EFFECT OF SUPERPHOSPHATE ON THE GROWTH OF CITRUS SEEDLINGS IN RELATION TO ITS REACTIONS WITH TWO ACID SOILS

(Met opsomming in Afrikaans)

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Abstract

The effects of superphosphate, its component compounds and comparable calcium and phosphate compounds, on the growth of sweet orange seedlings were tested in pot experiments using two acid soils. Superphosphate at high levels of application was found to be toxic and the toxicity was associated with the monocalcium phosphate in the fertilizer. Superphosphate was also compared with other phosphate fertilizers at two levels of application. Fertilizers containing no water-soluble but only two per cent citric acid-soluble phosphate showed no toxic effects and some forms stimulated growth of the plants. The reactions of superphosphate with the two soils were studied by using a fractionation technique. An immediate increase in insoluble aluminium phosphate following the application of the superphosphate, and a decrease in the difference between pH values in soil pastes made with water and 1 N KCl, indicates displacement of adsorbed aluminium and subsequent precipitation as a phosphate compound. The delayed and more gradual secondary increase in insoluble aluminium and iron phosphate indicates dissolution of aluminium and iron compounds in the soil through the action of the triple point solutions leading to the formation of soluble, unstable, aluminium and iron phosphate compounds that are subsequently precipitated after conversion to more stable compounds. The toxic effect is ascribed to high concentrations of aluminium or complex aluminium phosphate ions in the soil solution during this intermediary stage.

Introduction

Citrus grown on acid soils in the subtropical areas of the Republic of South Africa, requires regular applications of phosphate fertilizer for optimum production and fruit quality. The need for the application of phosphate fertilizers was first recognized by van der Plank & Turner (1936). In a fertilizer experiment with navel trees, Anderssen (1937), confirmed that applications of superphosphate improved the fruit quality. Rosselet, Hefer, Helff, Langenegger & le Roux (1962), found that applications of superphosphate increased the yield and improved the fruit quality of Valencia oranges.

Goldschmidt (1950) studied phosphate 'fixation' and movement in some of these acid citrus soils and found that the 'fixation' was high and the movement very slow. Superphosphate is applied to the soil surface without incorporation of the fertilizer into the soil (Naude, 1954) and therefore movement of the phosphate into the root zone is limited. Because of this lack of sufficient movement of the phosphate it became a general practice to apply substantial quantities of phosphate fertilizer to the planting hole when planting young citrus trees. Loss of young trees in new plantings

so treated, failure of young trees to grow satisfactorily and occurrence of severe copper and zinc deficiencies, indicated that these heavy phosphate applications might be harmful. Spencer (1960) found that heavy phosphate applications reduced grapefruit tree size and the concentration of feeder roots, especially in the top foot of soil.

In the present study the effects of large applications of superphosphate and other phosphate fertilizers on the growth and nutrient uptake of citrus seedlings were investigated. The reactions of superphosphate with two acid soils were studied to explain some of its effects on the growth of the seedlings.

Procedure

Two soils from the Eastern Transvaal Lowveld were used. The Nelspruit soil is an alluvial loamy coarse sand from granitic parent material, low in manganese, dark brown to reddish brown in colour, CEC of approximately 5 me/100 g, clay minerals predominantly kaolin with a 10 Å component (probably biotite) and traces of crystalline gibbside, and, pH (water paste) of the virgin soil 6.3. This soil was classified as an alfisol (probably a durustalf) according to the USDA classification system (7th approximation). The Alkmaar soil is a red alluvial loam on a river terrace along the Crocodile river. The original soil that was eroded to be subsequently deposited on this terrace was probably a latesol (oxisol). Properties of this soil are, CEC of approximately 11 me/100 g, pH of virgin soil 5.6, and clay minerals predominantly kaolin with crystalline gibbsite and traces of a 100 A component. Similar soils are known to contain low quantities of manganese and high quantities of iron and aluminium (van der Merwe, 1940).

