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## V. SUPPLEMENTARY PAPERS

### V.1. PRELIMINARY RESULTS OF LYSIMETER STUDIES ON THE DYNAMICS OF CALCIUM IN THE IRRIGATED CALCAREOUS SOILS OF SOUTH LEBANON

by

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#### 1.1. Introduction

The concept of active calcium carbonate generally used to define the quantity of  $\text{CaCO}_3$  which can be mobile in the soil, allows the taking into account of neither the calcium concentration in the soil solution (therefore the amount of calcium absorbable by the plant roots at a given moment), nor the movements to which this calcium can be subjected either by drainage or by being precipitated through heavy evaporation.

In a highly calcareous soil, the concentration of calcium in the liquid phase depends little on exchangeable calcium of an absorbant complex. The principal source is the carbonate of calcium existing in the solid state (mainly the  $\text{CaCO}_3$  called 'active') and the principal factor of solubility is the partial pressure of the carbon dioxide contained in the soil's atmosphere.

In this report are presented the experimental results concerning the calcium content of water which has passed through calcareous soil subjected to various treatments and these results are discussed in relation to the theoretical concentration of a saturated calcium solution.

The object of such work is to define the nature of the different phases in the calcareous environment in which the vegetation grows during the course of the year and to study some elements leading to a knowledge of the evolution of this environment under the effect of intensive irrigation and the application of fertilizers.

#### 1.2. Experimental Material

The material which served to support our efforts came from the experimental station of the National Litani Office at Lebna near Saïda. This material had been previously set in the soil enabling it to be linked with one of the inventory series at the time of the pedological study of the joint FAO-NARI(IRAL) project in the Daoudiyé trials. Its chief characteristics are: uniformly deep brown colour, differentiation of weakly defined horizons, depth varying between 50 and 80 cm, percentage of coarse material (before

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clearing of stones) of about 15%; the main analytical data are the following:

content of total $\text{CaCO}_3$	= 50%
content of active $\text{CaCO}_3$	= 22%
organic matter	= 1.5%
clay	= 48%
fine silt	= 33%

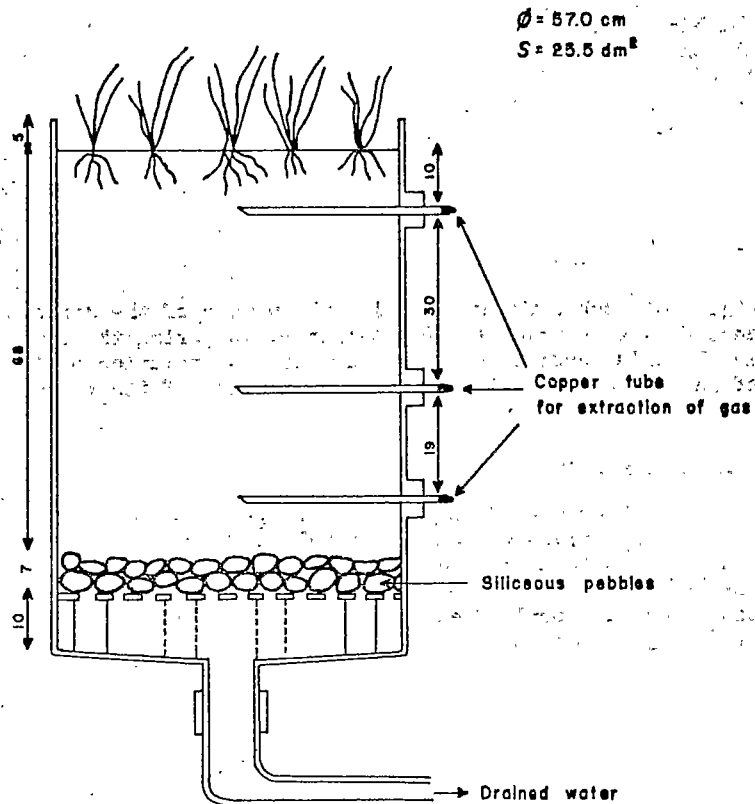
The clay fraction is composed of 21.8% calcium carbonate and 6.05% magnesium carbonate. In the rest (that is 72.2%) there are found mainly clay minerals of the type 2/1 (montmorillonite), a little kaolinite and some iron.

