

Table IV. Half-Life Values in Days for Residues of FW-293 in Peel of Field-Treated Citrus Fruits as Determined by Three Analytical Methods

Treatment	Colorimetric Method	Total Chloride Method	Total Ketone Method
Valencia Oranges			
1.6 pints 25% emulsifiable concentrate/100 gallons of water	320	350	...
1.6 pounds 25% wettable powder/100 gallons of water	200	170	220
Lemons			
1.6 pints 25% emulsifiable concentrate/100 gallons of water	150	150	...
1.6 pounds 25% wettable powder/100 gallons of water	120	140	...

appears that the residues of FW-293 from both emulsifiable concentrates and wettable powders on fruit harvested prior to 40 days after treatment may be reduced by a washing procedure.

From comparisons of the half-life values listed in Table IV of residue values accrued by the three analytical methods of gradient specificity, no appreciable residue metabolism or other degradation of the compound FW-293 is evident. Also, there is no evidence of appreciable physical losses through vaporization or

dislodgment (7) of the acaricide. FW-293 is remarkably stable as a residue on citrus fruit. This stability is further evidenced by the magnitudes of the residues remaining after the peel has been processed into dried citrus cattle feed (Table III). Citrus peel loses about 70% of its weight during this processing; simultaneously it loses less than 70% of the FW-293 residue as established by the chloroform method. As this manufacturing operation favors chemical loss of analytical identity of the residue from the

lime treatment, and for mechanical losses by solubility in the discarded press-oil emulsion and by volatilization during the forced-air drying, the magnitudes of these losses are low.

Acknowledgment

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FUMIGANT ADSORPTION BY SOILS

Adsorption of 1,2-Dibromo-3-Chloropropane Vapor by Soils

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The isothermal adsorption of 1,2-dibromo-3-chloropropane vapor by various dry soils was studied and the Brunauer, Emmett, and Teller equation applied to the data. The adsorption capacity of a dry organic soil was relatively low when compared with most mineral soils. Surface area measurements of the soils indicated that vapor adsorption was limited to the external surface of the clay fraction. The adsorption data reduced to unit surface showed that the adsorptive capacity of a dry soil is a function of the external surface area and the predominant clay mineral in the system. Kaolinitic and illitic soils adsorbed more fumigant, per unit surface, at higher P/P_0 values, but slightly less at lower P/P_0 values than montmorillonitic soils.

BECAUSE of its promising nonphyto-toxic properties, 1,2-dibromo-3-chloropropane is being utilized as a soil fumigant. The over-all effectiveness of dibromochloropropane as a fumigant will depend upon the ability of its vapor to diffuse through the soil. Thus, any factor that influences vapor diffusion will affect the efficiency of dibromochloropropane's fumigant action.

This study was initiated to observe the adsorptive capacities of seven soils for dibromochloropropane and to apply the

Brunauer, Emmett, and Teller (BET) equation (2) to the experimental data.

Materials and Method

Adsorption isotherm data were obtained by passing a stream of fumigant vapor of known relative pressure through a soil sample. The sample was housed in an adsorption chamber that could be removed from the system and weighed. When the weight remained constant with time, the state of equilibrium was as-

sumed to exist between the vapor stream and soil sample. The amount adsorbed was regarded as the weight difference of the soil sample prior to and after exposure to the fumigant. The apparatus used has been described (8).

The soils were ground to pass through a 60-mesh screen and were dried for 15 hours at 105° C. in air prior to adsorption measurements.

The predominant clay mineral in each soil was determined by x-ray diffraction and differential thermal analyses.

Table I. Brunauer, Emmett, and Teller Parameters and Surface Areas of Soils

Soil	Pred. Clay Mineral	BET Area, Sq. M./G.	Glycol Retention		$E_1 - L$ Cal./Mole	n
			Total area sq. m./g.	External area sq. m./g.		
Yolo silty clay	Mont.	32.6	200	47	1700	4
Meloland clay loam	Mont.	24.6	103	28	1600	4
Salinas clay	Mont.	20.5	145	35	1600	4
Yolo loam	Mont.	15.8	97	21	1600	4
Aiken clay loam	Kaolin	23.4	93	46	1200	∞
Hanford sandy loam	Illite	2.54	22	5.2	1400	∞
Staten peaty muck	Kaolin	4.18	264	20	1300	∞

The total specific surface and external areas of the soils were determined by the ethylene glycol retention method of Bower and Gschwend (7). The organic fraction was not removed from the samples before the total specific surface measurements.