A series of pot experiments was conducted in which finely ground fertilizers or salts were mixed with airdried soil that had been passed through a $\frac{1}{4}$ inch screen. The mixtures were placed in four-gallon containers and planted to sweet orange seedlings, selected for uniformity. Two seedlings were planted per container within about three hours after the soil-fertilizer or soil-salt mixture had been prepared. Throughout the experiments the plants were watered with distilled or rain water. No free drainage was allowed and the quantity of water applied was controlled so as to keep the soil moist throughout the container without excess water collecting at the bottom. All pots were given uniform applications of ammonium nitrate during the experiments.

In all three pot experiments a randomized complete block design was used with 12 treatments, replicated four times. Significant differences were calculated at the five per cent level of probability and the Duncan multiple range test was used for comparison of treatment means.

The plants were allowed to grow for nine months. At the end of this period the soil was washed from the containers and the plant roots. Each plant was divided into three sections, the roots, the leaves and the remainder of the above-ground section. These sections were washed free of dust and dirt, dried at 65°C for three days and weighed. The dry leaves were finely ground, dry-ashed and analysed for phosphorus by the vanadate method, for potassium by the flame photometric method and for calcium and magnesium by the EDTA titration method. Nitrogen was determined in the leaf-powder by the Kjeldahl method.

Two pot experiments were conducted, one with the Nelspruit soil and the other with the Alkmaar soil, to determine the effect of superphosphate, some of its chemical components and comparable chemical compounds containing either calcium or phosphate, on the growth and leaf composition of the sweet orange seedlings. The applications in all treatments were made at two levels. The treatments were superphosphate high grade fertilizer at 0.63 and 2.50 g per 100 g of dry soil (equivalent to 0.052 and 0.210 g, two per cent citric acid-soluble P per 100 g of soil); monocalcium phosphate at 0.23 and 0.90 g per 100 g of dry soil (equivalent to 0.052 and 0.21 g, two per cent citric acid-soluble P per 100 g of soil); calcium sulphate at 0.33 and 1.32 g per 100 g of dry soil (this provides the same quantity of calcium sulphate as that associated with the superphosphate in the first two treatments); calcium carbonate at 0.19 and 0.75 g per 100 g of soil (provides equivalent concentrations of calcium to that of the previous two treatments); mono-ammonium phosphate at 0.21 and 0.05 g per 100 g of dry soil (equivalent to 0.052 and 0.013 g soluble P per 100 g); a combination of 0.05 g mono-ammonium phosphate and 0.33 g calcium sulphate per 100 g of dry soil; and a control treatment.

In a third experiment, superphosphate was compared with other phosphate fertilizers when applied at two levels. At the different levels the quantities of fertilizer applied were calculated to provide near equivalent quantities of citric acid-soluble P. The treatments were superphosphate at 0.625, 0.312 and 0.156 g per 100 g dry soil; basic-slag at 0.742 and 0.371 g per 100 g of soil; super and raw phosphate (1:1 mixture), at 0.54 and 0.27 g per 100 g of soil; Calmafos at 0.33 and 0.66 g per 100 g of soil; Langfos at 1.98 and 0.99 g per 100 g of soil; and a control treatment.

The reactions of superphosphate with the two soils were studied in mixtures of finely ground high grade superphosphate with the dry soil that had passed through a 1mm sieve. Immediately after mixing, the mixtures were moistened by applications of distilled water and were kept moist for the duration of the experiment. Samples were withdrawn at regular intervals from the mixtures, starting 15 minutes after mixing, over a period of 65 days. The method of Chang & Jackson (1957) was used to determine the 'aluminium phosphate', 'iron phosphate' and 'calcium phosphate' fractions. pH values of the samples were determined in water and 1 N KCl solution pastes of the soils. The 'titratable acidity' was determined by titrating samples in 1 N KCl solution against 0.1 N NaOH solution to a pH of 8.5, as indicated by a pH meter.

Results and discussion

In the first two experiments the superphosphate and monocalcium phosphate treatments at the higher level of application, killed all the seedlings. As can be seen in Tables 1 and 2 none of the other treatments produced larger plants than the control treatment in either of the two soils.

