

Table I. Mortality Observed in Imported Fire Ants Fed and Incubated in the Dark with a Phloxin B Impregnated Bait Formulation^a

Days after mound collection	Total insects	Percent mortality ^b		
		Feeding period, days		
		1	2	10
1	50	1	0	40
2	130	0	0	50
3	59	0	2	71
4	32	0	14	88
5	57	0	4	72
6	67	1	10	96
8	62	11	13	58
9	137	0	1	45
10	74	0	3	66

^a Bait consisted of 850 parts corn cob grits, 147 parts soybean oil, and 3 parts phloxin B. ^b Uncorrected mortality was less than 10% after 10 days treatment for each group.

would be expected from the data of Broome et al. (1975b).

The light-independent lethal reaction was likewise investigated as a function of the energy level of the fire ants. Populations were removed from the mounds during the first 10 days after the insects were field collected and brought into the laboratory. Table I shows the observed mortality for fire ants exposed to the 0.30% phloxin B impregnated bait for 1, 2, and 10 days. For each population, there was less than 15% mortality after 48-h exposure to the bait. At 10 days exposure, there was a gradual increase in mortality over the first 6 days after mound collection after which a decrease was observed. The reason for the decrease in toxicity after the sixth day in the laboratory is unknown. A similar response was noted on ants fed dye on a sugar water medium (Broome et al., 1975b). The delayed toxicity which this represents satisfies one of the three criteria proposed for an effective fire ant bait (Stringer et al., 1964). This is the mechanism which would be depended upon to eliminate the queen(s) who lives in the deep recesses of the mound where light is minimal. The second toxicity mechanism (light de-

pendent) is much quicker acting. Mortalities are observed in terms of hours of light exposure. This will not affect the foraging of the worker ants until at least the second day. The observed mortality occurred in fire ants preincubated with the bait for 22 h in the dark. This allows the dye to be ingested in quantity and to be transported to critical tissues prior to the light exposure. In reality, the light-induced mortality occurred on the second day of exposure to the bait. Although this light-dependent mechanism will be effective in lowering the number of foraging worker ants in the colony, adequate foraging should be accomplished by those workers on their first day of contact with the bait.

These laboratory studies show that one of the xanthene dye sensitizers, phloxin B, can be incorporated into an acceptable bait for the control of the imported fire ant. The dye is ingested from this bait, penetrates to critical tissue, and causes mortality based on both the light-dependent and the light-independent mechanisms.

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LITERATURE CITED

- Broome, J. R., Callahan, M. F., Lewis, L. A., Ladner, C. M., Heitz, J. R., *Comp. Biochem. Physiol. C* **51**, 117 (1975a).
 Broome, J. R., Callahan, M. F., Heitz, J. R., *Environ. Entomol.* **4**, 883 (1975b).
 Callahan, M. F., Lewis, L. A., Holloman, M. E., Broome, J. R., Heitz, J. R., *Comp. Biochem. Physiol. C* **51**, 123 (1975).
 Callahan, M. F., Palmertree, C. O., Broome, J. R., Heitz, J. R., *Pestic. Biochem. Physiol.* **7**, 21 (1977).
Fed. Regist. **41**, 56694 (1976).
 Stringer, C. E., Jr., Lofgren, C. S., Bartlett, F. J., *J. Econ. Entomol.* **57**, 941 (1964).

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Sorption-Desorption of Parathion in Soils

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Sorption of parathion by soils differing widely in their physicochemical characteristics was investigated employing radiotracer technique. Organic matter was the most important single factor affecting parathion sorption in soils. The relationship between parathion sorption and organic matter content of soils was logarithmic. In soils oxidized with H₂O₂, parathion sorption was correlated with clay and free Fe oxides. Similarly, inorganic soil constituents influenced parathion sorption in soils with <2% organic matter, but their role was apparently masked by organic matter at levels above 2%. Desorption studies revealed that parathion sorption in soils high in organic matter content such as Kari and Pokkali soils of Kerala, South India, was almost irreversible. An equation, $\log x/m = \log [10.899 + 3.14 (\% \text{ organic matter})^2] + 1.05 \log c$, developed from the relationship between Freundlich constant, k , and soil organic matter would assist in predicting parathion sorption in soils with known organic matter content.