Equation

The general equation derived by Brunauer, Emmett, and Teller to account for multimolecular adsorption that produces the sigmoid type adsorption isotherm can be written as:

$$W = \frac{W_m X C}{1 - X} \times \frac{1 - (n + 1)X^n + nX^{n+1}}{1 + (C - 1)X - CX^{n+1}} \quad (1)$$

W is the weight of vapor adsorbed at pressure P , W_m is the weight adsorbed in forming the monolayer, $X = P/P_0$ where P_0 is the saturation pressure, C is related

to the heat of adsorption and heat of liquefaction of the vapor, and n is the number of adsorbed layers existing on the surface.

A relatively simple method for the determination of n as well as the parameters W_m and C has been presented by Joyner, Weinberger, and Montgomery (7). Equation 1 is algebraically rearranged as:

$$\Phi(nX) = \frac{1}{W_m C} \times \frac{\theta(nX)}{W_m} \quad (2)$$

where

$$\Phi(nX) = \frac{X(1 - X^n) - nX^n(1 - X)}{(1 - X)^2}$$

and

$$\theta(nX) = \frac{X(1 - X^n)}{1 - X}$$

If an appropriate value of n is selected and the values of W are taken from experimental data, a straight line should

result when $\Phi(nX)/W$ is plotted against $\theta(nX)$. The slope and intercept allow one to evaluate W_m and C .

Adsorption Isotherms

Figures 1 and 2 show the adsorption of dibromochloropropane on seven soils at 24.6° C. The isotherms show the marked difference in the adsorptive capacity of the soil, at zero relative humidity, for the fumigant. The relatively low adsorptive capacity of Staten peaty muck is of interest. Organic soils, when encountered in the field, are troublesome because they usually require considerably more fumigant to obtain the control that one obtains in mineral soils (9).

The value of n that produced the best straight line for each soil over the greatest P/P_0 range, when the adsorption data were plotted according to Equation 2, is given in Table I. When n equals 4, the adsorption isotherms of montmorillonitic soils can be reproduced by Equation 1 to a relative pressure of 0.6. When considering soils containing predominantly kaolin or illite clay minerals, the isotherms can again be reproduced to P/P_0 equals 0.6, but n assumes the value of ∞ . Hence, adsorption of dibromochloropropane on dry montmorillonitic soils tends to be restricted while adsorption on kaolinitic and illitic soils occurs on a free surface.

