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# BEHAVIOUR OF IRON AND MANGANESE CHELATES IN CALCAREOUS SOILS AND THEIR EFFECTIVENESS FOR PLANTS

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SUMMARY

The behaviour of the metal chelates Mn–EDTA, Mn–DTPA, Mn–EDDHA, Fe–EDTA, Fe–DTPA and Fe–EDDHA in calcareous soils and their availability to plants were studied.

The effectiveness of a metal chelate was shown to depend on its stability, the fixation capacity in the soil and its toxicity to the plant. Incorporation of Fe–DTPA into a framework of silica molecules prevents the fixation of Fe–DTPA in the soil.

Fe–DTPA and Fe–EDDHA cause a reduction in the manganese uptake of the plant.

The most striking result was the behaviour of Mn–DTPA in calcareous soils. Partial replacement of manganese in the chelate by iron from the soil makes this chelate useful for supplying the plant with both iron and manganese. Mn–DTPA appears to be the ideal type of chelate for the correction of chlorosis in the Netherlands, but unfortunately is not yet commercially available.

## INTRODUCTION

The use of chelated minor elements was pioneered by Jacobson with the introduction of the ferric iron chelate of ethylenediaminetetraacetic acid (Fe–EDTA) as an iron nutrient in water cultures.

In 1952, Stewart and Leonard[8] successfully applied Fe–EDTA for correcting iron deficiency of citrus in Florida. The trees on these acid sandy soils develop chlorosis as a result of copper toxicity.

In calcareous soils, however, the iron chelate of EDTA is not an efficient source of iron for plants. At high pH, OH-ions are attached to Fe–EDTA and the hydroxy-Fe–EDTA that is formed is much less stable than Fe–EDTA itself. Calcium from the soil will then replace the iron in the chelate making the iron ineffective.

Intensive research has resulted in the development of the very stable iron chelates of diethylenetriaminepentaacetic acid (Fe–DTPA) and ethylenediamine-di(o-hydroxyphenylacetic acid) (Fe–EDDHA) for the control of iron chlorosis under alkaline conditions. Fe–EDDHA has proved to be the better for use on calcareous soils.

In the Netherlands Fe–EDDHA is commonly used for chlorotic horticultural plants; because of its high cost it is only used on a limited scale in fruit culture.

Although the chelates of zinc, manganese and copper also are obtainable on the market their use is limited to special conditions. In many cases deficiencies in these trac-elements can be cured by soil dressing or by spraying with inorganic salt solutions. Moreover, most chelates of these trace elements have the disadvantage that they have a lower stability than the corresponding iron chelates. When a zinc chelate is added to the soil therefore, it will partly lose its effectiveness, because the zinc can be replaced by trivalent iron from the soil. Competition between the various metal ions can be explained by the stability sequence of Irving and Williams [3] which generally follows the order: Fe(III) $>$ Cu $>$ Ni $>$ Co $>$ Zn $>$ Fe(II) $>$ Mn $>$ Ca.

Besides the stability, other characteristics like fixation on the clay, leaching rate, microbiological attack and toxicity to the plant determine the value of a metal chelate for soil application.

In the present work a study was made of the behaviour of iron and manganese chelates in the soil and their effectiveness for plants.

## EXPERIMENTAL

### *Pot experiment with barley*

The experiment was performed in Mitscherlich pots with a manganese-deficient soil from the Wieringermeer Polder. This sandy clay soil contained 10 per cent of the fraction $<$ 16 microns, 1.8 per cent organic matter and 30 ppm manganese in an easily reducible form. The pH of the soil was 7.5. As a basal dressing each pot received adequate amounts of $NH_4NO_3$, $K_2HPO_4$ and $MgSO_4 . 7\,H_2O$. The metal chelates tested were Mn–EDTA, Mn–DTPA, Fe–EDTA, Fe–DTPA, and Fe–EDDHA applied at rates of 15, 75, 112.5, 150, and 225 kg iron or manganese per ha.

Before the barley (var. Agio) was sown, the chelates were incorporated into the soil by thorough mixing while the soil was dry. The treatments were replicated threefold and the pots in each replication were arranged randomly.