The distribution of calcium carbonate has also been studied and of magnesium among the different granular fractions: 53% calcium carbonate was found in the silt fraction, against only 24% in the clay fraction and 23% in the sandy fraction. It follows that the active  $\text{CaCO}_3$  comes more from the calcareous grains contained in the fine silt than from those contained in the clay. The silt seems to play an important role as well with regard to the hydraulic properties of the soil.

### 1.3. Experimental Apparatus

This consists of a battery of six lysimeters: small barrels of 200 litre capacity pierced underneath to allow the collection of drained water (Figure 1). In addition three copper tubes were introduced laterally at depths of 10, 40 and about 60 cm for the removal and the titration of the carbonic gas in the soil atmosphere.

Figure -1 - Cross section of a Lysimeter



The following treatments were carried out on each lysimeter:

Lysimeters No.	Pebbles		Irrigation		Minimum Fertilizer	
	with	without	with	without	with	without
1	+		+			+
2		+	+			+
3	+		+		+	
4		+	+		+	
5		+		+		+
6	+			+		+

Fescue grass (*Festuca arundinacea*) was sown in June 1970 on lysimeters 1, 2, 3 and 4, and lysimeters 5 and 6 were kept permanently without any vegetative cover.

The four irrigated lysimeters each received considerable and identical quantities of water: 1 400 mm in 1970 and 1 600 mm in 1971. The water came from the Karaoun dam and contained very little chlorine and sodium; on the other hand it was always super-saturated with calcium carbonate (between 51 and 65 mg/l of calcium).

Two applications of fertilizers were made on lysimeters 3 and 4, one in May 1970 (per hectare: ammonium nitrate 400 kg, triple superphosphate 2 000 kg and potassium chlorate 480 kg) and the other in November of the same year (ammonium nitrate 600 kg).

The amounts of water drained from each lysimeter were measured daily. Average samples of this water were taken and analysed about once a month. The CO<sub>2</sub> content of the soil atmosphere was determined every month from December 1970 onward with the Drager gas detection technique.

#### 1.4. Results obtained in 1970 and 1971

##### a) CO<sub>2</sub> content in the atmosphere of the lysimeters in 1971 (Figure 2)

A first fact is recognized which is valid for all the lysimeters except sometimes for No. 1: the CO<sub>2</sub> content increased with depth whatever the season.