TABLE 1 *Weight of plant parts in grams—Nelspruit soil*

Treatment		Weight of		
Quantities in g per 100 g dry soil		Roots	Tops	Total
Control	0.00	11.55^c	15.70^{ab}	27.88^{cd}
Superphosphate	2.50	0	0	0
Superphosphate	0.63	6.40^a	12.28^a	18.68^a
Ca(H$_2$PO$_4$)$_2$	0.90	0	0	0
Ca(H$_2$PO$_4$)$_2$	0.23	6.58^a	15.10^{ab}	21.68^{abc}
CaSO$_4$	1.32	10.93^{bc}	15.63^{ab}	26.55^{bcd}
CaSO$_4$	0.33	10.70^{bc}	11.60^a	22.30^{abc}
CaCO$_3$	0.75	8.48^{ab}	16.58^{ab}	25.05^{abcd}
CaCO$_3$	0.19	11.98^c	15.05^{ab}	27.03^{cd}
NH$_4$H$_2$PO$_4$	0.21	7.12^a	13.73^a	20.85^{ab}
NH$_4$H$_2$PO$_4$	0.05	10.80^{bc}	20.58^b	31.38^d
NH$_4$H$_2$PO$_4$ +CaSO$_4$	0.05 \ 0.33 ⌡	8.68^{ab}	20.78^b	29.45^d

NOTE: Where the figures in any column of Tables 1–6 contain the same letter (a, b, c, . . .) differences between those figures are not significant at the five per cent level.

TABLE 2 *Weight of plant parts in grams—Alkmaar soil*

Treatment		Weight of		
Quantities in g per 100 g dry soil		Roots	Tops	Total
Control	0.00	13.7^e	14.6^{bc}	28.3^c
Superphosphate	2.50	0	0	0
Superphosphate	0.63	7.8^b	11.7^b	19.5^b
Ca(H$_2$PO$_4$)$_2$	0.90	0	0	0
Ca(H$_2$PO$_4$)$_2$	0.23	9.8^{bcd}	15.8^c	25.7^c
CaSO$_4$	1.32	11.1^{cde}	14.1^{bc}	25.2^{bc}
CaSO$_4$	0.33	11.2^{cde}	13.8^{bc}	25.0^{bc}
CaCO$_3$	0.75	11.7^{cde}	16.9^c	28.6^c
CaCO$_3$	0.19	12.2^{de}	14.8^{bc}	27.0^c
NH$_4$H$_2$PO$_4$	0.21	4.9^a	6.4^a	11.3^a
NH$_4$H$_2$PO$_4$	0.05	9.3^{bc}	16.1^c	25.4^{bc}
NH$_4$H$_2$PO$_4$ +CaSO$_4$	0.05 \ 0.33 ⌡	11.5^{cde}	17.4^c	28.9^c

In both soils the treatments with calcium sulphate and calcium carbonate had no effect on top weight (weight of leaves plus twigs) or total weight of the plants, when compared with the plants of the control treatment. In the Nelspruit soil the heavier application of calcium carbonate reduced the root weight but the other treatments with calcium sulphate or carbonate, had no effect. The treatment with mono-ammonium phosphate at the higher rate of application, reduced growth of roots and tops, and at the lower rate of application it showed a tendency to reduce root weight but showed no effect on top or total weight.

Both the treatments with superphosphate and monocalcium phosphate at the lower rate of application, reduced the weight of the roots. The superphosphate treatment in addition showed a tendency to reduce the weight of the tops while the monocalcium phosphate treatment had no effect on the top weight.

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TABLE 3 . *Leaf Composition of seedlings grown in the Nelspruit soil*

Treatment		% N	% P	% K	% Ca	% Mg
Quantities in g per 100 g dry soil						
Control	0.00	3.02^a	0.137^a	1.50^d	3.11^b	0.39*
Superphosphate	0.63	3.11^a	0.364^b	1.21^{bc}	4.02^{cd}	0.28*
Ca (H$_2$PO$_4$)$_2$	0.23	2.98^a	0.366^b	1.24^{bc}	3.97^{cd}	0.41*
CaSO$_4$	1.32	2.89^a	0.139^a	1.32^{bc}	3.23^b	0.32*
CaSO$_4$	0.33	2.82^a	0.122^a	1.37^{cd}	3.51^{bc}	0.37*
CaCO$_3$	0.75	2.81^a	0.166^a	1.55^d	3.94^{cd}	0.33*
CaCO$_3$	0.19	2.72^a	0.151^a	1.49^d	4.12^d	0.30*
NH$_4$H$_2$PO$_4$	0.21	4.24^b	0.425^b	1.11^{ab}	2.36^a	0.44*
NH$_4$H$_2$PO$_4$	0.05	2.98^a	0.179^a	1.21^{bc}	3.32^b	0.52*
NH$_4$H$_2$PO$_4$ +CaSO$_4$	0.05 / 0.33	3.12^a	0.198^a	0.99^a	3.51^{bc}	0.29*