For comparison of the effect of the manganese chelates, the plants in three pots were sprayed twice with a 1.5 per cent manganese sulphate solution, the usual method for correcting manganese deficiency in field crops.

During growth, the pots were irrigated daily with abundant demineralized water. The leachates from each pot were collected and analysed for manganese, iron and chelate. After harvesting, grain yield, manganese and iron contents of the grain were determined.

*Pot experiment with roses*

A compost soil was prepared by mixing a sandy clay soil with peat in the ratio of 10:1. Since iron deficiency occurs especially on calcareous soils the compost soil was brought to pH 7.5 by liming with $CaCO_3$. In addition to fertilizing all pots with major elements (1.07 g N, 0.75 g $P_2O_5$, and 1.78 g $K_2O$ per 10 kg of compost soil, the following treatments were carried out in triplicate: (a) no chelate, (b) 5 g Mn–DTPA, (c) 5 g Fe–DTPA, (d) 2.5 g Mn–DTPA + 2.5 g Fe–DTPA, and (e) 13.16 g silica entrapped Fe–DTPA equivalent to 5 g Fe–DTPA on the basis of its iron content.

This last chelate was prepared in the laboratory according to Smith and Womersley[7] by neutralization of the acid form of Fe–DTPA with an equivalent amount of sodium silicate ($Na_2SiO_3$).

After planting the roses (var. Tawny Gold) the pots were irrigated and leached as in the previous experiment. The leachates were again analysed for manganese, iron and chelate.

At the end of the growth period, the youngest fully developed leaves were washed with a 0.2 per cent detergent solution, dried and analyzed for iron and manganese.

*Field trial with apple trees*

In an apple orchard (James Grieve) on a calcareous soil the trees showed symptoms of both manganese and iron deficiency.

In May 1964, the following treatments were applied: (a) no chelate; (b) 150 g Fe–EDDHA per tree; (c) 150 g Fe–DTPA per tree; (d) 250 g Mn–EDDHA per tree; (e) 250 g Mn–DTPA per tree. Each treatment was replicated eight times. So as to get a quick response the chelates were injected into the soil. To evaluate the effectiveness of the treatments, the trees were rated for iron and manganese deficiency after three months.

*Analytical methods*

Iron was determined by a modified *o*-phenanthroline method as described by Van Driel[1] after digestion of the leaf material and the leachate with sulphuric acid and perchloric acid according to Oosting.

The digestion for the manganese analyses was carried out with a mixture of concentrated sulphuric acid and nitric acid (1 vol. $H_2SO_4$ : 1 vol. $HNO_3$) and manganese was determined colorimetrically using formaldoxime.

The total chelate content in the leachates was estimated by an ultraviolet spectrophotometric method according to Hill-Cottingham. The method is based on the conversion of the chelates of other metals to iron chelates by use of the fact that the stability constants of the trivalent iron chelates exceed those of any other metal.

## RESULTS

Table 1 shows the results of the pot experiment with barley. Mn–DTPA causes a relatively large increase in grain yield and manganese content whereas the effects of Mn–EDTA are less pronounced. With respect to the iron chelates, the grain yield responds best to Fe–EDDHA.

TABLE 1

Yields, manganese and iron contents of the grain in the pot experiment with barley

