An Interpretation of the Cause of Waterrepellent Sandy Soils Found in Citrus Groves of Central Florida

I. W. Wander

Citrus Experiment Station, Lake Alfred, Florida

Several reports (3-5) have appeared in soil literature discussing the property which prevents the soil from being properly wetted by either rain or irrigation water. This property, water repellency, is widespread and quite pronounced in much of the citrus-growing area of Florida. Under many trees a large volume of soil remains dry even after prolonged periods of rainfall. A drop of distilled water, placed on the soil, behaves as if it were on a waxed surface. In some cases the drop of water will evaporate in place without any penetration; in other cases it will gradually penetrate the soil after several hours.

During the rainy seasons of 1947 and 1948, differences in the prevalence of water-repellent soil were noted in a group of plots having different fertilizer treatments, located at the Citrus Experiment Station at Lake Alfred, Florida. The treatments had been in effect 10 years. Determinations of the relative amounts of water-repellent soil were estimated by placing a drop of distilled water on soil samples taken from beneath trees and observing the time required for absorption. This was done by taking samples to a 6-in. depth with a stainless steel tube 1 in. in diam, turning the sample tube upside down and placing the drop of water on the exposed soil surface. If the drop of water did not soak into the soil within 10 sec, the soil was listed as water repellent; if it did soak in, it was listed easy to wet. Eighty examinations were made in each plot and the results from duplicate plots combined. The results of this investigation are shown in Table 1.

These results indicate that fertilizer practices influence the amount of water-repellent soil found under field conditions. It appears that the use of magnesium in the fertilizer, along with a separate application of ground limestone to control soil pH at about 5.8, is associated with the water-repellent phenomenon.

It is known that fatty acids form very insoluble soaps with calcium, magnesium, and other metals and that these soaps, when dry, are extremely water repellent. Waksman (6) had previously cited the presence of fatty acids, fats, and waxes in soils. With this in mind, several composite soil samples which exhibited the water-repellent property were checked for the presence of fatty acids. This was done by heating the soil in the presence of a strong sodium hydroxide solution, neutralizing with sulphuric acid, and steam-distilling in the presence of a slight excess of acid. A small amount of solid material was obtained which gave a test for a carboxylic acid group (1).

A dilute ether solution of the solid material obtained from this steam distillation, when added to subsoil, which wet very easily, had no effect on its wettability. However, when a dilute aqueous solution of calcium or magnesium hydroxide was added to the soil, which had been previously treated with the ether extract, the soil became very water repellent when it was dry.

This was further checked by treating an easily wetted soil with a dilute solution of stearic acid in ether. The ether was evaporated and then a dilute solution of either calcium or magnesium hydroxide was added and the soil dried. Following this treatment the soil became extremely water repellent. Evidently the formation under field conditions of metallic soaps results in water-repellent

TABLE 1

RELATIONSHIP OF FERTILIZER TREATMENT TO AMOUNT OF WATER-REPELLENT SOIL

Plot Nos.	Fertilizer treatment	July 1947 % water-repel- lent soil	August 1948 % water-repel- lent soil
1 and 12	3-6-8-4-1-12* 40% N organic source	23	18
2 and 11	nH 5.8; 3-6-8-0-1- <u>1</u> 100% N inorganic source nH 5.8;	4	1
3 and 10	3-6-8-2-1- <u>1</u> 100% N inorganic source pH 5.8 ⁺	29	30
4 and 9	3-6-8-4-1-½ 100% N inorganic source nH 5.8†	23	23
5 and 8	$3-6-8-4-1-\frac{1}{2}$ 100% N inorganic source pH not controlled (4.2)	0	1
6 and 7	3-6-8-0-0-0 100% N inorganic source pH not controlled (4.2)	5	8

* The figures refer to percentages of various constituents in the fertilizer in the following order: $N-P_2O_5-K_2O-MgO-MnO-$ CuO and as determined by A.O.A.C. methods for fertilizers. The fertilizers indicated were applied at 60 lb per tree per year.

† pH controlled with high Ca limestone.

soil and a similar water repellency can be produced in the laboratory by similar chemical combinations.