*Differences not significant

TABLE 4 *Leaf composition of seedlings grown in the Alkmaar soil*

Treatment		% N	% P	% K	% Ca	% Mg
Quantities in g per 100 g dry soil						
Control	0 00	3.00*	0.070^a	1.43^{bc}	3.37^{ab}	0.470^{abc}
Superphosphate	0.63	3.10*	0.201^d	1.29^{abc}	3.55^{abc}	0.654^d
Ca(H$_2$PO$_4$)$_2$	0.23	3.05*	0.199^d	1.17^{ab}	3.96^{bc}	0.437^{ab}
CaSO$_4$	1.32	3.08*	0 082^{ab}	1.44^{bc}	3.42^{ab}	0 491^{bc}
CaSO$_4$	0 33	3.07*	0.088^{abc}	1.46^{bc}	3.16^a	0 454^{abc}
CaCO$_3$	0.75	3.30*	0 090^{abc}	1.18^{ab}	3 96^{bc}	0 365^{ab}
CaCO$_3$	0 19	3.23*	0 073^a	1:21^{ab}	4 19^c	0 311^a
NH$_4$H$_2$PO$_4$	0 21	3 45*	0.309^e	1.55^c	3.73^{abc}	0 606^{cd}
NH$_4$H$_2$PO$_4$	0 05	2 89*	0.138^{abcd}	1.10^a	3 37^{ab}	0 428^{ab}
NH$_4$H$_2$PO$_4$ +CaSO$_4$	0.05 / 0.33	2.98*	0.158^{bcd}	1.22^{ab}	3.64^{abc}	0.531^{bc}

*Differences not significant

Less of the soluble phosphate applied was available to the seedlings in the Alkmaar soil than to those in the Nelspruit soil, as indicated by the phosphorus content of the leaves (Tables 3 & 4). Those treatments in the Nelspruit soil that reduced root weight are all associated with a high level of phosphorus in the leaves.

In the Alkmaar soil, treatments with soluble phosphate increased the P content of the leaves but not to the extent that it could be considered to be highly excessive as in the case of the Nelspruit soil. It would appear that the reduction in growth must be associated with other factors. None of the other leaf components analysed gave any indication of severe malnutrition. The nitrogen content in all cases was high and unaffected by most of the treatments applied. All calcium and magnesium values are well within a normal range for optimum growth and the potassium levels are satisfactory, though slightly below the optimum value of 1.5 — 2.0%. No visual symptoms of any trace element deficiency were observed during the experiments.

In the third pot experiment, superphosphate was compared with other phosphate fertilizers at two levels of application. In addition a third level of superphosphate was included at a rate of application equal to one quarter of that known to be toxic to seedlings in the first experiments. The Nelspruit soil was used in this experiment. Superphosphate at the higher rate of application killed all the seed-

lings in that treatment and also at a rate of 0.625 g per 100 g of soil. In the other experiment with the Nelspruit soil the 0.625 g per 100 g soil treatment killed only three of the eight seedlings.

TABLE 5 *Weight of plant parts in grams (Nelspruit soil) following applications of phosphate fertilizers*

Treatment		Weight of		
Quantities in g per 100 g dry soil		Roots	Tops	Total
Control	0 00	8.4^{bc}	8.1^a	16.5^{ab}
Superphosphate	0 625	0	0	0
Superphosphate	0.312	0	0	0
Superphosphate	0.156	5.0^a	9.0^a	14.0^a
Calmafos	0 66	6.9^{ab}	11.4^{ab}	18.3^{abc}
Calmafos	0 33	6.9^{ab}	13.1^{abc}	20 0^{abc}
Basic Slag	0 742	5.1^a	7.7^a	12.8^a
Basic Slag	0.371	6.9^{ab}	11.2^{ab}	20.6^{abc}
Langfos	1.98	8.6^{bc}	14 8^{bc}	23.4^{bc}
Langfos	0 99	9.5^c	16.1^{bc}	25.5^c
Super and Raw	0.54	4.9^a	10.7^{ab}	15.5^{ab}
Super and Raw	0.27	8.0^{bc}	17.4^c	25.4^c