Parathion (*O,O*-diethyl *O-p*-nitrophenyl phosphorothioate) is an important broad-spectrum organophosphorus insecticide. Persistence of this insecticide in soils was

reported to vary from a few weeks to several years (Sethunathan et al., 1977). Degradation of parathion in soil is mediated by both chemical (Adamson and Inch, 1973; Yaron, 1975) and biological (Sethunathan et al., 1975, 1977) reactions. The sorption-desorption pattern of a pesticide in relation to soil physicochemical characteristics would largely determine the amount of the chemical

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Table I. Physicochemical Characteristics of the Soils Used

Soil no.	pH ^a	E.C., ^a mmhos/ cm	Organic matter, %	CEC, me/ 100 g	Exchangeable cations (me/100 g)					Free Fe, %	Soil separates		
					K	Na	Ca	Mg	H		Clay, %	Silt, %	Sand, %
1	5.90	0.08	0.60	11.7	0.24	0.43	7.50	0.90	2.63	0.21	10.0	1.0	89.0
4	6.50	0.09	1.00	14.9	0.39	0.40	9.16	1.53	3.38	0.88	25.6	18.3	56.1
5	6.45	0.08	1.27	11.2	0.26	0.43	5.00	0.96	4.51	1.18	37.0	7.8	55.2
6	5.80	0.15	12.58	8.8	0.24	0.48	2.75	0.61	4.70	0.05	9.6	2.8	87.6
8	6.25	0.27	1.62	26.6	0.32	0.98	20.83	1.04	3.38	0.90	20.7	3.4	75.9
9	6.65	0.42	0.92	42.9	0.39	0.65	36.60	1.83	3.95	0.93	24.8	24.9	50.3
10	6.20	0.11	0.75	18.6	2.20	0.70	10.41	1.83	3.76	0.83	15.6	4.8	79.6
11	6.30	0.21	2.88	42.8	0.39	0.63	36.70	1.13	9.78	2.40	23.6	6.8	69.6
13	5.20	3.24	5.52	19.2	2.15	9.13	10.80	12.08	14.66	1.38	45.6	7.8	45.6
14	3.30	6.90	24.62	28.9	0.28	10.22	14.59	15.30	38.35	1.63	29.6	6.8	63.6
15	3.50	5.40	8.21	21.2	0.32	6.08	40.80	12.10	27.45	2.13	33.6	12.8	53.6
16	6.60	0.09	0.70	33.2	0.28	0.65	22.90	5.83	3.57	1.45	23.6	16.8	59.6

^a Soil-water suspension, 1:2.5.

available for losses due to volatilization, leaching, and chemical and biological degradation (Haque, 1975; Goring et al., 1975). As for parathion, clay content of the soils (King and McCarty, 1966, 1968) as well as both organic matter and clay mineralogy (Saltzman et al., 1972) have been implicated in the sorption process. Information on its desorption in soils is limited except for the work of Saltzman et al. (1972). The role of clay colloids and other soil inorganic constituents in parathion sorption is likely to be masked by organic matter since mineral adsorptive surfaces are actually covered up by the organic matter. This study employing [¹⁴C]ethyl-1-parathion was aimed at finding out the role of factors affecting sorption-desorption of parathion in 12 soils by correlating parathion sorption with 13 physicochemical characteristics of the soil. Also, sorption of parathion was compared in soils prior to and after oxidation with H₂O₂.