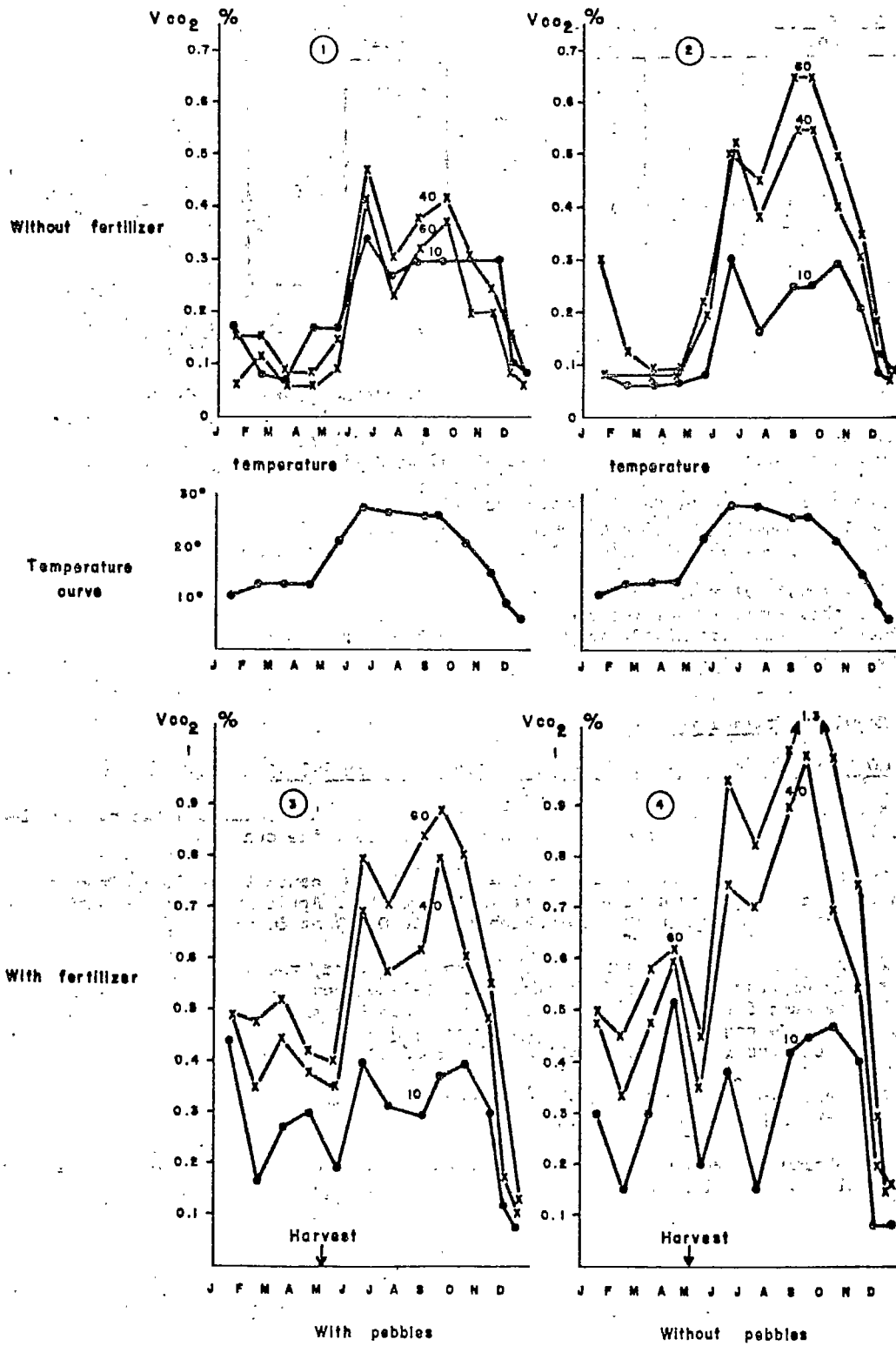
In the two non-irrigated trials (5 and 6), the CO<sub>2</sub> content was 0.03% from June to November. Then it increased slowly until in the month of April it reached a maximum which was no greater than 0.08% in 1971 but which rose to 0.35% at 60 cm in 1972.

In the four irrigated lysimeters, on the other hand, the quantity of CO<sub>2</sub> was slightly greater between June and November than between November and May. The curves had summarily the same form as the curve for the mean monthly temperatures. So the sharp decline in the CO<sub>2</sub> content observed between the 17 November and 7 December corresponds to a sudden coldness in the climate (from 20°C to 6°C).

Two maximums in the CO<sub>2</sub> content appeared at the same time in the 4 lysimeters, one in June and the other more noticeable in September.

The minimums came on the one hand in February-March and on the other in December. There was also a reduction, temporary but none the less obvious, in July.

Figure 2 Content in CO<sub>2</sub> in the atmosphere of the lysimeters at 10cm 40 cm 60 cm



It could be judged therefore that the application of fertilizers had the effect of increasing the CO<sub>2</sub> content, by stimulating bacterial activity and respiration of the roots.

Moreover, it seems that in lysimeters 3 and 4 the release of CO<sub>2</sub> linked with the biological activity is felt from the end of March. On the contrary, the cutting carried out in May would cause better diffusion of the carbonic gas in the outside atmosphere, therefore a lowering of the CO<sub>2</sub> content in lysimeters 3 and 4 in May and June.

Finally it should be noted that the May to September CO<sub>2</sub> contents at 40 and 60 cm are always higher in lysimeters 2 and 4 containing soil without pebbles, than in lysimeters 1 and 3 where the stones have not been removed.

b) Concentration of calcium in drainage water

Lysimeters with non irrigated trials

The only data obtained during the winter of 1970-1971 having proved insufficient we wished to complete them with data gathered during the course of the winter of 1971-1972. At the time of the first rain it was ascertained that the drained water and above all that which came from lysimeter 6 was turbid and very rich in solid matter in suspension. At the same time the strength of calcium was relatively high (50 and 70 mg/l). Then very rapidly the particles in suspension disappeared while the calcium concentrations were stable until February (60 to 70 mg/l).

In March there was a fall in the calcium concentration, the minimum reached at the end of March was between 35 and 50 mg/l.

