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SOIL FUMIGATION. III.*—The Sorption of Ethylene Dibromide by Soils at Low Moisture Contents

By PETER WADE

Isotherms of ethylene dibromide sorbed on two soils have been plotted at relative humidities between 0 and 98% of saturation. The sorptive capacities of the soils (an organic soil and a clay) decreased with increasing humidity, and the shape of the isotherms obtained changed from Type II (Brunauer, Deming, Deming & Teller[1] classification of isotherms) on the dry soils, becoming similar to Type III isotherms at humidities above 50%. The measurements were made with the aid of a helical spring balance, the construction of which is described.

Introduction

In the first paper in this series[2] an account was given of an investigation of the sorption of ethylene dibromide by three types of soil at moisture contents in the field range. Some further measurements have since been made on two of the soils at lower moisture contents by means of a helical spring balance. The apparatus was similar in principle to that used by Stark[3] in his investigation of the sorption of chloropicrin by soils.

Experimental

The spring balance was wound from 30-s.w.g. soft copper–beryllium-alloy wire and had 29 turns each of 23 mm. diameter. After being annealed at 315° for one hour the spring had a sensitivity of 5·86 cm./g. The spring was suspended from the hook A of the sorption tube illustrated in Fig. 1. A light aluminium bucket, 25 mm. in diameter and 5 mm. deep, weighing 0·4 g. and attached by fine copper–beryllium-alloy wire to the lower end of the spring, was used to carry the soil sample. The amount of fumigant sorbed by the soil sample was measured by observing the extension of the spring with a cathetometer reading to 0·01 mm. The minimum change in weight possible to detect was thus of the order of 0·2 mg.

Liquid ethylene dibromide was introduced into the apparatus *via* the straight-bore tap by means of a calibrated micrometer syringe fitted with a 20-cm. steel needle. The liquid was measured on to a strip of filter paper looped from two hooks at the lower end of the tube carrying the tap and allowed to evaporate.[2] When equilibrium was established between the fumigant in the vapour phase and that sorbed on the soil sample a further amount of ethylene dibromide was measured into the apparatus and the process repeated until an equilibrium concentration in the vapour phase of about 80 mg./l. was reached. The concentration in the vapour phase was calculated from the

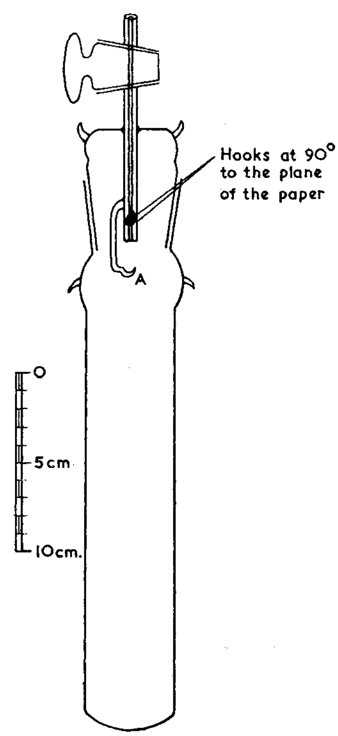


FIG. 1.—*Design of the sorption tube*

* Part II: *J. Sci. Fd Agric.*, 1954, **5**, 288

difference between the amount of fumigant introduced into the apparatus and the amount sorbed by the soil. The amount of fumigant introduced at each stage varied from 15 to 25 mg. according to the sorptive capacity of the soil.

The temperature of the apparatus was controlled by immersing the tube to just below the level of the tap in a water bath, the temperature of which could be regulated to within $\pm$ 0·05° of the desired temperature. All the measurements described in the present paper were made at 20°.

Control of the humidity of the air inside the sorption tube by means of sulphuric acid solutions was found to be impracticable, since measurements made by using a gas-sampling technique[2] in the absence of soil showed that, when the solution contained a high proportion of sulphuric acid, equilibrium between the ethylene dibromide in the vapour phase and that in solution was reached only after several hours. It was found that soil samples placed in the bucket and sealed into the apparatus in the absence of any humidity control showed small changes in weight during the first 5–6 hours, but no further changes were observed after standing for 18–24 hours. The soil samples were therefore placed in the apparatus overnight before sorption measurements were to be made. Usually 1-g. samples of soil were used in plotting an isotherm, and the change in the moisture content of the sample by evaporation or sorption of water vapour was small, being at most about 0·5%.

Measurements have been made on a clay soil (Bones Close) and on a soil with a high content of organic carbon (Black Fen). The compositions of these soils have been given in Part I.[2] A range of samples of varying moisture content were prepared by drying moist soil (passing a 2-mm.-mesh sieve) in a stream of warm air for varying periods of time. Thoroughly dry samples were prepared by drying under vacuum over concentrated sulphuric acid for one week.