Weights of root sections, top sections and total weights of plants for this experiment are present-phate fertilizers produced better root systems than the control treatment. Superphosphate at 0.156 g per 100 g, basic slag and super & raw mixture at 0.742 and 0.540 g per 100 g of soil respectively reduced the root weight. Both treatments with Langfos and the super and raw treatment at 0.54 g per 100 g of soil produced seedlings with larger

TABLE 6 *Leaf composition of seedlings grown in Nelspruit soil treated with different phosphate fertilizers*

Treatment	Quantities in g per 100 g dry soil	%N	% P	% K	% Ca	% Mg
Control	0.00	3.86^d	0.078^a	2.34^f	2.66^a	0.58^b
Superphosphate	0.156	3.14^{bc}	0.310^g	1.39^{cd}	3.58^{bcd}	0.55^b
Calmafos	0.66	2.78^a	0.158^c	0.85^a	3.16^b	0.90^c
Calmafos	0.33	3.15^{bc}	0.219^e	1.05^{ab}	3.35^{bc}	0.97^c
Basic Slag	0.742	3.37^c	0.119^b	1.39^{cd}	4.44^e	0.42^a
Basic Slag	0.371	3.02^{ab}	0.184^{cd}	1.24^{bc}	3.80^d	0.42^a
Langfos	1.98	3.04^{abc}	0.229^{ef}	1.57^{de}	3.37^{bcd}	0.48^{ab}
Langfos	0.99	3.13^{bc}	0.200^{de}	1.38^{cd}	3.43^{bcd}	0.53^{ab}
Super and Raw	0.54	3.09^{abc}	0.354^h	1.72^e	3.35^{bc}	0.49^{ab}
Super and Raw	0.27	3.16^{bc}	0.243^f	1.39^{cd}	3.65^{cd}	0.53^{ab}

tops than the seedlings in the control treatment. Only Langfos and super and raw at 0.99 and 0.27 g citric-soluble P per 100 g soil respectively produced plants with a greater total weight than that of the plants of the control treatment.

The inorganic leaf composition (Table 6) of the seedlings was influenced by all the treatments. All forms of phosphate fertilizer increased the percentage phosphorus in the leaves, highest values being found in leaves of plants in the superphosphate and super and raw treatments at the higher rate of application. With both Calmafos and basic slag, higher P contents were found in the leaves of seedlings from the treatments at the lower than at the higher rates. Neutralizing substances known to be present in these fertilizers, apparently change the soil acidity and reduce the availability of the phosphate. Correlation coeffi-

cients were calculated for the correlations of leaf P with root weight (-0.3913), top weight ($+0.2693$) and total weight ($+0.0438$) and none of these are significant.

Calcium content of the leaves was increased by all the treatments. The highest value was found in the basic slag treatment at 0.75 g per 100 g. The results indicate that the fertilizers all provide plant available calcium, the uptake of which does not correspond with the uptake of the accompanying available phosphate. Calmafos is known to be a source of magnesium and the results show that this magnesium was readily available to citrus seedlings. The leaf composition bears no evidence of any severe malnutrition and during the experiment no visual symptoms of trace element deficiencies were observed.

