yerseke in 1963. Each bicarbonate value is the mean of two replicates.

Tholen the bicarbonate contents decreased towards the ditch, whereas the bicarbonate contents in the row at Yerseke showed an increase in this direction. In the first case far from the ditch the water cannot be drained away and on these places high bicarbonate contents arose. It is clear that from the viewpoint of iron chlorosis the water management must be corrected in this orchard. In the orchard at Yerseke, however, the level of underground water was high near the ditch as a result of a too high water level in the ditch and consequently high bicarbonate contents arose near the ditch. Generally the seasonal fluctuations of the bicarbonate content obtained in 1963 are the normal ones, but deviations in rainfall and evaporation may disturb this picture.

In comparison with 1963 there was considerably less rainfall in the spring of 1964 (Table 3). This difference is reflected in the bicarbonate values and also in the degree of iron chlorosis in the experimental rows. On the other hand the spring of 1965 was wet, just as in 1963, resulting in higher bicarbonate contents and more iron

TABLE 3

Fluctuations of rainfall and bicarbonate contents in the spring of 1963, 1964 en 1965

Year	Rainfall (mm) over March, April and May	HCO_3^- content in the spring at Tholen expressed as the average of 7 tree plots (ppm)	HCO_3^- content in the spring at Yerseke expressed as the average of 7 tree plots (ppm)	Degree of iron chlorosis
1963	166	407	409	severe
1964	121	337	331	moderate
1965	180	414	370	severe

TABLE 4

Contents of bicarbonate, calcium carbonate and acidity in the orchard soil of the Betuwe in the spring of 1970

Location of the orchard plots and degree of iron chlorosis in the trees		HCO_3^- content of the soil (ppm)	$CaCO_3$ in the soil (per cent)	pH of the soil
Echteld;	healthy	76	0,1	5.4
	moderate	262	0,2	6.9
Ochten;	healthy	153	0,0	6.4
	mild	184	0,2	6.7
Kesteren;	mild	179	0,3	6.9
	severe	516	1,5	7.3
Beuningen;	mild	144	0,3	6.7
	severe	340	1,2	7.4
Millingen;	healthy	169	0,1	6.8
	moderate	316	2,0	7.3
Lent;	moderate	204	0,1	6.9
	severe	287	0,9	7.2
Ommeren;	moderate	340	0,1	7.1
	severe	399	1,7	7.3
Winssen;	moderate	290	5,5	7.7
	severe	340	3,8	7.4

chlorosis than in 1964. The results of the field trial in the Betuwe are given in Table 4 and demonstrate again a close relationship between bicarbonate content of the soil and iron chlorosis in the trees.

Although the drainage in most orchards was unsufficient, no local variations in water regime could be found to give an explanation of the differences in bicarbonate content and iron chlorosis of the two plots in the same orchard. An explanation of why these differences occur is given here by the local pH variations in the orchards. At the pH range from weakly acid to neutral the bicarbonate content is greatly affected by variations of the pH in the soil and so it can happen, that in spite of poor drainage a locally lower pH value prevents the development of a high bicarbonate content on this plot in the orchard. These local differences of the pH in the orchards are possible because the river clay region of the Betuwe finds itself on the border-line of decalcification as appears from the calcium carbonate contents in Table 4.

DISCUSSION

The system $CaCO_3$–CO_2–H_2O has been the subject of many studies [5 9]. However, the equilibrium considerations of calcite cannot be simply transferred to calcareous soil systems. Besides differences in solubility of the various carbonate forms (aragonite, dolomite, monohydrate and hexahydrate) other ions in the soil like magnesium sulphate and phosphate and also the clay minerals complicate the carbonate equilibria in the soil.

For a better understanding of the pH effect on bicarbonate concentration in soils two differents soil types are considered.

In a weakly acid soil the following equilibrium reaction will dominate:

$$H_2O + CO_2 \rightleftarrows H^+ + HCO_3^-$$

This relations shows, that a rise of the pH will increase the bicarbonate concentration.

In an alkaline soil, however, the following equilibria will determine the bicarbonate concentration:

$$OH^- + CO_2 \rightleftarrows HCO_3^- \qquad [1]$$

$$HCO_3^- + OH^- \rightleftarrows CO_3^{2-} + 2H_2O \qquad [2]$$

From Equation [1] it is seen, that a rise of pH will cause an increase of the bicarbonate concentration. On the contrary Equation [2] shows that an increase of pH will decrease the bicarbonate concentration. Therefore in calcareous soils the curve pH versus HCO_3^- concentration shows a maximum HCO_3^- concentration at a definite pH-value and a fall or rise of this value will cause a decrease of the bicarbonate concentration.

This pH-value can be different for each calcareous soil because the value is also influenced by the solubility of the carbonate form and the above-mentioned ions involved in the bicarbonate equilibria. In view of this some relation would be expected to exist between HCO_3^- content and pH in the weakly acid to neutral soils of the Betuwe, but this relation is absent in the calcareous soils of Yerseke and Tholen. The failure of any interaction between high soil pH and the occurrence of lime-induced chlorosis is also supported by the pot experiments where high soil pH in absence of high bicarbonate content was not able to induce iron deficiency. Of course a high pH reduces the solubility of inorganic iron but probably the most calcareous soils contain sufficiently available organic iron for healthy growth.

On wet calcareous soils the development of a high bicarbonate content must be seen as the interaction of three factors, namely, a high CO_2 pressure in the soil, hydrolysis of $CaCO_3$ and the pH. The effects of high CO_2 pressure in the soil and $CaCO_3$ hydrolysis are favoured by the high soil moisture and can be represented by the following reaction:

$$CaCO_3 + H_2O + CO_2 \rightleftarrows Ca^{2+} + 2HCO_3^-$$

Often it is assumed that lime-induced chlorosis only occurs on soils having a high calcium carbonate content. In the Betuwe, however, it has been found that a content of 0.1 per cent $CaCO_3$ was sufficient to cause lime-induced chlorosis.

Some workers [3] [6] suggest that high levels of calcium also contribute to lime-induced chlorosis. The fact, that a decreased calcium content of the leaf is a characteristic of much iron chlorosis, does not support this suggestion.

The possibility that a decrease in oxygen level as a result of high soil moisture content may be a causal factor in chlorosis appears also unlikely since in the second pot experiment a combination of $Ba(OH)_2$ and high soil moisture did not induce iron chlorosis.

The correlation found between lime-induced chlorosis and the bicarbonate values in the spring suggests a way in which the chlorosis susceptibility of calcareous soils may be predicted. Also annual variations in the degree of chlorosis can be predicted by means of the bicarbonate contents in the spring.

In field experiments with calcareous soils it has been shown that defects in the draining system may cause locally high bicarbonate contents in the orchards. Other defects such as an impermeable layer in the soil, improper land leveling and a poor soil structure leading to locally improper water management were observed in various orchards. Here iron chlorosis and high bicarbonate contents were found where these defects were observed. The irregularity with which chlorosis often occurs on calcareous soils now becomes clear because the chlorosis has been closely related to local variations of the water management in the soil. Therefore careful attention should be given to the water management of the soil before planting of a new orchard.

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