water were diethyl phosphate, cyclic *S,S*-propylene dithiocarbonate and 2-imino-5-methyl-1,3-dithiolane, suggesting that the major photolytic process involved hydrolysis of the phosphorus–nitrogen bond. In acetone, the major products were diethyl phosphate and cyclic *S,S*-propylene dithiocarbonate. This suggests that acetone, in addition to accelerating the photohydrolysis of mephosfolan, also effectively sensitized the photohydrolysis of II to III. A suggested scheme for the photolysis of mephosfolan appears in Figure 5.

ACKNOWLEDGMENT

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Sorption–Desorption of α, β, and γ Isomers of Hexachlorocyclohexane in Soils

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Sorption and desorption of α, β, and γ isomers of hexachlorocyclohexane (HCH) by 12 soils of varying characteristics were studied using uniformly ^{14}C-labeled isomers. Soils showed striking differences in their ability to sorb HCH with sorption ranging from 40 to 96% of the total HCH added. At low equilibrium concentrations no appreciable differences in sorption occurred between the three isomers with respect to individual soil samples; but at higher concentrations sorption of the three isomers within a soil was not always comparable. Organic matter was the most important factor governing the sorption and desorption of HCH isomers. Sorption increased and desorption decreased with increasing soil organic matter content. The sorption of HCH isomers with unit increase of soil organic matter content from 0 to 3.4% was 41 times more than at organic matter contents over 3.4%. In the absence of organic matter, clay content and free iron oxide were implicated in γ-HCH sorption and free iron oxide alone in β-HCH sorption, while no significant correlation existed between α-HCH sorption and clay content or free iron oxide. Desorption of all three isomers showed a hysteresis effect.

Hexachlorocyclohexane (HCH) is used widely for controlling major insect pests of rice. Commercial and technical formulations of HCH are comprised of α, β, δ, ε, and γ isomers of which the γ isomer alone is insecticidal. The β isomer is a minor constituent, but, following extensive use of HCH in Japan, it accumulated through the food chain because of its persistence and, as a result, occurred more frequently and in larger amounts than other isomers in agricultural commodities, milk samples in particular (Tomizawa, 1977). Consequently, the use of HCH was banned or restricted in Japan in recent years. In tropical developing countries, such a ban on HCH use would adversely affect the intensive crop production and health programs because HCH is relatively cheap, highly effective, and indigenously available. Price considerations and nonavailability of substitutes would thus delay the replacement of HCH in most of the developing countries. For example, India has the capability of producing HCH in surplus of the projected demand and HCH alone accounts for more than 50% of all pesticides used in the country. In view of the overall importance of HCH to Indian agriculture, an isotope study was undertaken to

compare the relative sorption/desorption of α, β, and γ isomers of HCH in Indian rice soils, widely differing in their physical and chemical characteristics.

MATERIALS AND METHODS

Soils. Twelve soils from rice-growing tracts in India were the same as used in an earlier study (Wahid and Sethunathan, 1978) and differed widely in their physicochemical characteristics. The soils have been identified by number and their physicochemical characteristics have been described earlier (Table I, Wahid and Sethunathan, 1978). Included were a Pokkali soil (13) and two Kari (14 and 15) soils from the major rice-growing tract of coastal Kerala in India which have extractable S contents of 0.2, 0.8, and 0.5% and are characterized as acid sulfate soils (Bloomfield and Coulter, 1973). Soils were air-dried, ground to pass a 100-mesh sieve, and stored in air-tight bottles.

Labeled HCH Isomers. Uniformly labeled α, β, and γ isomers of HCH were obtained from Amersham Radiochemical Centre, Bucks, United Kingdom, and had specific activities of 48, 33, and 45 mCi/mmol. The purity of all isomers was confirmed by thin-layer chromatography. The benzene carrier was evaporated and the [^{14}C]HCH isomers were equilibrated with distilled water for 24 h prior to their addition to the soils.

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Sorption–Desorption of HCH Isomers in Soils

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Table I. Sorption of HCH Isomers by Soils before and after Oxidation with H_2O_2 (%)

soil no.	natural soil			H_2O_2-oxidized soil		
	α-HCH	β-HCH	γ-HCH	α-HCH	β-HCH	γ-HCH
1	43	47	46	27	18	8
4	54	52	50	46	22	6
5	48	46	47	31	39	37
6	91	93	89	32	22	16
8	49	58	65	35	27	25
9	54	59	55	36	23	26
10	40	46	48	9	15	8
11	77	84	76	5	58	33
13	87	91	87	16	42	27
14	95	96	96	23	37	25
15	91	92	91	34	36	28
16	54	46	44	27	14	20

Factors Affecting HCH Sorption. In this experiment, the sorption of the three isomers was studied in all 12 soils at one concentration (1 $\mu g/g$ of soil). Preliminary experiments showed that sorption equilibrium for the three isomers was attained within 2 h of shaking at a soil–solution ratio of 1:10. Hence the following procedure was adopted. One-gram soil samples were equilibrated with 10 mL of an aqueous solution of each isomer of HCH in glass centrifuge tubes by shaking on a wrist-action shaker for 2 h at room temperature (26 ± 1 °C). Then the suspension was centrifuged at 8000 rpm for 5 min and radioactivity in the supernatant determined. The decrease in the radioactivity in the supernatant was attributed to sorption by soil. The percentage sorption of HCH isomers by soils was subjected to simple correlation analyses. Similarly, sorption of HCH isomers was studied in the same soils after treatment with H_2O_2 (Black, 1965). The organic matter contents of the H_2O_2-oxidized soils were less than 0.1%.

Sorption and Desorption Isotherms. Sorption isotherms for the three isomers of HCH in soils were obtained at concentrations of 0–2.5 $\mu g/g$ of soil for α-HCH and from 0 to 3.0 $\mu g/g$ of soil for β- and γ-HCH. The experimental conditions and procedure were as decribed in the previous experiment.