TABLE 7 *Changes in pH, titratable acidity and phosphate fractions in the Nelspruit soil following applications of superphosphate*

Time of sampling relative to the time of mixing soil and superphosphate (in hours)	pH water	pH 1N KCl	Titratable acidity me/100 g	P in ppm as AlPO$_4$	P in ppm as FePO$_4$	P in ppm as Ca$_3$(PO$_4$)$_2$	P in ppm as Total
Before	6.3	5.3	1.30	5	22	50	77
3	4.7	4.5	—	—	—	—	—
5	4.7	4.4	—	19	23	38	80
24	4.8	4.5	3.53	56	25	59	140
48	4.8	4.5	3.82	57	41	45	143
72	4.8	4.6	4.32	—	—	—	—
96	—	—	—	45	44	40	129
120	5.0	4.8	3.89	38	53	33	124
168	4.9	4.7	4.65	—	—	—	—
192	—	—	—	127	66	27	220
240	4.9	4.6	2.59	113	49	33	195
336	—	—	—	105	67	38	210
360	5.0	4.7	4.00	—	—	—	—
432	—	—	—	132	78	44	254
480	4.9	4.6	2.33	—	—	—	—
552	—	—	—	169	61	37	267
600	5.0	4.6	3.28	—	—	—	—
672	—	—	—	182	46	40	268
720	4.9	4.6	3.61	—	—	—	—
840	—	—	—	206	48	42	296
888	4.7	4.7	3.96	—	—	—	—
1 512	—	—	—	342	84	40	466
1 584	4.8	4.5	4.12	—	—	—	—

TABLE 8   Changes in pH, titratable acidity and phosphate fractions in the Alkmaar soil following application of superphosphate

Time of sampling relative to the time of mixing soil and superphosphate (in hours)	pH		Titratable acidity me/100 g	P in ppm as			
	water	1N KCl		AlPO$_4$	FePO$_4$	Ca$_3$(PO$_4$)$_2$	Total
Before	5.8	4.7	5.4	8	55	22	85
3	4.7	4.3	—	—	—	—	—
5	4.6	4.2	—	74	60	30	164
24	4.7	4.3	14.1	69	63	36	168
48	4.9	4.5	9.8	87	79	39	205
72	4.9	4.5	8.5	—	—	—	—
96	—	—	—	91	79	35	205
120	5.0	4.6	7.7	105	80	48	233
168	4.9	4.4	9.3	—	—	—	—
192	—	—	—	141	90	52	283
240	4.9	4.4	4.2	140	93	78	311
336	—	—	—	163	91	62	316
360	5.0	4.5	3.7	—	—	—	—
432	—	—	—	187	114	70	371
480	4.9	4.4	5.9	—	—	—	—
552	—	—	—	227	150	60	437
600	4.9	4.4	7.6	—	—	—	—
672	—	—	—	289	173	89	551
720	4.9	4.4	5.5	—	—	—	—
840	—	—	—	400	173	66	639
888	4.8	4.4	4.0	—	—	—	—
1 512	—	—	—	407	216	72	695
1 584	4.8	4.4	5.3	—	—	—	—

Some of the reactions of superphosphate with the two soils were followed in the mixtures of fertilizer and soil. In Tables 7 and 8, the pH changes, as determined in soil pastes made with water and 1 N KCl solution over a period of 65 days, are graphed. A very rapid change in pH takes place within 15 minutes after mixing the fertilizer and soil. The pH of the Nelspruit soil as determined in a paste made with water dropped from 6.30 to 4.80 during the first day, gradually rose to 4.90 on the second and third days and remained more or less at that value for the remainder of the period. In the Alkmaar soil the pH dropped from 5.80 to 4.55, then increased gradually to 4.90 by the third day and remained there for the remainder of the period.

Initial differences between the pH values determined in a paste made with water and a paste made with 1 N KCl solution were 1 pH unit for the Nelspruit soil and 1.1 pH unit for the Alkmaar soil. Immediately following the application of superphosphate however, there was a greater reduction in the pH measured in water than in the pH measured in 1 N KCl. After this initial rapid reduction, the differences between the two pH values for each soil remained more or less constant at 0.30 pH unit for the Nelspruit soil and 0.40 pH unit for the Alkmaar soil. This indicates that in both soils there was a reduction in the exchangeable acidity immediately following the application of superphosphate.

The values for the 'titratable acidity' for the two soils are presented in Tables 7 and 8. This acidity increased two and a half fold in the Alkmaar soil during the first day and then gradually returned to the initial value in approximately 35 days. In the Nelspruit soil an initial increase of about the same magnitude was recorded although the values were considerably lower than those of the Alkmaar soil. However, in the Nelspruit soil the value remained at this raised level and failed to return to normal during the experimental period.

