Reply to "Comments on The DTPA-Extractable Iron, Manganese, Copper, and Zinc from Neutral and Calcareous Soils Dried Under Different Conditions."

Dr. Benians' letter prompts the following concerning his comments on the paper by Leggett and Argyle (1983).

Our report dealt only with neutral and calcarious soils, as explicitly stated in the title. It was not intended for acid or highly weathered soils without further testing, although our experience indicates that some of these soils are affected by drying and heating in the same way as calcarious soils. Benians indicates that we "berated" Standard Works for their lack of sample drying information. We did not intend to berate anyone (see Webster, 1965 - berate is to chide vehemently; to scold). We stated the facts as we saw them. Quite likely the main reason the subject was not covered more extensively in the Standard Works is the lack of specific information in the literature.

We were well aware of the consequences of drying or heating some samples as indicated by our list of references cited. Thus, we are happy that we arrived at the same "inevitable conclusion" as did Benians that drying or heating affects the results of many analyses of soils.

The field conditions of soils at sampling time is an important problem as indicated by Benians. Shuman's (1980) comprehensive study adequately points out differences that can be encountered when sampling soil in the field at different times and under different moisture conditions. We did not attempt studies of this kind.

The opening sentence of the third paragraph in Benians' letter introduces the subject of changes occurring for di-ethylenetriaminepentaacetic acid (DTPA) extractable Fe and Mn on storing dried samples. In the discussion following this opening sentence we are not sure whether he refers to changes in already dried samples or changes encountered upon drying. In our view the fact that DTPA-extractable Fe and Mn change markedly after drying i.e., while stored dry in waterproof containers, is unusual and a serious limitation that needs to be recognized. Such changes preclude the use of quality control samples over long periods of time that are necessary in laboratory operation. We recognize, however, that this problem may not be unique for Fe and Mn determined by DTPA-extraction. Bartlett and James (1980) showed similar changes for Mn extracted by 1.2 M NH₄OAc, pH 4.8 on samples stored dry for various lengths of time.

Benians asks "Why dry samples?" We did not try to settle this issue with publication of our paper. Our purpose was to point out some of the changes that occur during drying or drying and heating so that others should be aware of the consequences associated with arbitrarily selecting sample drying conditions. Our experiences indicate that many people testing soil are not aware of changes that can take place during drying, nor what effects it will have on the analytical results.

In addition, many of our commonly used analytical procedures specify dry samples and that they be ground to specified fineness (e.g., Chapman, 1965). It is difficult to grind moist samples.

We feel that our "quest for correction factors" was worth trying and had it been successful it would have been useful. Soil testing laboratories receive samples of varying degrees of dryness, some have been dried or partially dried under conditions not adequately specified. We recognize that the lack of standard sample handling procedures and drying temperatures leads to diverse soil test values and confusion on the part of the recipient of the tests, especially when samples from the same fields are submitted more than once during the year or at different times of the year in subsequent years. The final paragraph in our paper suggests that routine samples be handled in the same way as the calibration samples used for relating soil tests to fertilizer response. At the present time most calibration samples are air-dried before analysis whereas a great many routine samples are dried at elevated temperatures.

This exchange of letters points out the need for standardization of sample handling and drying procedures. We thank Dr. Benians for helping call attention to the problem.

Received 27 Aug. 1984

G. E. LEGGETT

Agricultural Testing & Consultants, Inc. D. P. ARGYLE

Twin Falls, ID 83301

References


Comments on "Multifactor Kinetics of Phosphate Reactions with Minerals in Acidic Soils: I. Modeling and Simulation"

The following suggests a disagreement between Langmuir plots and the two-surface Langmuir equation as discussed by Lin et al., (1983).

In Case 5

The adsorption isotherm for the reaction sequence:

\[
[\text{Al(OH)}_3] + [\text{P}]_{\text{Lat}} \rightarrow [\text{P\text{\~\text{}}}\text{Al(OH)}_3]_{\text{R}} + [\text{P\text{\~\text{}}}\text{Al(OH)}_3]_{\text{R}}
\]

at defined initial and final states we have an adsorption isotherm of Fig. 5 and Fig. 6 (at \( R_2 = 0.3 \)). I question how the authors could raise the value of \( R_2 \) by 10 times (\( R_2 = 3 \)) without simultaneously changing the values of \( R_1 \), \( R_2 \), and \( R_3 \) under the defined situation that the initial and final states are maintained unchanged. This is the result obtained in Fig. 7.

Such treatment will violate the rate law and the second law of thermodynamics (Rosenberg, 1977; Butt, 1980). That is, if a single step controls the rate of reaction, all other steps must be at equilibrium. Actually Fig. 7 is not perfectly curvilinear, it comprises two sections of plots; the lower portion of the curve (between points 4 to 8) is curvilinear, whereas the upper portion of the curve (between points 9 to 18) is perfectly linear. A very careful plotting technique must be exercised in order to distinguish these two portions of the plot.

Furthermore, the final P concentration in Fig. 7 is only extended to about 13 \( \mu \text{g/mL} \); suppose the final P concentration was extended to 40 \( \mu \text{g/mL} \) (same as in Fig. 6), the perfect linearity may be even more evident in this portion. Then the curvilinear portion observed in Fig. 7 is not due to the properties of Langmuir plot (Butt, 1980; Rosenberg, 1977),