MATERIALS AND METHODS

Soils. Twelve soils from rice growing tracts in India, differing widely in their physicochemical characteristics (Table I) were used in the study. Among the soils included were Pokkali (soil no. 13) and two Kari (no. 14 and 15) soils from major rice growing tracts of coastal Kerala in South India; these soils have extractable S contents of 0.2, 0.8, and 0.5%, respectively, and are characterized as acid sulfate soils (Bloomfield and Coulter, 1973). Pokkali and Kari soils were selected because of a steady increase in the use of pesticides in the areas comprised of these soils in recent years, but the behavior of pesticides in such unique soils is little understood. Lateritic (no. 1, 4, 5, 8, 9, 11), alluvial (no. 10, 16), and organic matter rich sandy (no. 6) soils were also included in the study.

Labeled Parathion. [¹⁴C]Ethyl-1-parathion obtained from Amersham Radiochemical Centre, Bucks., England, had a sp act. of 54.4 μ C/mg. The radiochemical purity of the chemical was confirmed by thin-layer chromatography as 98%. The benzene carrier was evaporated off and [¹⁴C]parathion was equilibrated with distilled water for 24 h prior to its addition to the soils.

Sorption and Desorption Isotherms. To determine sorption pattern in soils, 1-g soil samples were shaken in a wrist-action shaker with 10 mL of an aqueous solution of parathion at five concentrations ranging from 2 to 10 μ g/g of soil. After 2 h of shaking to attain the equilibrium, the soil suspension was centrifuged and the radioactivity in the supernatant determined by liquid scintillation.

For desorption studies, the method was essentially the same as adopted by Swanson and Dutt (1973) for atrazine. After the initial equilibration of 1 g of the soil sample with 10 mL of an aqueous solution of parathion to allow

sorption, the suspension was centrifuged. Five milliliters of the supernatant was replaced with 5 mL of distilled water, and the contents were shaken again for 2 h, followed by centrifugation, and 5 mL of the supernatant was replaced with 5 mL of distilled water. This process was repeated three times. After each centrifugation, the radioactivity in 0.5 mL (out of 5 mL removed) of the supernatant was assayed.

To study the sorption-desorption process in the absence of organic matter, the same procedure was followed except that the soil samples were pretreated with H₂O₂ to oxidize organic matter (Black, 1965). The desorption was determined only at one sorption maximum.

Factors Affecting Parathion Sorption. In this experiment, the sorption of parathion was studied in 12 soils at one concentration (1 μ g/g of soil). One gram of soil was shaken for 2 h with an aqueous solution of parathion, the suspension centrifuged and the reduction in the radioactivity in the supernatant determined. The parathion sorbed by the soils was correlated with 13 soil physicochemical characteristics by simple and multiple correlation analyses using an IBM computer. Similarly, sorption of parathion was studied in the same soils after pretreatment with H₂O₂.

Determination of Radioactivity. To determine the radioactivity, 0.5 mL of the supernatant was mixed with 5 mL of liquid scintillator which consisted of 60 g of naphthalene, 4 g of PPO (2,5-diphenyloxazole), 0.2 g of POPOP [1,4-bis[2-(5-phenyloxazolyl)]benzene], 100 mL of methanol, and 20 mL of ethylene glycol, brought to 1 L with dioxane. The radioactivity was assayed in a liquid scintillation system LSS 20 (Electronics Corporation of India Ltd., Hyderabad, India).

Soil Analyses. Organic carbon was estimated by the Walkley and Black method and organic matter (O.M.) was calculated by multiplying the values of organic carbon with 1.72 (Jackson, 1967). Exchangeable Na, K, Ca, and Mg were extracted with 1 N ammonium acetate (pH 7.0); Na and K were estimated by flame photometry and Ca and Mg by atomic absorption spectrophotometry. Exchange acidity was determined after extraction with BaCl₂-triethanolamine (pH 8.2) (Black, 1965). Free Fe was obtained by treatment with sodium dithionite and then estimated colorimetrically using KCNS (Jackson, 1967). The soils were analyzed for clay, silt, and sand by the Bouyoucos hydrometer method (Black, 1965). The CEC of most soils was obtained by summation of exchangeable Na, K, Mg, and H (Black, 1965), while for acid sulfate soils rich in soluble salts, the ammonium acetate method using K as saturating cation was followed. Sulfur was determined turbidimetrically after extraction with ammonium ace-

