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The Copper-retaining Powers of Different Cacao Soils

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Brun (1945) has shown that soil organic matter (SOM) holds copper in a complex, non-leachable form; the work of Hasler (1943) suggests that most metallic trace elements are so retained in soil, the order of their retention being roughly parallel to their power of forming metallo-organic complexes (Mellor & Maley, 1948). From such complexes between trace elements and SOM (Bremner, Mann, Heintze & Lees, 1946) the trace elements presumably become slowly available to plants growing in the soil. In view of the fact that Trinidad cacao soils have been exploitatively cropped for 150 years, a depletion of trace elements in these soils may, in part, be responsible for the general drop in cacao yields apparent over the last 25 years. The present work was therefore begun in order to discover whether 'good' cacao soils (i.e. those on which the decline has been least marked) had a greater power than 'bad' soils to retain a trace element against leaching, and to establish a relation between the percentage of SOM in a soil and the power of the soil to retain a trace element. The trace element chosen was copper, in which cacao is rich (Lindow, Elvehjem & Peterson, 1929).

EXPERIMENTAL

Copper was determined by the method of Sherman & McHargue (1942). Soil organic matter was estimated by the method of Hardy (1929). Because the upper layers of a cacao soil probably play the dominant part in cacao nutrition (McCreary, McDonald, Mulloon & Hardy, 1943), the top 3 in. of soil, air dried and ground to a powder, have been used in all experiments. The soils were divided into 'good' soils and 'bad' soils on the basis of planters' estimates of the cacao yields to be expected from them. Good soils were those estimated to yield 7 or more bags of cacao

per 1000 picquets, bad soils were those estimated to yield less.

The Cu-retaining powers of different soils (Fig. 1) were determined as follows. A 5 g. sample of soil was shaken, over a period of 30 min., with 15 ml. 0.5M-Na₂SO₄ containing 1.0 mg. Cu as CuSO₄ after which the soil was centrifuged down, and the supernatant liquid poured off. The soil was then again shaken with 15 ml. 0.5M-Na₂SO₄ containing no Cu and, after 30 min., again centrifuged down, the supernatant liquid being added to the initial one. After 7 such washings, all exchangeable Cu was presumed to have been removed from the soil. The amount so removed was determined by analysis of the bulked supernatant liquids and the amount retained determined by difference.

The data on which Fig. 3 is based were obtained in two different ways on each soil:

(a) Either 1, 2, 4, 8, or 16 g. of soil were mixed with 50 ml. 0.33M-Na₂SO₄ containing, as CuSO₄, either 1.0 mg. Cu (for the bad soil) or 5.0 mg. Cu (for the good soil). After intermittent shaking over a period of 1 hr. the soil was centrifuged down, and the equilibrium concentration of Cu in the supernatant liquid determined.

(b) Either 1, 2, 4, 6, 8, or 10 mg. Cu as CuSO₄, contained in 30 ml. 0.33M-Na₂SO₄, were mixed with 5 g. soil. Procedure then followed that described in (a).

Preliminary tests showed that equilibration of Cu between soil and solution was attained in less than 5 min. The longer equilibration periods used were adopted as a safety measure.

RESULTS

The relation between the estimated percentage of SOM and the copper-retaining power of the soil is shown for thirty-two different cacao soils in Fig. 1. Some 2.5% of the estimated SOM of the soils is apparently inactive in retaining copper; moreover, the percentage of the active SOM (total SOM % - 2.5) is not linearly related to copper retention. In fact the curve of Fig. 1 closely follows the relation

Fig. 1. The retention of copper by different cacao soils (5 g. samples) treated with 1 mg. of copper as CuSO_4 and then well leached with 0.5M- Na_2SO_4 . Crosses, good cacao soils; dots, bad cacao soils.

Fig. 2. Freundlich isotherm derived from Fig. 1; a , copper ($\mu\text{g.}$) retained by soil; m , active SOM (total $\text{SOM}\%$ - 2.5); C , copper removed by Na_2SO_4 leaching.

Fig. 3. Freundlich isotherm of copper retention, derived from two different cacao soils equilibrated with different concentrations of copper contained in 0.33M- Na_2SO_4 . Dots, data from a bad soil (active SOM , 3.4%); crosses, from a good soil (active SOM , 8.3%).

