

## Technical Papers

### Absorption of Radioactive Zirconium and Niobium<sup>1</sup> by Plant Roots from Soils and Its Theoretical Significance

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In the last few years certain by-products of atomic fission have been made available for studying the mechanisms of ion uptake by plants and soils. In particular, a mixture of radioactive zirconium ( $Zr^{95}$ ) and niobium ( $Nb^{95}$ ) has been used by Sengupta (5) to study ion exchange between colloidal materials. This carrier-free mixture is received as the oxalate in the form of a complex

TABLE 1

RADIOACTIVE ZR AND NB REMOVED FROM YOLO SOIL BY VARIOUS LEACHING REAGENTS

5 g Soil with an activity of 780 counts per minute leached with 100 ml of each solution. Radioactivity data from Geiger counter.								
Acid reagent	Normality of acid							
	.001		.01		0.1		1.0	
	Initial pH	cpm*	Initial pH	cpm	Initial pH	cpm	Initial pH	cpm
HCl ....	3.1	0	2.2	0	1.2	0	0.3	21
H <sub>2</sub> SO <sub>4</sub> ...	3.1	0	2.2	0	1.3	5	0.5	35
Acetic ...	3.9	0	3.5	0	3.0	0	2.4	0
Oxalic ..	3.4	4	2.4	49	1.6	226	0.9	209
Citric ...	3.6	15	3.0	55	2.4	143	1.9	281
Lactic ...	3.6	1	3.0	4	2.4	35	1.8	221
Malic ...	3.6	8	3.0	57	2.5	128	2.0	137
Tartaric .	3.6	5	2.9	16	2.3	38	1.7	125

\* Counts per minute.

which can be destroyed by the action of hydrogen peroxide in strong sulfuric acid. A product is obtained which is adsorbed very easily by clay and soil. Once adsorbed, the Zr and Nb are held very tenaciously and resist leaching by many reagents. For instance, dilute HCl and H<sub>2</sub>SO<sub>4</sub> and up to 1*N* acetic acid fail to remove any of the adsorbed radioactive ions. Some organic acids are more efficient and their relative efficacy is illustrated by the data in Table 1. The relations indicated have been used by Tompkins *et al.* (6) as a means of separating several by-products of atomic fission by adsorption on cation exchange Amberlite, followed by leaching with various reagents. With this technique they leached out Zr and Nb, using 0.5% oxalic acid and 5% citric acid. In their

<sup>1</sup> Formerly known as columbium (Cb) before revision by the International Union of Pure and Applied Chemistry in September, 1949.

opinion the successful leaching agents were those capable of forming complexes with these ions. It will be noted that at least five of the organic acids listed in Table 1 have been found to occur in plant tissues (?).

Radioactive Zr and Nb were added to 900 g of Yolo soil and carrots were grown in this medium for 8 weeks. Control plants were grown in the same type of soil without Zr and Nb. The radioactivity measured in the plants at the end of the growth period is given in Table 2. These results confirm the observations of Jacobson and Overstreet (1), who found a high activity in roots and a weak activity in the shoots. There is no doubt that plants can assimilate Zr and Nb from soils.

Two main theories have been advanced to account for the mechanism of release of adsorbed ions by plant roots: the soil solution theory and the contact theory.

TABLE 2

RADIOACTIVITY OF ASHED CARROT TISSUES GROWN ON YOLO SOIL CONTAINING  $Zr^{95}$  AND  $Nb^{95}$  AS MEASURED ON GEIGER COUNTER

Sample	Dry wt in g	Radio-activity cpm/g	Remarks on apparent contamination with radioactive soil
Soil .....	900	212	.....
Leaves			
Active .....	3.4	26	None
Control .....	3.9	0	None
Fibrous Roots			
Active .....	1.3	106	Considerable
Control .....	1.4	0	None
Peeled Tap Root			
Active .....	1.8	0	None
Control .....	1.5	0	None
Tap Root Peelings			
Active .....	0.6	52	Slight
Control .....	0.6	0	None

The original version of the soil solution theory postulated that roots absorb ions present in the liquid phase of a soil system. The solvent action of water was held responsible for the transfer of ions from the unavailable solid phase to the available liquid phase. Later, the theory was modified to assign a role to respiratory carbonic acid excreted by roots into the soil solution. The H<sup>+</sup> in solution was exchanged for cations adsorbed on soil colloids, and these ions, now part of the soil solution, became available to plant roots. This mechanism does not require direct action of roots on soil colloids.

On the other hand, the contact theory of Jenny and Overstreet (3), while recognizing the existence of absorption from the soil solution, holds that many aspects of mineral absorption by plants growing in soils can be better explained by assuming direct transfer of ions from the soil colloid to the plant root also behaving as a col-

loidal particle. This mechanism by-passes the soil solution and postulates that hydrogen ions on the roots exchange directly for cations on the clay. The theory for cation exchange by contact is supported by theoretical considerations (4). A detailed account of both theories discussed briefly here was given recently by Jenny (2).