Surface Area

The surface area of the adsorbent that is available for adsorption of dibromo-

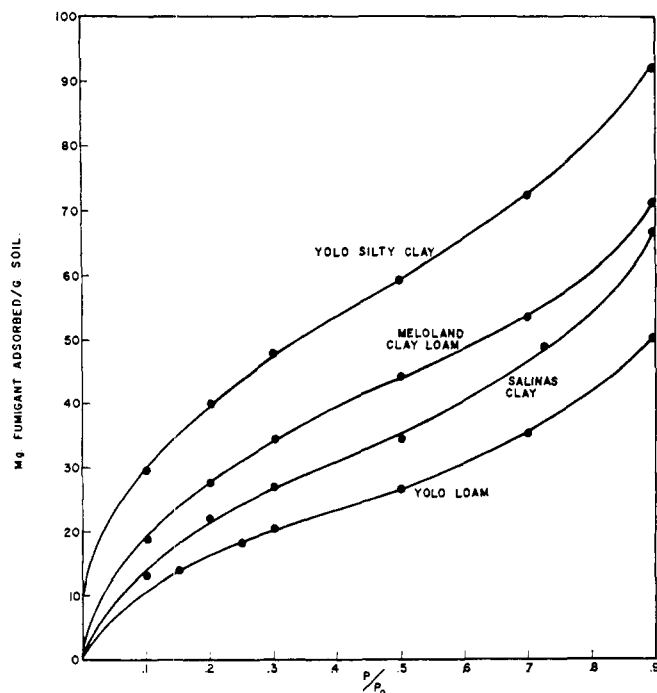


Figure 1. Adsorption of 1,2-dibromo-3-chloropropane by montmorillonitic soils

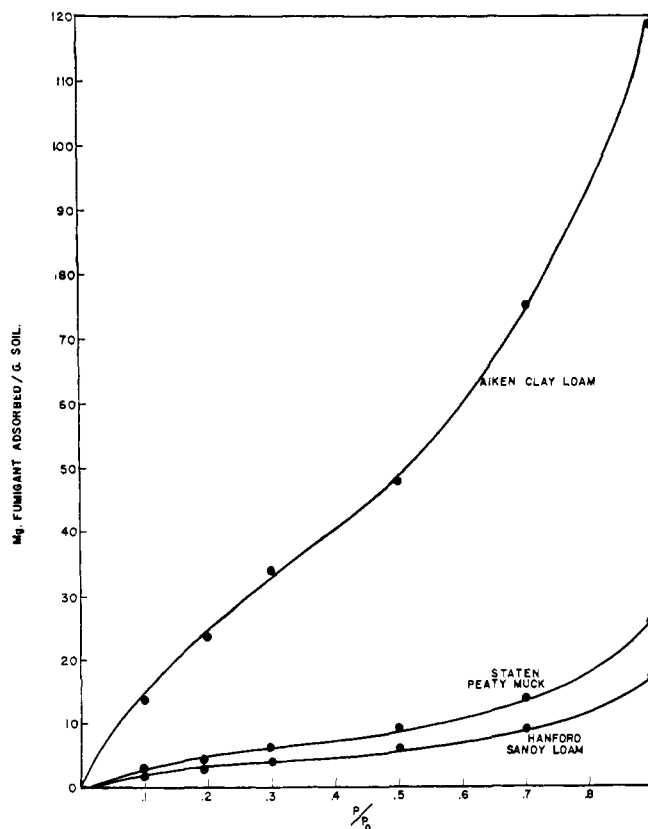


Figure 2. Adsorption of 1,2-dibromo-3-chloropropane by kaolinitic and illitic soils

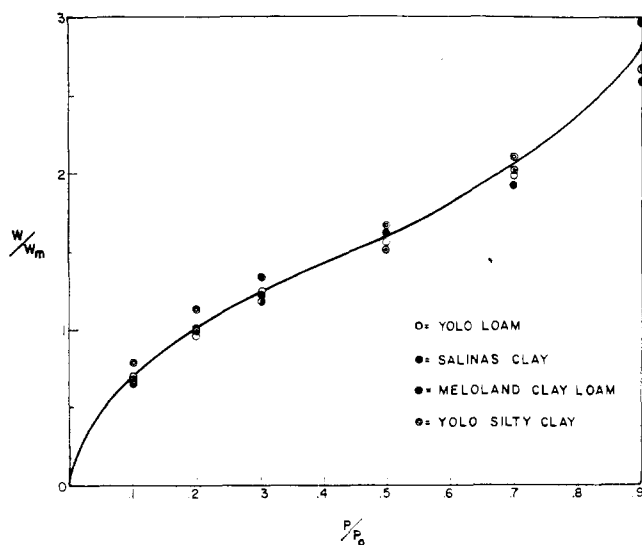


Figure 3. Adsorption on montmorillonitic soils reduced to unit surface

chloropropane can be determined by the evaluation of W_m and the area covered by an adsorbed molecule. The calculated molecular area (4) of adsorbed dibromochloropropane—assuming that the adsorbed molecules are close packed, spherical, and have liquid density—is 36.4 sq. A.

Comparison of the surface areas of the soils as determined by the ethylene glycol retention method and as predicted by the Brunauer-Emmett-Teller equation (Table I) shows that the area available to the adsorption of fumigant vapor is limited to the external surface of the clay minerals. The pre-

treatment of the sample (drying at 105 °C. for 15 hours) is assumed to be only of sufficient severity to remove surface water and some interlayer water, and not irreversibly collapse the clay lattice (6). Hence the unavailability of the internal clay surface is a property of the vapor molecule-clay surface interaction.

The low adsorptive capacity of dry Staten peaty muck, containing 35% of organic matter, is ascribed to the presence of microcapillary pores whose size prevent the entrance of the vapor molecule. Thus adsorption occurs only in the larger capillaries of the organic matter and on the surface of the clay minerals. The low adsorption capacity also indicates that no specific interaction occurs between the dry organic fraction and the organic vapor.