Lastly, in April at the time when the contents of CO<sub>2</sub> are highest, the calcium concentrations again became identical to those observed in January-February. Thus in uncultivated and non irrigated calcareous soils the leaching of CaCO<sub>3</sub> during the first rains should be considered in relation to the drying that the earth has undergone during the summer and with the settling which has resulted.

This is the mechanism of pelicular alteration to calcareous stones which happens in this medium which is porous, inflated and poor in organic matter. The calcium carbonate goes into suspension rather than dissolves in the water.

In April, on the contrary, it is the presence of carbonic gas which causes a dissolution of the "carbonate reserve" which was extant in the soil.

Irrigated lysimeters (Figures 3 and 4)

The influence of irrigation and the application of fertilizers on the concentration of calcium in the drainage water is illustrated by the curves in Figures 3 and 4.

No matter what the material (earth with or without pebbles) and whether fertilizer has or has not been added, periodical variations exist in the calcium concentration. These differences are based in the first estimate in the same way as the variations in the CO<sub>2</sub> content of the atmosphere.

Although the minimums were observed at the same time (April) and had appreciably the same value of nearly 10 mg/l for the two years, in contrast there was a clear enough difference between the maximums of 1970 and those of 1971. In 1970 the maximums in lysimeters 1 and 2 were observed in June (87 and 100 mg/l) and September-October (78 and 94 mg/l). In 1971 in the same lysimeters the maximums were respectively no more than 60 to 65 mg/l and 70 to 75 mg/l during a period stretching from August to December. The measurements taken in the first seven months of 1972 confirm that there is from one year

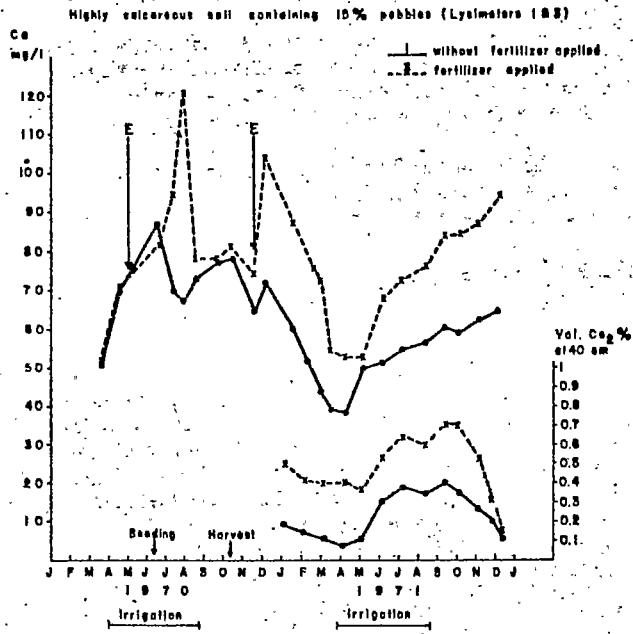


Figure 3 Concentration of calcium in the drained water

Average content of CO<sub>2</sub> in the atmosphere of the Lysimeters (at 40 cm)

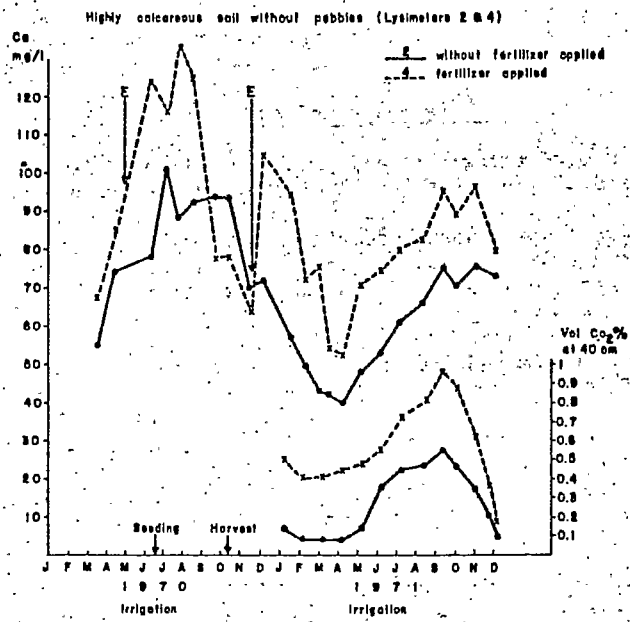


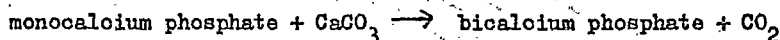
Figure 4 Concentration of calcium in the drained water.