Table II. Pertinent Correlations (*r*) between Parathion Sorption and Soil Characteristics

	Organic matter	pH	Exchange acidity	Exchangeable bases		
				Na	Mg	E.C.
Parathion sorbed	0.841 ^b	-0.830 ^b	0.804 ^b	0.782 ^b	0.721 ^b	0.797 ^b
Organic matter		-0.806 ^b	0.830 ^b	0.714 ^b	0.671 ^a	0.786 ^b

^a Significant at 5% level. ^b Significant at 1% level.

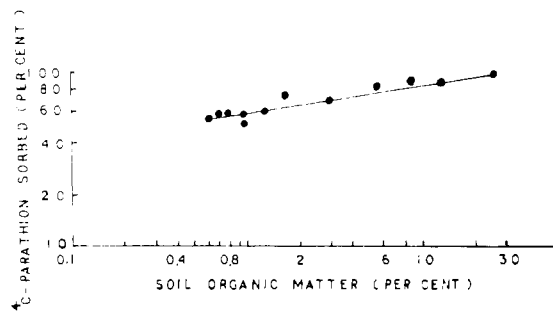


Figure 1. Log-log plot of organic matter vs. parathion sorption in soils.

tate-acetic acid solution (Black, 1965).

RESULTS AND DISCUSSION

Factors Affecting Parathion Sorption. The quantity of parathion sorbed by 12 soils was correlated with 13 physicochemical characteristics of the soils (Table I). In simple correlation analysis (Table II), six characteristics, viz., organic matter content, pH, exchange acidity, exchangeable Na and Mg, electrical conductivity, gave significant correlations, while in multiple correlation analysis, only organic matter yielded significant partial regression coefficient. Interestingly, the five parameters significant only in simple correlations were characteristics of organic matter rich soils, Pokkali and Kari (no. 13, 14, 15). Contrary to the expectation of a simple linear relationship, the plot of organic matter vs. percent parathion sorbed was curvilinear. The regression equation, $\log \text{parathion sorbed (\%)} = 1.763 + 0.15 \log \text{organic matter (\%)}$, accounted for 91% ($r^2 = 0.91$) of the variability in parathion sorption by organic matter alone as compared to 70.7% by the simple linear regression. The data when plotted on a log-log scale yielded a straight line (Figure 1).

The foregoing results suggest that the organic matter content is the most important single factor involved in parathion sorption by soils. It is likely that in organic matter rich soils, the contribution of other factors affecting parathion sorption may be masked, because the inorganic adsorption surface is covered up by organic matter in addition to the tighter adsorption of parathion by the organic matter. The role of other factors in parathion sorption may be best illustrated with soils pretreated with H_2O_2 . The sorption of parathion in soils pretreated with H_2O_2 is shown in Table III. Sorption decreased considerably following oxidation although, as an exception, Pokkali (no. 13) and Kari (no. 14 and 15) soils showed considerable sorption ranging from 53 to 72% after oxidation as compared to 85 to 90% in natural soils. The organic matter content in Pokkali and Kari soils, as in other soils, decreased to less than 0.1% following oxidation. Evidently, factors other than organic matter participated in sorption processes in oxidized soils. Thus for oxidized soils, correlation analysis yielded a significant "*r*" value of 0.79 (significant at the 1% level) for parathion sorption vs. clay content as against a value of 0.24 in natural soils. Also, a significant "*r*" value of 0.807 (significant at the 1% level) was noticed between parathion sorption and free Fe