Jacobson and Holmes (2) found that metallic soaps, such as magnesium stearate, are practically insoluble in ether, but that magnesium stearate is relatively soluble in methyl alcohol. Jamison's work (4) indicated that a water-repellent soil, extracted with ether, remains water repellent. With these facts in mind a sample of waterrepellent soil was extracted first with ether to remove any free fats and waxes, then with methyl alcohol. This treatment left the soil readily wettable. The methyl alcohol extract, when evaporated on an easily wetted soil, left the soil water repellent, whereas the ether extract had no effect. When a portion of the methyl alcohol extract was evaporated to dryness, nitric and perchloric acids added for destruction of organic matter, and heat applied, small globules of fat were released. Further heat oxidized the fat, and the residue, when taken up in distilled water, gave strong magnesium and calcium tests.

This indicates that calcium and magnesium soaps had been dissolved by the methyl alcohol.

From this and other corollary information, it has been concluded that it is the formation of a water-repellent coating of metallic soaps on the soil particles (98% silica) that causes the water-repellent property found in many Florida soils. The source and identity of the particular fatty acids involved have not yet been determined.

References

- 1. FEIGL, F. Qualitative analysis by spot tests. New York: Elsevier, 1946. P. 357.
- JACOBSON, C. A. and HOLMES, A. J. blol. Chem., 1916, 25, 29.
- 3. JAMISON, V. C. Soil Sci. Soc. Amer. Proc., 1942, 7, 36.
- 4. _____. Soil Sci. Soc. Amer. Proc., 1945, 10, 25. 5. SCHREINER, O. and SHOREY, E. C. Bul. No. 74, U. S.
- Dept. of Agric., Bureau of Soils, 1910, 8.
- WAKSMAN, S. Humus, (1st Ed.) Baltimore: Williams and Wilkins, 1936.

Near Infrared Absorption Spectra of Uracil, 5-Chlorouracil, and Thymine¹

J. R. Lacher, D. E. Campion, and J. D. Park

University of Colorado, Boulder

Infrared spectrometry has proved very useful in studying biologically active materials (5), particularly if they are soluble in solvents which are transparent in the same region of the spectrum. In proteins (1, 4) and the components of nucleic acids $(\mathcal{Z}, \mathcal{Z})$, the lack of solubility in other than aqueous solvents has made it necessary to use thin films, powders, suspensions, and the like. We have found that fused antimony trichloride is a powerful solvent for some of these materials and nearly 0.2 molar solutions of uracil, 5-chlorouracil, and thymine were readilv prepared at 100° C. After a vacuum distillation, the fused antimony trichloride was suitably transparent and showed only two small absorption peaks at 1.93 and 1.42 μ (believed to be an O-H stretching overtone). These peaks cause no trouble, since their effect is subtracted out with the background. We have not investigated the absorption spectra of antimony chloride beyond 2.3 µ, but one might reasonably expect it to be transparent as far out as carbon tetrachloride or perhaps silver chloride. This aspect of the problem is being studied further.

The near infrared spectra of the compounds reported in this paper were measured with a Perkin-Elmer spectrometer model 12-B. A flint glass prism and tungsten light source were used, with a constant slit width of 0.475 mm. The absorption cell was constructed of Monel metal and had a diameter of 2.5 and a length of 4.0 cm. Glass windows were used with Teflon gaskets. The cell was heated electrically to 100° C.

The results obtained are shown in Fig. 1 and tabulated in Table 1. For comparison we have included the absorption spectra of phenol and acetamide. The concentrations are about 0.2 molar. In addition, chlorouracil

¹Supported in part by the Atomic Energy Commission and the Office of Naval Research.



INFRARED ABSORPTION SPECTROGRAM

FIG. 1.

absorption curves were run at 0.18, 0.28, and 0.43 molar. The effect of increasing the concentration of chlorouracil is simply to deepen the various absorption bands. No broadening characteristic of hydrogen bonding was obtained, and we infer that in this solvent compounds are present in a monomeric form.

TABLE 1

NEAR INFRARED ABSORPTION BANDS (IN ANTIMONY TRICHLORIDE)

Uracil	5-Chloro- uracil	Thymine	Phenol	Acet- amide	Assignment
ab	ab	ab	1.43	ab	0-Н
1.50	1.50	1.51	ab	1.49	N-11
1.65	1.65	1.68	1.67	ab	C-II (ring)
ab	ab	1.75	ab	1.75	C-II (aliphatic)
1.99	1.99	2.00	ab	2.00	C= O ?
2.13	2.13	2.14	2.14	ab	C-H (combination. ring)

Uracil, chlorouracil, and thymine all show sharp, deep bands at 1.50 μ . Bath and Ellis (1) concluded from a study of various proteins that absorption at this wavelength corresponds to the first N-H overtone. The very deep band at 1.49 μ in the spectrum of acetamide confirms

ŀ