In Tables 7 and 8 the changes in the 'aluminium phosphate', 'iron phosphate' and 'calcium phosphate' are tabulated for both soils. Although the phosphate fractionation method of Chang & Jackson (1957) has some error in assigning the P from a particular extraction to a discrete compound, Laverty & McLean (1961) concluded after a critical study of the method that there seemed to be no valid reason why the method should not be used empirically in studying the fate of phosphate applied to soils.

The Nelspruit soil showed a small reduction in the 'calcium phosphate' with time. The 'iron phosphate' content increased from 22 ppm P to 65 ppm and then fluctuated around this value for the remainder of the period. P as 'aluminium phosphate' increased from 10 ppm to 55 ppm in the first day, decreased to 40 ppm at the fifth day, increased rapidly to 126 ppm and then more gradually to 341 ppm at the end of the experimental period.

In the Alkmaar soil the 'calcium phosphate' increased gradually from 20 ppm P to 70 ppm during the first 10 days and then remained more or less constant at that value. The 'iron phosphate', initially twice as high as the corresponding value in the Nelspruit soil, increased from 55 ppm to 173 ppm during the first 28 days, and then increased at a slower rate to 215 ppm at the end of the period. The quantities of 'iron phosphate' precipitated in the soils are apparently related to the iron contents of the soils. The 'aluminium phosphate' increased rapidly from 10 ppm to 70 ppm P within the first few hours and thereafter continued to rise sharply for 35 days to a value of 400 ppm P at which it remained for the last 28 days.

For both soils the total increase in three forms of phosphate as determined, exceed the quantity of soluble phosphate added. While 320 ppm of soluble phosphorus was added to both soils, the increase in insoluble phosphate compounds was

389 ppm P for the Nelspruit soil and 610 ppm P for the Alkmaar soil. Through the reactions of the superphosphate in the soil more phosphate is involved in the precipitation of aluminium, iron and calcium phosphates than the 'soluble P' in the superphosphate applied.

The values in Tables 7 and 8 suggest that at least two mechanisms are involved in the formation of insoluble aluminium phosphate. The initial rapid increase of aluminium phosphate, associated with the reduction in the difference between the pH values in soil pastes made with water and 1 N KCl, apparently follows the displacement of, and phosphate sorption by the exchangeable aluminium. Coleman, Thorup & Jackson (1960) and Franklin & Reisenauer (1960) indicated that phosphate sorption by soils was highly correlated with the exchangeable aluminium content of the soils. The reaction scheme suggested by Coleman et al (1960) for a pure clay system was:

$$Al-clay + MH_2PO_4 + 2MOH \underset{\longrightarrow}{\overset{\longleftarrow}{MCl}}$$

$$M_3-clay + Al(OH)_2H_2PO_4 + H_2O$$
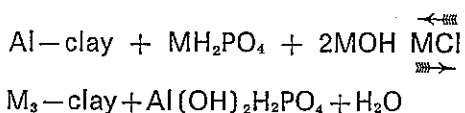
Alternatively they indicated that a compound with composition $AlPO_4.H_2O$ could be formed. The 'solubility product' for the reaction product calculated by them was between 1 and 2×10^{-28}. When salt was added to displace aluminium the reaction was complete at pH 4.0 The rapid initial increase in the insoluble aluminium phosphate in the two soils used in the present study is attributed a similar reaction taking place in these soils.

The second mechanism, apparently, is associated with the formation of the metastable triple point solution and triple point solution following the reaction of the superphosphate, as indicated by Lindsay & Stephenson (1959 a). The rapid reduction in pH and increase in titratable acidity of the mixtures during the first few hours of the reaction, suggests that the metastable triple point solution forms rapidly and is followed by dissolution reactions with the subsequent formation of iron, calcium and aluminium phosphates (Lindsay & Stephenson, 1959 b; Lindsay, Lehr & Stephenson, 1959). Formation of insoluble aluminium phosphate by this mechanism increased rapidly after an initial delay of four to five days. Taylor, Gurney & Lehr (1963), found that complex iron and aluminium phosphates formed by reaction of the metastable triple point solution or triple point solution with soil minerals, were unstable in acidic soil environments and that they hydrolysed with release of part of their phosphate to the soil and formation of simpler iron and aluminium phosphates. Lindsay, Frazier & Stephenson, (1962), identified some of the reaction products or superphosphate fertilizer with soils and indicated that considerable quantities of Fe and Al go into solution. The initial reaction products are mainly $CaHPO_42H_2O$, $CaHPO_4$ and colloidal [Fe Al X] PO_4 nH_2O together with various acidic calcium iron phosphates and calcium phosphates. In subsequent reactions the soluble products are transformed to less soluble iron and aluminium phosphates. The delay of four to five days is ascribed to the initial formation of more soluble but unstable aluminium phosphates that are subsequently converted to stable and less soluble compounds.