Table III. Sorption of Parathion by Soils before and after Oxidation with H_2O_2

Soil no.	Parathion sorbed, %	
	Natural soil	Oxidized soil
1	53.5	17.8
4	51.9	38.6
5	59.7	31.3
6	84.9	10.6
8	72.2	29.7
9	55.3	34.3
10	57.5	30.6
11	68.3	55.6
13	84.5	68.5
14	95.6	53.1
15	87.9	71.9
16	57.0	26.1

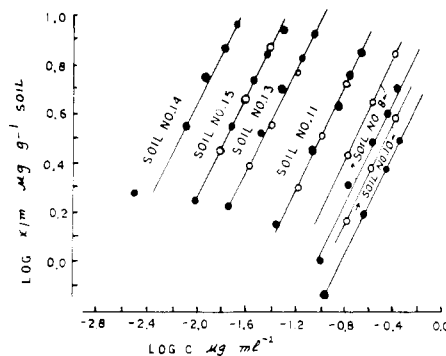


Figure 2. Experimental (●) and predicted (○) Freundlich isotherms for parathion sorption in soils.

oxides in oxidized soils as compared to a value of 0.042 in natural soils. These results demonstrate the relative importance of inorganic soil constituents in parathion sorption in soils. Involvement of clay in parathion sorption has been indicated in studies with pure clay mineral systems (Saltzman et al., 1974).

Sorption Isotherms. The Freundlich isotherm has been used to describe sorption of pesticides by soils using the formula:

$$x/m = kc^{1/n} \quad (1)$$

or

$$\log x/m = \log k + 1/n \log c \quad (2)$$

where x/m is the pesticide sorbed in $\mu\text{g/g}$ of soil, k is a distribution coefficient representing the pesticide sorbed at an equilibrium concentration (c) of 1 ppm, and $1/n$ is the slope indicating the variability in the amount of pesticide sorbed at different pesticide concentrations.

When n is equal to unity, the isotherm is a simple linear relationship as in:

$$x/m = kc \quad (3)$$

In the present study, the amount of parathion available for sorption was in the range of 0 to 10 $\mu\text{g/g}$ of soil, a concentration normally encountered in the agricultural environment after field application. The Freundlich isotherms for soils differing in organic matter content from 0.75 to 24.6% were nearly parallel (Figure 2). The Freundlich constants $1/n$ and k are presented in Table IV.

Table IV. Freundlich Isotherm Constants for Parathion Sorption by Soils

Soil no.	Soil organic matter, %	Natural soils		Oxidized soils	
		<i>k</i>	1/ <i>n</i>	<i>k</i>	1/ <i>n</i>
10	0.75	7.67	1.04		
8	1.62	12.80	1.05	3.16	1.33
11	2.88	38.02	1.11	10.72	1.33
13	5.52	125.90	1.05		
15	8.21	213.80	1.03		
14	24.62	457.10	1.02		

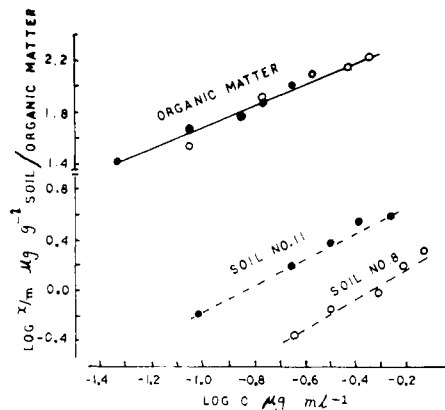
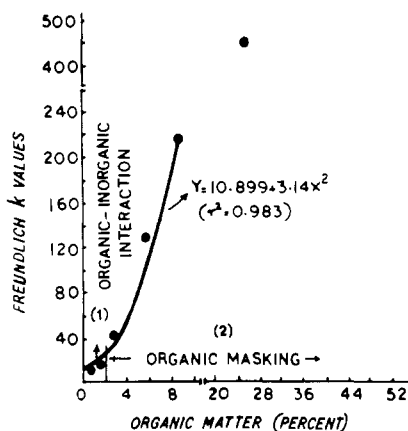


Figure 3. Freundlich isotherms for parathion sorption in oxidized soils and organic matter alone.

