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THAT chemical reactions take place on an equivalent basis has long been known. The soil chemist has found this relationship useful in studies of cation exchange. Only recently, however, has it come to be generally realized that this principle applies also to plants. Liebig long ago had implied that cations replace each other equivalently in plants, but little attention was paid to his statement. It was not until Van Itallie (6)<sup>3</sup> published his paper on this subject in 1938 that the principle was accepted in plant studies. Since then a number of scientists have demonstrated its importance (4).

This subject has been under intensive study at the New Jersey Agricultural Experiment Station for the past 9 years. Most of the work has been done with alfalfa. Plants have been grown under solution-culture techniques, in potted soils, and under field conditions. Early in this work it was reported that the number of me. of K + Ca + Mg + Na per unit weight of the top portions of alfalfa plants that had been grown *under uniform environmental conditions* tended to be a constant (2).

These nutrient cations replaced each other to a considerable degree in alfalfa plants without interfering with growth in any noticeable way. For example, the K content of alfalfa was made to vary between 1 and 3% without materially affecting the yield. As the plant's content of K increased, its content of Ca + Mg + Na decreased. But a point was eventually reached at which no further replacement of one cation for another could be effected without injury to the plant.

Although the cation me. sums<sup>4</sup> of the top portions of alfalfa plants tended to be constant for any given harvest, no matter whether they were grown on different soils or on the same soil under different fertilizer treatments, marked variations were noted for the different cuttings (8). These variations were closely related to the plant's content of carbohydrates, which serve as a dilution factor for the mineral elements. Under field conditions, the second crop tended to be lower in cations than the first or third.

Further study of the mineral composition of alfalfa revealed that the me. sums of the N, P, S, Cl, and Si anions tended to be equally as constant as those of the cations, even though the me. of the individual anions varied greatly. Finally, it was discovered that the ratios of the cation me. sums to the anion me. sums for the different cuttings tended to be constant, regardless of the date of harvest and of the carbohydrate dilution factor.

The following equation may be used to express the overall cation-anion equivalent relationship in plants at any given pH value:

$$\frac{K + Ca + Mg + Na}{N + P + S + Cl + Si} = Constant^{5}$$

A detailed study of uninoculated alfalfa in sand culture (7, 8) revealed that cation-anion equivalent ratio values varied from one part of the plant to another. In the leaves, they decreased with increasing K and decreasing Ca. The reverse was true for the stems and roots. But the cation-anion equivalent ratio values for the whole plant tended to remain constant.

The substitution of one cation or anion for another cation or anion may have important effects on the animals that consume the plants. The ratio of K to Ca is of special interest. Quantitatively, Ca is a much more important element to animals than K. As more K is applied to the soil and taken up by crops, the consuming animal gets less Ca, perhaps less than it requires.

Economy of production is also important. Ca is a much less expensive element than K. It can be supplied in the form of pulverized limestone at one-twentieth the cost of an equivalent quantity of K in muriate of potash. Na is another relatively inexpensive element that can be used as a partial substitute for K.

A survey of New Jersey alfalfa fields during recent years revealed that the K content of the plants was entirely too low in about half the fields inspected. In 20% of them, however, it was above 3%, which is known to be unnecessarily high. In such cases, Ca could have been substituted for the excess K to advantage, both in terms of feeding quality of the crop and economy in its production.

If Cl is applied in such materials as KCl, a reduction in the absorption of N, S, and P by plants will occur. Cl values as high as 7% have been reported, or nearly 200 me. per 100 gm dry matter. Cl is a very mobile ion and its substitutive effect, when applied in large amounts, is considerable. In field alfalfa that was grown without the use of a K fertilizer, N constituted 85.8% of the anion me. sum. Where a topdressing of 300 lbs. KCl per acre had been applied, N made up

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<sup>&</sup>lt;sup>3</sup>Figures in parentheses refer to "Literature Cited", p. 178.

<sup>&</sup>lt;sup>4</sup>By cation me. sum and anion me. sum is meant the summation values of the cations and anions, respectively, per 100 grams dry matter.

<sup>&</sup>lt;sup>5</sup>Although a considerable number of other mineral elements are present in plants, their quantities are too small to be of significance in this equation.

only 79.8% of the anion me. sum and Cl 6.4%. Since N, S, and P are the important protein elements, this substitution of Cl for them results in a lower protein content of the plant and, in many cases, a lower nutrient value.