Conclusions

Superphosphate applications resulting in fertilizer concentrations in excess of 625 mg per 100 g of soil, are toxic to sweet orange seedlings. At lower rates of application the superphosphate markedly reduces the root development of these seedlings. Phosphate fertilizers containing acid-soluble phosphate can be applied at high rates without significant reduction in growth of the seedlings. Relatively large phosphate reserves can be incorporated into the soil through the use of these fertilizers without subsequent damage to the young plants. Phosphate applications in the desired form and quantity result in increased growth of seedlings planted in the two acid soils.

The reactions of superphosphate with these two soils are characterised by an initial rapid increase in insoluble aluminium phosphate believed to be associated with the displacement of exchangeable aluminium and the subsequent precipitation thereof as aluminium phosphate. This reaction is followed by a series of dissolution reactions in which iron and aluminium compounds in the soil are dissolved with the formation of unstable complex metallic phosphate compounds. These unstable compounds are converted to more stable insoluble compounds. The toxic effect of superphosphate is associated with this dissolution reaction during which toxic concentrations of metallic ions or complex metallic phosphate ions may occur in the soil solution (Tayler & Gurney, 1962). The high concentrations of precipitated aluminium phosphate, found in the soil after this reaction would indicate that the aluminium ion or complex aluminium phosphate ions may be largely responsible for the phytotoxic reaction.

Opsomming

DIE INVLOED VAN SUPERFOSFAAT OP DIE GROEI VAN SITRUS SAAILINGE IN VERHOUDING TOT DIE REAKSIE MET TWEE SUUR GRONDE

Die invloed van toedienings van superfosfaat en ander fosfaatmisstowwe teen relatief hoë hoeveelhede, op die groei en anorganiese blaarinhoud van soetlemoensaailinge is ondersoek. Twee suur gronde wat aangetref word in die subtropiese sitrusproduserende dele van die Oos-Transvaal is gebruik. Toedienings van superfosfaat waarin die konsentrasie van die misstof 625 mg per 100 g grond oorskrei, was toksies vir soetlemoensaailinge. Toedienings van ander fosfaatmisstowwe wat nie wateroplosbare fosfor bevat nie, het geen nadelige uitwerking gehad nie. Indien fosfaat toegedien is in die regte vorm en teen 'n redelike hoeveelheid is die groei van die saailinge daardeur bevorder. Die fosfaat en kalsium in die misstowwe wat gebruik was, is geredelik toeganklik vir die saailinge.

Die reaksies van superfosfaat met die twee gronde is ondersoek deur die fraktioeringsmetode van Chang & Jackson (1957) te gebruik. In beide gronde word die verplaasbare aluminium verplaas, en dan neergeslaan as aluminiumfosfaat. Hierna volg 'n reeks van reaksies waarin yster- en aluminiumverbindings in die grond opgelos word deur die inwerking van die suurfosfaat-oplossing gevorm van die superfosfaat. Aanvanklik word onstabiele oplosbare verbindings gevorm wat omsit in meer stabiele minder oplosbare yster- en aluminiumfosfate.

Die toksiese reaksie word toegeskryf aan die teenwoordigheid van hoë kosentrasies van metaal- of kompleks metaal-fosfaatione in die grondvogoplossing tydens die oorgangsfase na minder oplosbare stowwe. Die hoë konsentrasie aluminiumfosfaat wat in die grond gevind word na verloop van die reaksie laat vermoed dat dit veral aluminiumione of kompleks aluminiumfosfaatione is wat vir die toksisiteit verantwoordelik is.

Acknowledgement

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