| Metal chelate | Application rate of metal chelate kg Fe or Mn per ha | Dry-weight yield per g/pot | Mn, ppm dry weight | Fe, ppm dry weight |
|---|---|---|---|---|
| No chelate | 0 | 11.6 | 7.7 | 60.6 |
| Mn–EDTA | 15 | 12.7 | 9.8 | |
| | 75 | 13.3 | 11.1 | |
| | 112,5 | 12.3 | 11.0 | |
| | 150 | 12.8 | 9.5 | |
| | 225 | 12.8 | 9.4 | |
| Mn–DTPA | 15 | 12.8 | 10.3 | |
| | 75 | 14.8 | 14.5 | |
| | 112.5 | 15.6 | 18.5 | |
| | 150 | 15.0 | 25.5 | |
| | 225 | 14.5 | 39.4 | |
| Fe–EDTA | 15 | 11.2 | | 59.5 |
| | 75 | 13.7 | | 64.7 |
| | 112.5 | 13.1 | | 65.6 |
| | 150 | 12.2 | | 65.6 |
| | 225 | 7.2 | | 60.0 |
| Fe–DTPA | 15 | 11.2 | | 76.4 |
| | 75 | 13.2 | | 77.1 |
| | 112.5 | 10.7 | | 80.9 |
| | 150 | 8.9 | | 69.4 |
| | 225 | 6.7 | | 65.1 |
| Fe–EDDHA | 15 | 10.0 | | 68.2 |
| | 75 | 14.5 | | 90.2 |
| | 112.5 | 13.8 | | 111.9 |
| | 150 | 14.0 | | 135.6 |
| | 225 | 13.7 | | 149.5 |
| 2 sprays with 1,5% $MnSO_4$-solution | | 13.1 | 12.6 | |

TABLE 2

Recoveries of chelate, manganese and iron in the pot experiment with barley expressed as average percentages of all rates

| Treatment | Chelate, % leached | Manganese, % leached | Iron, % leached |
|---|---|---|---|
| Mn–EDTA | 83 | 0.2 | 3.7** |
| Fe–EDTA | 81 | 0.1* | 10 |
| Mn–DTPA | 97 | 11.1 | 63** |
| Fe–DTPA | 80 | 2.6* | 65 |
| Fe-EDDHA | 47 | 0.1* | 47 |

* Manganese recovery has been calculated as a percentage of the total amount of manganese, which can be chelated by the free ligand.

** Iron recovery has been calculated as a percentage of the total amount of iron, which can be chelated by the free ligand.

Low rates of Fe–EDTA and Fe–DTPA increase the grain yield, but the higher rates depress it relative to the control. This last effect may be due to toxicity of Fe–EDTA and Fe–DTPA. From the iron contents it will be seen that the effectiveness of Fe–EDTA as a source of iron in this soil is very poor whereas Fe–DTPA was very effective. However, the largest iron uptake is obtained with Fe–EDDHA without any toxic effect.

The analytical results for the leachates are given in Table 2. The percentages of metals and chelates are average values of all rates. The data show that the manganese and iron recoveries of Mn–EDTA and Fe–EDTA in the leachates are very small. With Fe–DTPA, however, 65 per cent of the iron remains soluble. The same percentages of EDDHA and iron in the leachate indicate that Fe–EDDHA is extremely stable in calcareous soils.

In comparison with the other chelates Fe–EDDHA shows the lowest leaching rate. That the remaining Fe–EDDHA in the soil was not fixed was proved by liberating the chelate after continued leaching.

The behaviour of Mn–DTPA in the soil is quite different from that of the other chelates. Besides giving a better soluble manganese supply than Mn–EDTA, this chelate mobilizes a considerable amount of iron in the soil.

TABLE 3

Iron and manganese contents of the youngest leaves and deficiency ratings in the pot experiment with roses

| Treatment | Fe, ppm dry weight | Mn, ppm dry weight | Fe-deficiency rating* | Mn-deficiency rating* |
|---|---|---|---|---|
| Control | 50 | 46 | 3 | 1 |
| Mn–DTPA | 105 | 130 | 0 | 0 |
| Mn–DTPA + Fe–DTPA | 107 | 86 | 0 | 0 |
| Fe–DTPA | 107 | 32 | 0 | 3 |
| Silica-entrapped Fe–DTPA | 140 | 40 | 0 | 1 |

* 0–3, no-severe deficiency symptoms.

TABLE 4

Recoveries of chelate, manganese and iron in the pot experiment with roses, expressed as percentage of the rates

| Treatment | Chelate, % leached | Manganese, % leached | Iron, % leached |
|---|---|---|---|
| Mn–DTPA | 98 | 30 | 68** |
| Mn–DTPA + Fe–DTPA | 67 | 11* | 66** |
| Fe–DTPA | 42 | 3.6* | 37 |
| Silica-entrapped Fe–DTPA | 88 | 4.4* | 97 |

* Manganese recovery has been calculated as a percentage of the total amount of manganese, which can be chelated by the free ligand.