Average content of CO<sub>2</sub> in the atmosphere of the Lysimeters (at 40 cm)

to another a progressive decrease in the concentration of calcium in the drained water especially during the irrigation period. It was also noted that the first rain in November-December seemed to elicit a more intense but ephemeral enough dissolution of the calcium carbonate rather as in the test lysimeters, although this period corresponds to a sharp decrease in the CO<sub>2</sub> content.

In May 1970 fertilizer application to Nos. 3 and 4 caused a strong rise in the concentration of calcium in the drained water in July-August. The same thing happened, although not so severely, after the second application of nitrate in December 1970. This influence from the fertilizers was still to be seen in 1971, but it was much less obvious. The absence of data concerning CO<sub>2</sub> in 1970 allowed us to make only two observations regarding the action of the fertilizers. These occurred in two ways:

- indirectly by stimulating bacterial activity and root growth. The resultant carbonic gas caused intense solubility of the calcium carbonate.
- directly with regard to the monocalcium phosphate (triple superphosphate). In effect this reacted rapidly on the calcium carbonate in the following pattern (ARVIEU 1972):



The carbonic gas which was released reacted in its turn with the lime and caused its dissolution (peak in June-July 1970).

In a second stage the bicalcium phosphate reacted slowly with calcium carbonate to create octocalcium phosphate at first and then apatite calcium, both of them insoluble therefore unavailable to plants. During the course of this second stage, which was slower than the first, there was also a release of CO<sub>2</sub>. According to ARVIEU the two stages happen far more quickly and with a far greater speed when the temperature is higher and the quantity of CaCO<sub>3</sub> is greater.

At the limit the two stages occur simultaneously, the bicalcium phosphate reacting on the calcium carbonate at the same time as it forms.

c) Comparison between the concentrations of calcium measured and the theoretic concentrations of saturated calcium (Figures 5 and 6)

The concentration of theoretic calcium in a saturated solution in the presence of pure calcite is linked with the partial pressure of CO<sub>2</sub> by the following relation:

$$\log [\text{Ca}^{++}] = 0.33 \log P_{\text{CO}_2} + b \quad (1)$$

the value of b varies in terms of the temperature according to the following relation established by T. Stchouskoy-Muxart

$$\log b = -0.055 \log t + 0.4605$$

if it is admitted that the atmospheric pressure is constant and equal to 1 atmosphere, the following is given:

$$P_{\text{CO}_2} = \frac{V_{\text{CO}_2}}{100}$$

V<sub>CO<sub>2</sub></sub> being the volume of CO<sub>2</sub> in the soil atmosphere expressed in percent; the equation (1) becomes:

$$\log [\text{Ca}^{++}] = 0.33 \log V_{\text{CO}_2} + (b - 0.66)$$

to simplify the calculations the variable log 1000V<sub>CO<sub>2</sub></sub> has been used in the place of log V<sub>CO<sub>2</sub></sub>. Therefore the relation obtained is:

$$\log [\text{Ca}^{++}] = 0.33 \log V_{\text{CO}_2} + b - 1.32 \quad (2)$$

the right side terms in equation (2) for different temperatures have been shown in Figure 5.

Figure 8 Concentration of calcium in the drained water  
in relation to the CO<sub>2</sub> content at 60 cm