Examination of the cation-anion equation suggests some interesting possibilities. For example, absorption of N in the  $NH_4$  form should result in a reduction in the K + Ca + Mg + Na content of plants, and this has been found to occur. It should also result in an increase in the content of P + S + Cl + Si, and this has been demonstrated.

Whatever the cation-anion equivalent relationship may be, electrostatic balance must be maintained. When a nitrate ion is assimilated into protein, it would appear that an organic anion must arise or a H-ion must disappear to compensate. In keeping with this reasoning, high-protein plants may well have high contents of organic acids. This theory has recently been confirmed by Ergle and Eaton with cotton plants (3).

Careful consideration of the cation-anion equation explains many irregularities in the response of plants to fertilizer applications. Thus a Mg-P relationship has long been believed to exist in plants (5), although there are many reports to the contrary. The discrepancies can be explained on the basis of competition between other anions and P and other cations and Mg for absorption. For example, heavy applications of KCl will result in lowering the uptake of both Mg and P. But absorption of N as  $NH_4$ , rather than as  $NO_3$ , tends to decrease the uptake of Mg and increase that of P.

Analyses of 204 samples of snapbeans, tomatoes, cabbage, lettuce, and spinach, obtained from Georgia, South Carolina, Virginia, Maryland, New Jersey, New York (Long Island), Ohio, Indiana, Illinois, and Colorado (1), are of special interest in connection with the quality factor in plants. The cation me. sum of these vegetables tended to increase from south to north and from east to west. For snapbeans, this range was between 95 me. for Virginia and 149 me. for Ohio. For tomatoes the range was between 117 me. for Maryland and 160 me. for Colorado. The relationships for the anions have not been fully explored. But there is every reason to believe that protein and P relationships follow the same trend as those of the cations in these vegetables. Otherwise the cation-anion ratios would not tend to be constant.

Since our plant breeding and plant selection program is based primarily on yield, it is apparent that we are tending to produce larger percentages of carbohydrates at the expense of protein and mineral matter. If the yield of corn, for example, is stepped up from 50 to 100 bushels, this carbohydrate dilution factor tends to operate, and this has been observed in the lower protein content of hybrid corn as compared to the older field-pollinated varieties.

If the yield of corn is stepped up from 100 to 200 bushels, this means still further dilution with carbohydrates, and further reduction in protein. But it also means a lowered mineral content. It may reduce the trace element content of the produce to the point that the lack of one or another of these elements becomes a seriously limiting factor in the growth or production of the consuming animal. If the 300-bushel yield that is being aimed for by a few farmers is attained, it seems quite evident that the food value of the corn is very likely to be greatly lowered. Thus the question may well be raised as to how high acre yields should be pushed. For highest quality of food crops, we would do well to stop far short of the yield potentialities, at least until such time as some better provision is made for control of the mineral elements, and especially those of the minor element group. For fiber crops, however, our aim might well be exactly the opposite.

## **Summary and Conclusions**

Under uniform environmental conditions, alfalfa plants tend to maintain constant me. sums of K + Ca+ Mg + Na per unit dry matter, regardless of wide variations in the number of me. of the individual cations.

A similar tendency toward constancy obtains for the me. sums of N + P + S + Cl + Si, when expressed as anions.

The ratios between the cation me. sums and the anion me. sums tend to be constant, irrespective of environmental conditions.

Marked variations in the cation and anion me. sums occur from harvest to harvest because of change in environmental conditions.

The second cutting of alfalfa in New Jersey tends to have a lower protein and mineral content than the first or third.

Replacement of the nutrient cations and anions by each other may have important effects on the nutritional value of plants and in the economy of their production.

Quantitatively, Ca is a much more important element to animals than K, and it is much less expensive, and this suggests substituting Ca for K in alfalfa, insofar as possible.

When Cl is applied to soils in KCl, it tends to substitute for N + S + P in the plants growing on that soil, and thus to lower their protein content.

Substitution of  $NH_4$  for  $NO_3$  nitrogen in fertilizers may lower the intake of mineral cations and increase that of the mineral anions.

When a nitrate ion is utilized in protein production, it would appear that an organic anion must arise or a H-ion must disappear, if electrostatic balance is to be maintained.

## Plants that are high in mineral cations tend to be high in protein and organic acids.

The mineral and protein content of vegetables tends to increase from south to north and from east to west.

As yields of crops are stepped up to increasingly high levels, their mineral and protein values per unit of dry material tend to be lowered by carbohydrate dilution.

For the highest quality of food crops, it may be necessary to stop far short of the yield potentialities.

For the highest quality of fiber crops, our aim might well be exactly the opposite.

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