** Iron recovery has been calculated as a percentage of the total amount of iron, which can be chelated by the free ligand.

The results of the pot experiment with roses are presented in Table 3. The treatment with Fe–DTPA corrects the iron deficiency in the plants, but aggravates the symptoms of manganese deficiency. On the other hand, Mn–DTPA not only cures the manganese deficiency but also the iron chlorosis. The iron and manganese contents of the young leaves are in agreement with these observations.

Fertilizing with silica-entrapped Fe–DTPA gives complete suppression of the iron deficiency symptoms but has little influence on the manganese disorder.

The data on the leachate analyses (Table 4) again confirm that

TABLE 5

Deficiency ratings of apple trees three months after treatment with different metal chelates

| Treatment | Fe-deficiency rating* | Mn-deficiency rating* |
|---|---|---|
| Control | 2 | 1 |
| 150 g Fe-EDDHA | 0 | 3 |
| 150 g Fe–DTPA | 0 | 3 |
| 250 g Mn–EDDHA | 1 | 1 |
| 250 g Mn–DTPA | 0 | 0 |

* *0–3, no–severe deficiency symptoms.*

Mn–DTPA dissolves a large amount of iron from the soil. In this experiment the recovery of Fe–DTPA is much lower than in the previous one. Continued leaching showed that the remaining Fe–DTPA had been fixed in the compost soil. The incorporation of Fe–DTPA into a silica framework greatly decreases the fixation of the chelate.

The effectiveness of the iron and manganese chelates in the field trial with apple trees is demonstrated in Table 5. Both Fe–EDDHA and Fe–DTPA correct the iron deficiency in the trees, but they aggravate the manganese deficiency. Mn–EDDHA slightly reduces the iron chlorosis, but fails to correct the manganese deficiency. Complete control of iron and manganese deficiency is obtained with Mn–DTPA.

## DISCUSSION

Most of the results in this study can be explained by stability considerations and competition for chelating sites by different metals.

In general, the experiments show that the effectiveness of the chelate increases with its stability. In calcareous soils the stabilities of Mn–EDTA and Fe–EDTA are too low to supply the plants adequately with manganese and iron. Both alkaline hydrolysis and the substitution of iron and manganese by calcium in the chelates decrease their effectiveness. Similar results were obtained by Hill-Cottingham [2] and Wallace *et al.*[9].

Although in most cases Fe–DTPA is very successful for correcting iron chlorosis it may have some unfavourable effects. As was found in the pot experiment with roses this chelate depresses the manganese uptake, hence it is possible that Fe–DTPA induces manganese deficiency. Another deterrent to its use could be the toxicity to the plant at high levels as we have seen in the pot experiment with barley. Furthermore, the fixation of Fe–DTPA which occurred in the compost soil (Table 4) reduced the value of this chelate as a source of iron. When Fe–DTPA is incorporated into a silica framework, fixation is largely prevented; further study may show whether this will lead to a better response.

Fe–EDDHA overcomes the two last mentioned objections to Fe–DTPA. It is true that this chelate can also induce manganese deficiency, but Fe–EDDHA is the least toxic of all iron chelates and it is not fixed in the soil. Moreover, the low leaching rate guarantees that the iron chelate remains available in the root zone for a period of at least three months.

It is rather surprising that Mn–DTPA not only corrects manganese deficiency, but also iron deficiency. The higher stability of Mn–DTPA confirms that it is a better manganese dressing on calcareous soil than Mn–EDTA. On the other hand, Mn–DTPA is also very effective as an iron supplier, because the manganese in the chelate is partially replaced by iron from the soil. The application of Mn–DTPA therefore offers the advantage of a well-balanced iron and manganese supply to the plant and in this respect it is preferable to Fe–EDDHA for the correction of iron chlorosis in plants, which are susceptible to manganese deficiency.

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