Figure 4. Soil organic matter vs. Freundlich *k* values for parathion sorption in soils.

In spite of the variations of 0.75 to 24.62% in organic matter content, the values of $1/n$ remained close to unity while the values of k varied considerably depending on the organic matter content of the soils. In oxidized soils, k values were relatively low and $1/n$ values high as compared to their respective values in natural soils (Table IV, Figure 3).

The data in Figure 4 show k values plotted against the organic matter content of the soils. Expressed in terms of an empirical equation fitted by least-squares method as in:

$$k = 10.899 + 3.14(\% \text{ organic matter})^2 \quad (4)$$

This relationship accounted for a variation of 98% up to a soil organic matter level of about 10%, a range normally encountered in agricultural soils. At higher organic matter levels, this relationship does not seem applicable. The intercept, 10.899 in the equation is the theoretical value of k when no organic matter is present in the soil.

Furthermore, Figure 4 could be resolved into two regions, 1 and 2. At lower organic matter levels <2% (designated as region 1), the sorption of parathion is

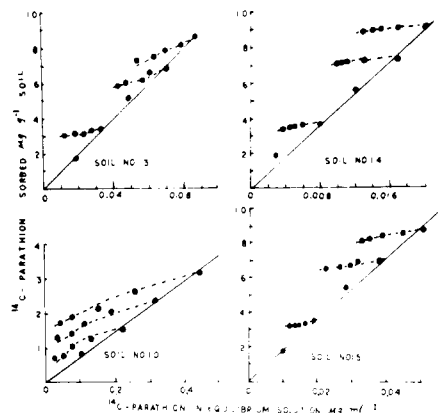


Figure 5. Sorption (—) and desorption (-----) isotherms for parathion in soils.

apparently governed by an interaction between inorganic and organic components. In region 2 (>2% organic matter), the role of inorganic soil constituents in parathion sorption is not manifested, perhaps because of "organic masking".

The Freundlich constant, $1/n$ was close to unity in all soils tested as reported earlier by King and McCarty (1968) for other soils. Assuming these variations in $1/n$ as negligible, a prediction equation for determining parathion sorption isotherms for soils was arrived at using a value of 1.05 for $1/n$ (mean for all soils) and substituting k in eq 2 with eq 4 as follows:

$$\log x/m = \log [10.899 + 3.14 (\% \text{ organic matter})^2] + 1.05 \log c \quad (5)$$

Interestingly, the experimental isotherms based on eq 2 and theoretical isotherms from eq 5 were in close agreement (Figure 2). This has applied significance since parathion sorption in soils can be predicted using isotherms derived from eq 5, provided the organic matter content of the soil is known.

Desorption of Parathion in Soils. The desorption pattern of parathion was studied in four soils at three sorption maxima (Figure 5). The sorption isotherms were apparently linear, because the values of $1/n$ were close to unity. Least desorption occurred with one Kari soil (no. 14) which has an abnormally high organic matter content of 24.6%, regardless of the quantity of parathion initially sorbed. Pokkali (no. 13) and another organic matter rich Kari soil (no. 15) showed poor desorption characteristics. Desorption of parathion from mineral soil (no. 10) was considerable. Following four repeated extractions with water, 48.2% of initially sorbed parathion was released from mineral soil, 12.4% from Pokkali soil, 7.3% from Kari soil no. 15, and 2.7% from Kari soil no. 14. Even after ten repeated extractions with water at a 1:25 soil-water ratio, the total parathion desorbed was 29.2% for Pokkali soil and 8.9% for Kari soil no. 14. These results reflect strong binding of the insecticide to organic matter. This was confirmed when more than 34 to 42% of initially sorbed parathion was desorbed from Kari and Pokkali soils pretreated with H_2O_2 as compared to only 2.7 to 12.4% from natural soils. Moreover, the sorption and desorption isotherms did not overlap, but exhibited a "hysteresis effect" as reported earlier (Saltzman et al., 1972).