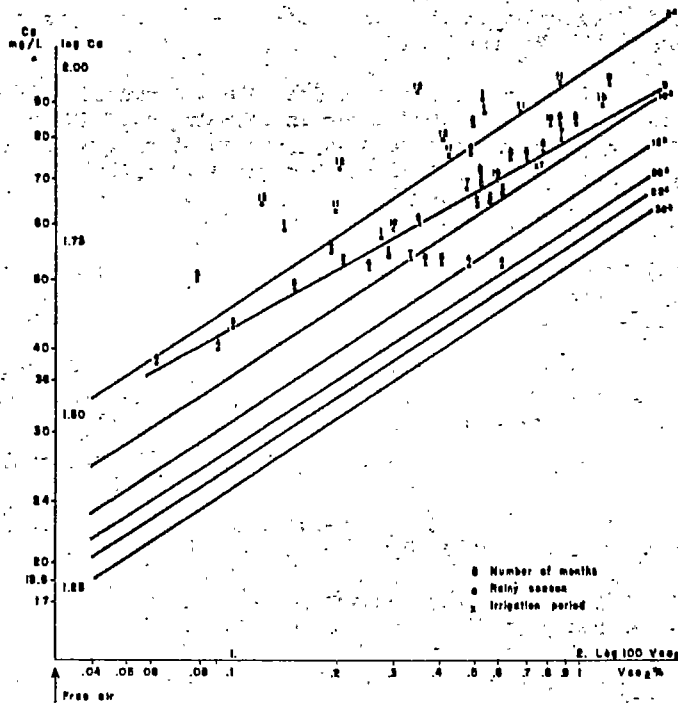
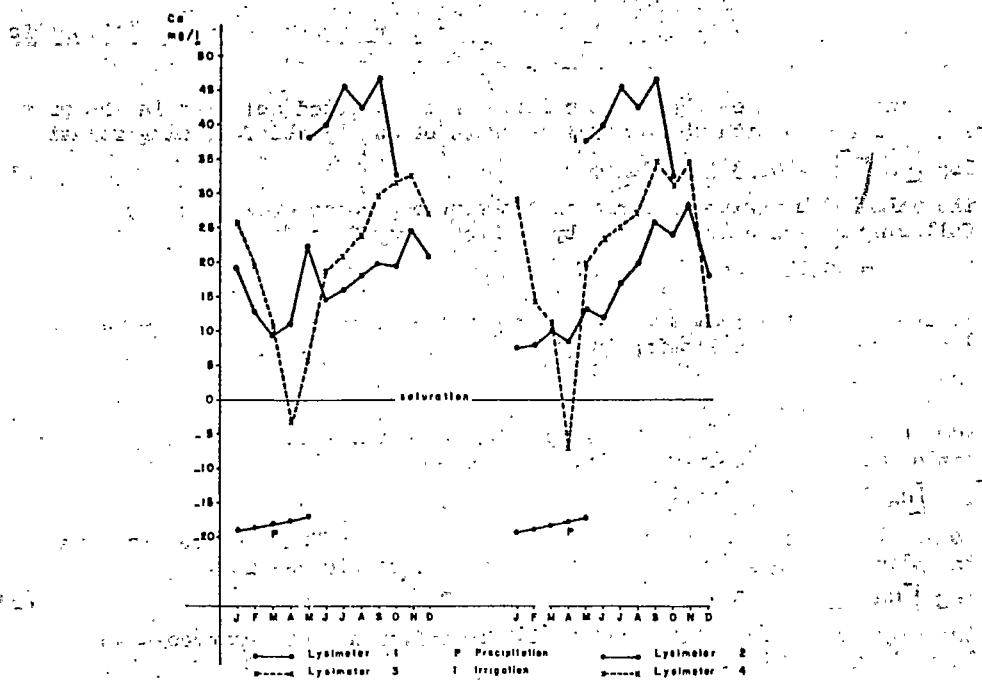


Figure 9 Excess or deficit of calcium in the water  
in relation to the saturation





One can therefore, knowing  $t$  and  $VCO_2$  calculate  $[Ca^{++}] = S$ : concentration of theoretical calcium from the water of the saturated soil.

The difference C-S between the concentration measured and the theoretical concentration, for the same content in  $CO_2$  of the atmosphere and for the same temperature, allows the estimation of the excess or deficit of calcium in the water having passed through the lysimeters and the comparison of this to the values obtained for the rain-water and for the irrigation water. All these values collected in 1971 are given in Figure 6. It can be calculated that in the four irrigated lysimeters the values of C-S were at a minimum in April and at a maximum in November. The drained water from lysimeters 1 and 2 was constantly supersaturated with calcium whilst in lysimeters 3 and 4, which had received fertilizers in 1970, this water showed in April a loss of calcium in relation to the saturation; on the contrary from June to December the excess of calcium was higher than in the water coming from lysimeters 1 and 2. It seems, therefore that nearly always the percolation water is supersaturated with calcium; in other words, only part of the calcium was found in solution in the form of bicarbonate of calcium whilst the other part was in the form of very fine calcareous particles in suspension in the water. It is moreover the same thing for the water used for irrigation which is, as shown by the I curves, extremely supersaturated with regard to an equilibrium content of calcium in natural water. From this fact irrigation water has a very different action on calcareous soil to that exercised by rain water which has a stronger dissolving action.