Adsorption per Unit Surface

When adsorption per unit mass (Figure 1) is reduced to adsorption per unit surface as shown in Figure 3, the difference in the adsorptive capacities of the montmorillonitic soils disappears. These data show that the adsorptive capacities of these soils for dibromochloropropane are an expression of the difference in the external surface area of the soil. Within the vapor pressure range studied, the various montmorillonitic soils exhibited

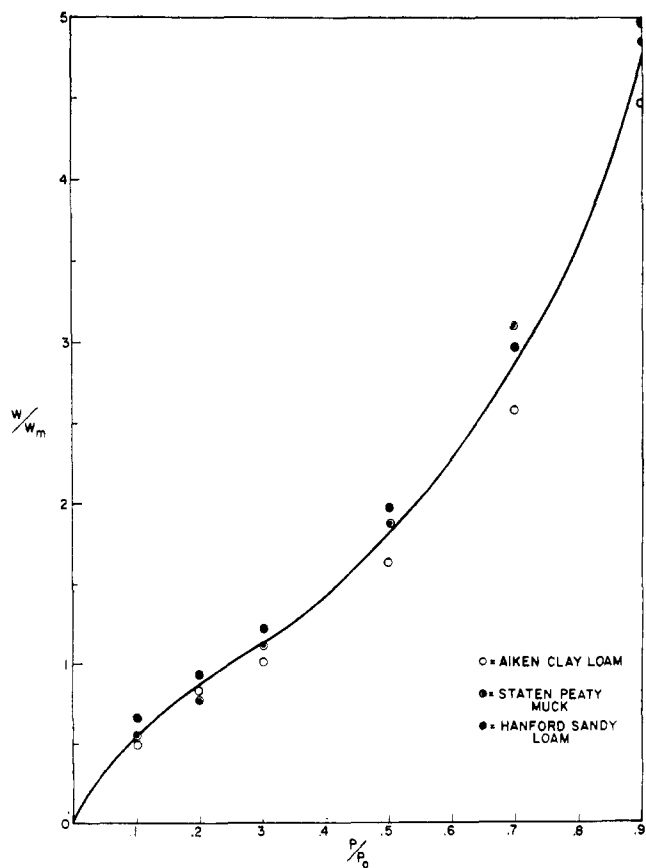


Figure 4. Adsorption on kaolinitic and illitic soils reduced to unit surface

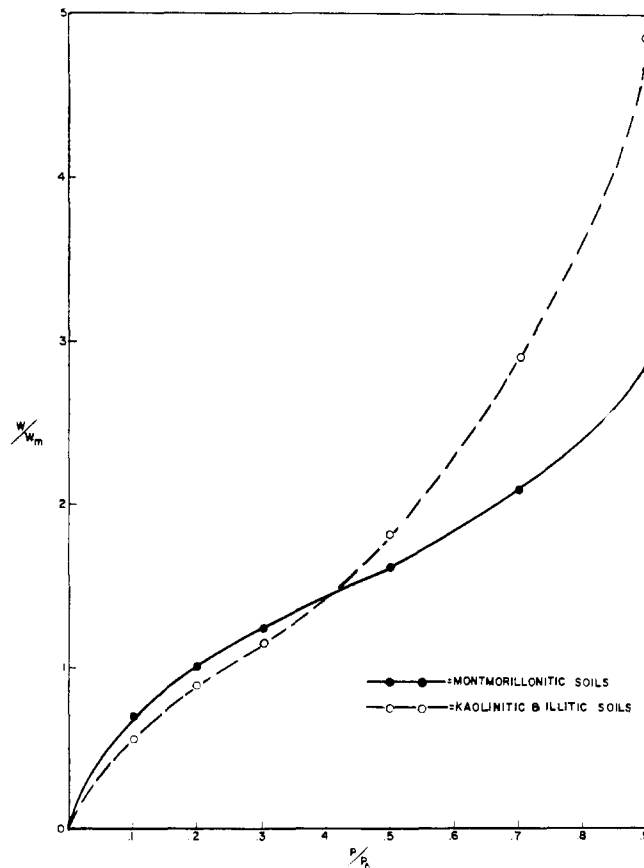


Figure 5. Comparison of mean adsorption isotherms based on unit surface

no specificity for the fumigant vapor. Figure 4 shows similar results when adsorption data of Figure 2 are reduced to a unit surface basis. These data also indicate that, when adsorption is considered on a unit surface basis, kaolinitic and illitic soils tend to act similarly toward the dibromochloropropane molecule.