Results

The initial rate of sorption of ethylene dibromide by the soils was rapid, gradually falling off and becoming imperceptible over a period of 30 minutes after 15–120 minutes according to the amount sorbed. A further increase in the amount sorbed (of the order of 3–6% of the total amount sorbed) was noted after 24 hours, in agreement with the results previously obtained at moisture contents in the field range. Equilibrium in the present experiments was taken as the amount sorbed when the rate of increase became imperceptible during 15–30 minutes.

The isotherms obtained on the Black Fen soil at various moisture contents are shown in Fig. 2. A similar series of curves were obtained with the clay soil. It has been shown previously (Part I, Fig. 6) that the sorptive capacity of the soils for ethylene dibromide increased rapidly with decreasing moisture content at moisture contents below the usual field range. The present results show this increase to continue until the soils are in equilibrium with a relative humidity of 0%. At the lowest moisture content the isotherms obtained were sigmoid, or Type II in the B.D.D.T. classification,[1] but as the moisture content increased the shape of the isotherms changed, becoming similar to Type III at moisture contents in equilibrium with relative humidities above 50%.

One isotherm was obtained on the Black Fen soil at a moisture content of 32%, corresponding with a relative humidity of approximately 98%. Attempts to carry out measurements at still higher moisture contents were unsuccessful, as distillation of water from the soil to the walls of the apparatus occurred.

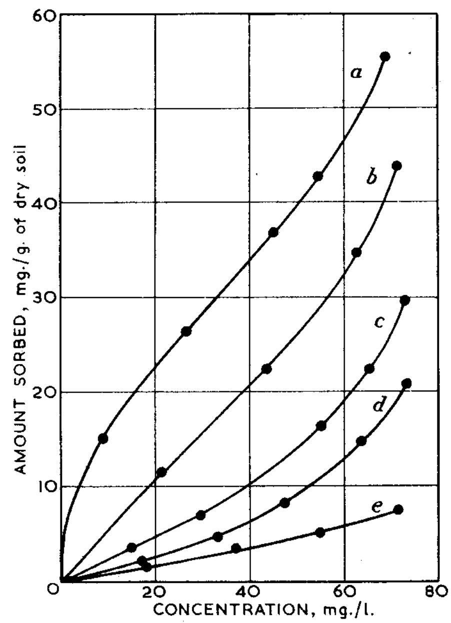
Discussion

The apparatus described above is limited in its applications to measurements on soils having an appreciable sorptive capacity under the conditions of the experiment, and to investigations where the small uncertainty in the final moisture content of the sample is not important. Within these limitations the apparatus provides a convenient method for measuring the sorption of ethylene dibromide by soils at low moisture contents. The isotherms obtained with it have been found to be closely reproducible.

The amount of fumigant sorbed by a soil of a given moisture content at a fixed concentration was found to be less when measured by the present method than when determined by the

FIG. 2.—*Sorption isotherms of ethylene dibromide on Black Fen soil, measured at 20°*

Curve	Moisture content, %	Approx. r.h., %
a	0	0
b	8	10
c	13	50
d	20	90
e	32	98



analytical technique used in the earlier investigation (e.g. compare Fig. 2 curve '*e*' with the corresponding isotherm I in Fig. 5 of Part I). This difference is partly caused by the different conditions taken as equilibrium in the two methods, the remaining difference probably being an artifact.

The change in shape of the isotherms from Type II to Type III as the moisture content of the soils increased is similar to the change in shape observed by Stark[3] for the isotherms of chloropicrin sorbed on soils at increasing moisture contents. The change can be explained by the Brunauer[1] theory of multimolecular adsorption as being caused by a change in the heat of adsorption of the first layer of fumigant molecules. Some change in the heat of adsorption would be expected as the moisture content of the soils rises since the surface of the soil particles will become covered with an increasing number of layers of water molecules, the fumigant molecules being subsequently sorbed on top of the water layer.

The observed high sorptive capacity of the dry Black Fen soil for ethylene dibromide is not in agreement with Stark's observation that a dry muck soil had a low sorptive capacity for chloropicrin. The shapes of the isotherms obtained on the dry soils (Type II in the present case, Type III obtained by Stark) are also at variance.

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THE FREE AMINO-ACIDS OF FISH. I.—Taurine in the Skeletal Muscle of Codling (*Gadus callarias*)

By N. R. JONES

Taurine is present in the free amino-acid fraction of codling muscle. Considerable losses of the amino-acid occur during storage in ice. These apparently result from the combined actions of 'drip' on gutting and leaching by ice-melt water.