One can interpret the curves in Figure 6 in the following way. In the autumn the soil encloses a high reserve "of easily soluble calcium carbonate" (calcium carbonate carried by the irrigation water or coming from the alteration of the pre-existing  $CaCO_3$ ). Rain water carries away during the course of its passage through the soil not only calcium bicarbonate but also some very fine particles in suspension. Gradually as the winter passes, the reserve of  $CaCO_3$  diminishes and the quantities of calcium carried away show a noticeable reduction. In lysimeters 3 and 4, the content in  $CO_2$  being higher, the reserve of "easily soluble calcium carbonate" is more rapidly reduced so that in April the drained water is under-saturated. From May onwards there is not only a carrying away of calcium but also a depositing in the soil of a part of the calcium contained in the irrigation water. The difference between the saturation curves of the irrigation water and those of the drained water represented on Figure 6 illustrates the quantities of calcium which have remained in the soil. One can estimate that these quantities are higher in lysimeters 1 and 2 than in lysimeters 3 and 4.

d) Deposits and losses of calcium between June 1970 and October 1971

Table 1

Additions (+) and losses (-) of the quantity of calcium in the irrigated and non irrigated lysimeters in 1970 and 1971

Lys. No.	from 1. 6.70 to 10.11.70	from 11.11.70 to 19. 4.71	from 20. 4.71 to 19.10.71	Total
1	+ 14.7	- 8.9	+ 17.0	+ 22.8
2	+ 13.8	- 9.3	+ 14.8	+ 19.3
3	+ 23.0	- 14.4	+ 15.4	+ 24.0
4	+ 21.6	- 15.0	+ 14.0	+ 20.6
5	- - -	- 9.7	- - -	- 9.7
6	- - -	- 8.5	- - -	- 8.5

The figures in the preceding table represent the difference between the quantities of calcium supplied (with the water and with the mineral fertilizers) and the quantities carried away by lixiviation and in the harvest.

During the winter of 1970-71 lysimeters 1, 2, 5 and 6 released into the drained water about the same quantity of calcium (9 to 11 g), while Nos. 3 and 4 lost a lot more (15 g about).

During the two summers, lysimeters 1, 2, 3 and 4 were watered with the following significant quantities: 355 and 426 litres. Owing to the intense evapotranspiration the volume of drained water only represents about a third of the irrigation water. For this reason and also because the drained water is clearly less saturated than the irrigation water, the quantities of calcium lost are hardly significant (13 to 17 g) when considered against the quantities of calcium added (45 g). Irrigation for lysimeters 1 and 2 definitely indicates an increase in calcium of 31.7 and 28.6 g and for lysimeters 3 and 4 an increase of 28.6 and 26.2 g. But to these last two figures should be added also 9.4 g of calcium coming from the phosphate fertilizer in 1970 (the triple superphosphate used included 18.7% Ca). In relation to the calcium phosphate ammonium phosphate would introduce the double advantage of not increasing the calcium content of the soil on one side and on the other of lasting much longer in an assimilable form (Arvieu 1972).

Finally the overall balance (last column in the table) demonstrates, and it could not be clearer, that the irrigation of calcareous soils with water supersaturated with calcium bicarbonate, causes an enrichment of calcium which is not compensated by the lixiviation in winter under the influence of rain water.

#### 1.5. Conclusion

It appears from the preliminary studies undertaken in the lysimeters that the carbonic gas contained in the soil body, the content of which varies considerably during the course of the year as a result of the processes undergone by the soil, is an important factor in the solubility or precipitation of calcium. But this is not the only factor which interferes with the dynamics of the calcium. Account must be taken of the existence of very fine calcareous particles in suspension in the gravitational water.

From the practical point of view it confirms that irrigation of calcareous soils with water containing high percentages of calcium carbonate shows a clear enough increase in the quantity of  $\text{CaCO}_3$  in the soil, an increase which in the long term could have a harmful effect on the plants. Furthermore, the use of calcium phosphate as a fertilizer must be reconsidered in the light of its contribution to the increase in calcium and the rapidity with which this fertilizer is rendered unavailable in a calcareous soil.

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