The adsorption capacity of soil for dibromochloropropane, however, cannot be fully explained by the external surface area. Figure 5 shows that adsorption is also influenced by the clay mineral present in the soil. Comparison of the two mean adsorption isotherms based on unit surface indicates that montmorillonitic soils adsorb slightly greater amounts of dibromochloropropane vapor at lower P/P_0 values, but kaolinitic and illitic soils possess greater adsorptive capacities at higher P/P_0 values. These data on dibromochloropropane adsorption by dry soils correspond closely with the adsorption data of ethylene dibromide (8) indicating similarity in the adsorption mechanism of these two molecules. Additional studies are now in progress to determine the clay mineral effect on vapor adsorption.

Heat of Adsorption

The parameter C of Equation 1 is

related to the average heat of adsorption, E_1 , of the first layer by $2.30 RT \log C = E_1 - L$, where R is the gas constant, T is absolute temperature, and L is the heat of liquefaction of the adsorbent. The value of C is obtained when experimental data are plotted according to Equation 2. The usefulness of E_1 as a measure of surface energetics, is limited to a qualitative index because of the simplified model used in the derivation of Equation 1 (5). The $E_1 - L$ values, shown in Table I, indicate that montmorillonitic soils have a slightly greater adsorptive force for the fumigant molecules than do kaolinitic or illitic soils. The heat of liquefaction of dibromochloropropane is approximately 12 kcal. per mole at 23° C. (3). Therefore, the average heat of adsorption on the less active, roughly homogeneous, fraction of the surface varied from 13.2 to 13.7 kcal. per mole on the seven soils studied.

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INSECTICIDE DETERMINATION

Color Reaction of 2,6-Dibromo-*N*-chloro-*p*-quinoneimine with Thiophosphate Insecticides on Paper Chromatograms

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A simple and rapid detection paper chromatographic method for sulfur-containing phosphate ester insecticides was found by spraying the developed chromatogram with 2,6-dibromo-*N*-chloro-*p*-quinoneimine. As low as 1 γ of material was detected for some of the insecticides studied. This color reaction is useful for rapid identification of a wide variety of thiophosphate insecticides from plant or animal residues.

PAPER CHROMATOGRAPHY is widely used for separation and identification of mixtures of organic insecticides and their metabolites, but the detection of spots on chromatograms is often difficult. Many useful insecticides are esters of phosphoric acid. These can be detected by oxidation to inorganic phosphate and formation of molybdenum blue (6), but this method usually requires several hours for the hydrolysis and fails to detect quantities of less than 25 γ .

The sulfur-containing phosphate ester insecticides can be detected by spraying the chromatogram with *N*-bromosuccinimide (2). The spots react with the active bromine, and subsequent spraying with fluorescein gives yellow fluorescent

Table I. Detection of Various Phosphate Ester Insecticides on Paper Chromatograms at 110° C. for 7 Minutes

Compound ^a	Micrograms	Color
Systox	1	Red-brown
Isosystox	2	Yellow
Parathion	2	Red-brown
Isoparathion	20	None
Trithion	1	Orange-brown
Thimet	1	Orange-brown
Malathion	2	Orange-brown
Dow ET-14	5	Red-brown
Guthion	2	Orange-brown
Dipterex	20	None
Phosdrin	20	None

^a Structures of these insecticides are as follows: Systox is *O,O*-diethyl *O*-ethyl-2-mercaptoethyl phosphorothionate. Isosystox is *O,O*-diethyl *S*-ethyl-2-mercaptoethyl phosphorothiolate. Parathion is *O,O*-diethyl *O*-*p*-nitrophenyl phosphorothioate. Isoparathion is *O,S*-diethyl *O*-*p*-nitrophenyl phosphorothioate. Trithion is *S*-(*p*-chlorophenylthio)-methyl *O,O*-diethyl phosphorodithioate. Thimet is *O,O*-diethyl *S*-(ethylthio)methyl phosphorodithioate. Malathion is *S*-[1,2-bis(ethoxycarbonyl)ethyl] *O,O*-dimethyl phosphorodithioate. Dow ET-14 is *O,O*-dimethyl *O*-(2,4,5-trichlorophenyl) phosphorothioate. Guthion is *O,O*-dimethyl *S*-(4-oxo-3*H*-1,2,3-benzotriazine-3-methyl) phosphorodithioate. Dipterex is *O,O*-dimethyl 2,2,2-trichloro-1-hydroxyethyl phosphonate. Phosdrin is *O,O*-dimethyl (1-carbomethoxy-1-propen-2-yl) phosphate.