One difficulty in appraising these two mechanisms arises from the fact that ions exist in both the liquid phase, or soil solution, and in the solid phase, or soil colloid. From the data already presented, the possibility was considered that it might be possible to identify from which of the two phases the plants absorbed Zr and Nb. This prospect was explored experimentally in the following way. Five-gram samples of soil containing radioactive Zr and Nb with an activity comparable to that in which the plants were grown, were leached with a liter of each of the following solutions: Hoagland's solution in equilibrium with atmospheric CO<sub>2</sub>, giving a pH of 5.0, and a similar solution saturated with CO<sub>2</sub>, giving a pH of 3.9. Distilled water, under the same two CO<sub>2</sub> pressures, was also used as a leaching agent. Of the two leaching agents, Hoagland's solution was considered the more reasonable facsimile of what is understood by a soil solution. The use of CO<sub>2</sub> is an attempt to simulate the respiratory excretion of roots.

The leachings were evaporated to dryness and measured for activity on the Geiger counter. No activity was detected with any of the leaching solutions. From this it was concluded that no Zr and Nb were present in the soil solution and therefore the CO<sub>2</sub>-soil solution theory was inadequate to explain the uptake of these radioactive substances by plants from soils.

However, from the leaching experiment with organic acids (Table 1) it is entirely within the realm of possibility that a soil solution theory incorporating as an important feature the excretion of organic acids by plant roots could very nicely explain the absorption of Zr and Nb. Such a theory might conceivably account for the uptake from soils of such ions as iron made available by complex formation with the same organic acids as were used in our leaching test. It is common practice in the water culture of plants to supply iron in the form of citrate or tartrate. So the organic acid theory offers a possible explanation, even though it has not been advanced very seriously as a mechanism for ion uptake. For instance, a recent review of organic acids in plants (7) considers their role as intermediates in respiration, as agents in the maintenance of cation-anion balance, and as participants in protein metabolism, but no mention is made of their possible excretion by roots in connection with ion availability.

Of course, it is not strictly necessary that plants themselves excrete organic acids, inasmuch as microorganisms in soils could perform this function just as well, to their mutual advantage. The biological excretion of organic acids has been demonstrated (8) and their function in increasing the availability of phosphate and potassium in soils has already been considered (9). Obviously, the possibilities of organic acids require serious consideration and investigation in relation to ion availability.

Another mechanism for explaining these results is offered by the contact theory. According to this idea, it is not necessary to have ions in solution in order for plants to absorb them. All that is required for an exchange of ions is the intermingling of the electric double layers between two colloidal particles. In this connection, some interesting results were obtained by Sengupta (5). He was able to remove Zr<sup>95</sup> and Nb<sup>95</sup> from clay by synthetic cation exchange resins such as Amberlite IR-100. This behavior would be analogous to the activity of a root acting in accordance with the contact exchange concept.

It is concluded that insofar as the absorption of radioactive Zr and Nb is concerned, the CO<sub>2</sub>-soil solution theory does not offer a satisfactory explanation. The only possible mechanisms are offered by the contact theory or by a soil solution theory postulating the excretion of organic acids by plant roots or microorganisms growing in the same environment.

#### References

1. JACOBSON, L. and OVERSTREET, R. *Soil Sci.*, 1948, **65**, 129.
2. JENNY, H. *Symposium on plant nutrition*, Madison: Univ. of Wisc., 1949. In press.
3. JENNY, H. and OVERSTREET, R. *J. phys. Chem.*, 1939, **43**, 1185.
4. OVERSTREET, R. *Soil Sci.*, 1945, **59**, 265.
5. SENGUPTA, K. Ph.D. thesis, Univ. of Calif., 1949.
6. TOMPKINS, E. R. et al. *J. Amer. chem. Soc.*, 1947, **69**, 2769.
7. VICKERY, H. B. and PUCHER, G. W. *Ann. Rev. Biochem.*, 1940, **9**, 529.
8. VIRTANEN, A. I. et al. *Suomen Kemist.*, B, 1946, **19** (7/8), 83. (Abstract.)
9. WAKSMAN, S. A. *Principles of soil microbiology*. Baltimore: Williams & Wilkins, 1932.

## New Method for Studying Electrical Orientation and Relaxation Effects in Aqueous Colloids: Preliminary Results with Tobacco Mosaic Virus

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Various investigators have observed the double refraction effects produced by the application of sinusoidal electric fields to suspensions of anisometric colloidal particles. Lauffer (3) studied by a visual method the birefringence produced in aqueous tobacco mosaic virus (TMV) solutions by 60-cycle sinusoidal fields. Mueller (4) and Norton (5) observed in bentonite aquasols birefringence which varied in magnitude and sign with the frequency of the applied sinusoidal voltage and the concentration of the sol. Although the phenomena are similar to the Kerr effect (2), a number of interesting anomalies have been reported which suggest the existence of orienting mechanisms other than those due to permanent or induced dipoles.

It seems clear that data obtained with sinusoidal fields