Parathion was desorbed effectively from the soils when chloroform-diethyl ether was used instead of water. About 29 and 39% of sorbed parathion was released from Pokkali and Kari (no. 14) soils by one extraction with chloroform-diethyl ether (1:1); the corresponding values for one aqueous extraction were 6.4 and 0.6%. Low desorption

of parathion in water may be attributed to its reported sorption onto hydrophobic sites of soil colloids (Leenheer and Ahlrichs, 1971).

The sorption isotherm for organic matter alone was determined based on the differences in the amount of parathion sorbed between natural and oxidized soils (Figure 3). Considering the high affinity and large surface area of organic matter, a higher k value for organic matter alone can be expected. However, the results showed that the k value obtained for organic matter alone was only 354.8 as compared to 457.1 for Kari soil (no. 14). This discrepancy might result from underestimating the role of organic matter in situations where considerable sorption of the insecticide can occur even in oxidized soils, as in soil no. 11, due to an increase in the inorganic adsorption surface effected by H_2O_2 treatment possibly by (a) exposing surface previously covered by organic matter and (b) changing the inorganic surface qualitatively as well as quantitatively. Perhaps, 68% sorption noticed in soil no. 11 with 2.88% organic matter prior to oxidation may be largely due to organic matter alone while 56% sorption in oxidized soils could be attributed to inorganic soil surface. As a result, Freundlich k values for organic matter alone based on sorption differences in natural and oxidized soils would be misleading. Such a discrepancy may also be expected when sorbed parathion and organic matter do not follow a simple linear relationship (Figure 1).

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LITERATURE CITED

Adamson, J., Inch, T. D., *Proc. Brit. Insectic. Fungic. Conf.*, 7th

65-72 (1973).

Black, C. A., "Methods of Soil Analysis", Part 2, American Society of Agronomy, Madison, Wis., 1965.

Bloomfield, C., Coulter, J. K., *Adv. Agron.* **25**, 266 (1973).

Goring, C. A. I., Laskowski, D. A., Hamaker, J. W., Meikle, R. W., in "Environmental Dynamics of Pesticides", Haque, R., Freed, V. H., Ed., Plenum Press, New York, N.Y., 1975, pp 135-172.

Haque, R., in "Environmental Dynamics of Pesticides", Haque, R., Freed, V. H., Ed., Plenum Press, New York, N.Y., 1975, pp 97-114.

Jackson, M. L., "Soil Chemical Analysis", Prentice-Hall of India, 1967.

King, P. H., McCarty, P. L., *Proc. Purdue Univ. Ind. Wastes Conf.* **21**, 156 (1966).

King, P. H., McCarty, P. L., *Soil Sci.* **106**, 248 (1968).

Leenheer, J. A., Ahlrichs, J. L., *Soil Sci. Soc. Am. Proc.* **35**, 700 (1971).

Saltzman, S., Klinger, L., Yaron, B., *J. Agric. Food Chem.* **20**, 1224 (1972).

Saltzman, S., Yaron, B., Mingelgrin, U., *Soil Sci. Soc. Am. Proc.* **38**, 231 (1974).

Sethunathan, N., Rajaram, K. P., Siddaramappa, R., in "Origin and Fate of Chemical Residues in Food, Agriculture and Fisheries", International Atomic Energy Agency, Vienna, Austria, 1975, pp 9-18.

Sethunathan, N., Siddaramappa, R., Rajaram, K. P., Barik, S., Wahid, P. A., *Residue Rev.* **68**, in press (1977).

Swanson, R. A., Dutt, G. R., *Soil Sci. Soc. Am. Proc.* **37**, 872 (1973).

Yaron, B., *Soil Sci. Soc. Am. Proc.* **39**, 639 (1975).

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