Table 1. *Equilibrium distribution of copper between 5 g. of a good cacao soil (8.3% active SOM) and various volumes of 0.33M- Na_2SO_4 solution*

(Total copper (as CuSO_4) in soil and solution: 5.0 mg. (157 $\mu\text{-equiv.}$.)

Vol. of Na_2SO_4 solution (ml.)	Equilibrium concn. of Cu in solution ($\mu\text{-equiv./l.}$)	Equilibrium concn. of Cu on active SOM ($\mu\text{-equiv./g.}$)
20	33	377
40	37	376
60	31	374
80	31	374
100	34	371
120	30	370

Cu (mg.) retained by soil

Active $\text{SOM}\%$

$= \alpha$ (Cu (mg.) released by Na_2SO_4 extraction)^k.

This is one form of the adsorption isotherm suggested by Freundlich (1930)

$$a/m = \alpha C^{1/n},$$

where a = amount of solute adsorbed, m = weight of adsorbent, C = equilibrium concentration of solute, and α and n are constants. Expressed logarithmically this gives

$$\log a/m = 1/n \log C + \log \alpha.$$

If $\log a/m$ is plotted against $\log C$, a straight line should result. A plot of the appropriate data derived from Fig. 1 does in fact yield a straight line (Fig. 2).

At moderate concentrations of copper in the equilibrium solution (less than 100 $\mu\text{-equiv. Cu/l.}$),

the same equation was found to apply to data from experiments in which the equilibrium distributions of copper between soil and 0.33M- Na_2SO_4 solution were determined for both a good and a bad soil under wide variations of experimental conditions (Fig. 3).

Data in Table 1 show, as might be expected, that the equilibrium concentration of copper in 0.33M- Na_2SO_4 against a given concentration of copper on the *SOM* is independent of the solution volume.

DISCUSSION

In comparison with good Trinidad cacao soils, bad cacao soils are characterized by a low power to retain copper in complex with the *SOM*. Although the copper-retaining power of a soil is clearly related to its *SOM* content, the relation is not linear, and nearly all the bad soils lie on or near the steeply descending portion of the curve relating copper retention and percentage of *SOM* in the soil. Trace-element deficiencies, induced either by leaching or by a too great uptake of trace elements by past cacao crops, are, therefore, far more likely to occur in bad than in good soils.

Although difficulties in estimating small percentages of *SOM* in all probability caused the scatter

of the points on the descending part of the copper-retention curve (Fig. 1), there is reason to believe that of the total value for percentage of *SOM*, as given by the method used, some 2.5% represents absorptively inactive *SOM*. If it be assumed that some 2.5% of the *SOM* is adsorptively inactive, two widely different soils give the same adsorption isotherm (Fig. 3), a fact that suggests there is no basic difference between the absorptive capacities of the organic fractions of the two soils.

It is reasonable to infer from Fig. 3 that the saturation capacity of *SOM* is about 1400 μ -equiv. Cu/g., to which value the logarithmically plotted Freundlich isotherm, known to be non-linear near saturation of the adsorbent, is asymptotic.

SUMMARY

1. Some bad Trinidad cacao soils have lower contents of organic matter, and lower copper-retaining powers than good soils.
2. The distribution of copper between a soil and a solution in equilibrium with it follows a Freundlich isotherm.
3. The significance of the results is discussed.

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The Secondary Oxidation of Amino-acids by the Catechol Oxidase of Belladonna

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The purpose of this investigation was to examine more fully than has hitherto been done the manner in which a plant polyphenolase is able to oxidize amino-acids in the presence of phenols. It was further hoped to discover which of the common amino-acids are liable to oxidation by the system, and the nature of the oxidation products. *Atropa belladonna* L. was known to possess an active polyphenolase system and was used because the nitrogen metabolism of this plant is under general investigation, and large quantities of reasonably homogeneous material were available.

EXPERIMENTAL

Preparation of the enzyme. Young leafy shoots of belladonna up to about 20 cm. long were harvested in May or June; 120–150 g. were disintegrated in a Waring Blendor with two successive portions of 350 ml. acetone. The acetone was filtered off, and the residue air-dried on a Buchner funnel and ground to a fine powder in a Wiley mill.

This crude powder had considerable polyphenolase activity; 50 mg. powder suspended in 2.5 ml. 0.01M-catechol at pH 6 gave an O_2 uptake of over 200 μ l. in 10 min. After three successive extractions with water at room temperature the powder still retained a high oxidase