Desorption isotherms were obtained following the method of Swanson and Dutt (1973). After equilibration of 1 g of soil with 10 mL of aqueous solution of each HCH isomer to allow sorption, the suspension was centrifuged. Five milliliters of the supernatant was replaced with 5 mL of distilled water, the contents shaken again for 2 h and centrifuged, and 5 mL of the supernatant again replaced with 5 mL of distilled water. This process was repeated once more. After each centrifugation, the radioactivity was measured in 0.5 mL of the supernatant. The desorption isotherms of all the isomers were obtained with four soils (10, 11, 13, and 14: Table I, Wahid and Sethunathan, 1978) after sorption at three different concentrations.

In another experiment, desorption of HCH isomers from the same four soils was studied at one concentration (1 $\mu g/g$ of soil) before and after treatment with H_2O_2. After equilibration and centrifugation the supernatant was
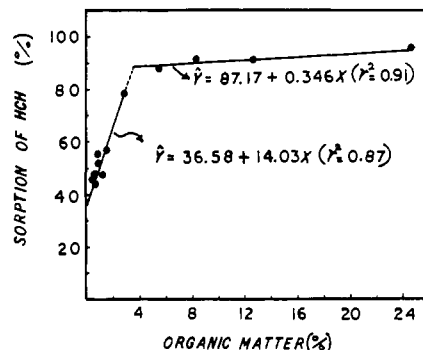

Figure 1. Organic matter vs. HCH sorption in soils. Mean of the pooled values for α, β, and γ isomers of HCH.

discarded and the soil-sorbed isomers were equilibrated with 20 mL of distilled water for 2 h for desorption. The suspension was centrifuged and an aliquot removed for radioactivity measurement.

Determination of Radioactivity. To determine the radioactivity, 0.5 mL of the supernatant was mixed with 5 mL of a liquid scintillation cocktail 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 measured using a liquid scintillation system LSS 20 (Electronics Corporation of India Ltd., Hyderabad).

RESULTS AND DISCUSSION

Sorption Pattern in Natural and Oxidized Soils. The relative sorption of α, β, and γ isomers of HCH by 12 soils at a low concentration of 1 $\mu g/g$ of soil before and after oxidation with H_2O_2 is presented in Table I. The differences in sorption of the three isomers in each of 12 natural soils (prior to oxidation with H_2O_2) were not found to be statistically significant by the "t" test. The sorption data for individual isomers when subjected to simple correlation analysis with 13 physicochemical characteristics of the soil (Table I, Wahid and Sethunathan, 1978) yielded significant correlations with six characteristics: soil organic matter, pH, exchange acidity, exchangeable Na and Mg, and electrical conductivity (Table II). The nature and magnitude of these relationships are similar among the isomers. Significant r values obtained in simple correlation analysis for five characteristics (pH, exchange acidity, exchangeable Na and Mg, and electrical conductivity) may be due to their interrelationships with organic matter (Table II) as reported for parathion (Wahid and Sethunathan, 1978).

Contrary to expectations, plots of the sorption of the three HCH isomers against soil organic matter exhibited two linear branches. As the differences in sorption among the isomers were negligible, the pooled mean values were obtained and are presented in Figure 1. The two portions of the curve shown in Figure 1 are best expressed by two separate linear regression equations which account for a variation of 87 and 91%, respectively, in the first and second portions of the curve. Attempts to describe the

Table II. Correlation (r) between Sorption of HCH Isomers and Soil Characteristics[a]

HCH isomer	org. matter	pH	exchange acidity	exchangeable bases		EC
				Na	Mg	
α	0.784**	−0.740**	0.749**	0.713**	0.683*	0.720**
β	0.757**	−0.723**	0.723**	0.699*	0.624*	0.699*
γ	0.792**	−0.774*	0.759**	0.734**	0.653*	0.744*
org. matter		−0.805*	0.830*	0.714**	0.671*	0.786*

[a] Significant at the 5% level (*). Significant at the 1% level (**).
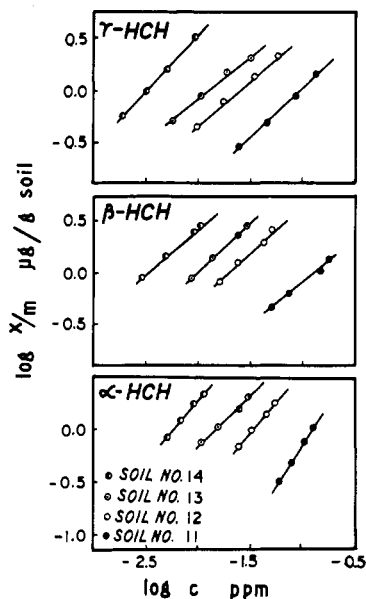
Figure 2. Freundlich isotherms for α, β, and γ isomers of HCH in soils.

relationship by a single equation using logarithmic models were not successful. Adams and Li (1971) derived a curvilinear equation for lindane sorption by soil organic matter of the form $y = ax + bx^2 + c$, where y is percent lindane sorbed, x is the organic matter content of soil, and a, b, and c are constants. A disadvantage of this model is that it is too empirical to explain the behavior of y as a function of x with two exponents, 1 and 2, and with two coefficients, a and b. From the two equations given in Figure 1, it is possible to compare the rate of increase in sorption of HCH within two ranges of organic matter, viz., 0–3.4% and 3.4–24.6%, using the ratio of the slopes of the curves in the respective ranges, i.e., 14.03/0.35 = 40.9. This means that the increase in sorption of HCH with unit increase in organic matter within a range of 0–3.4% is approximately 41 times over that in the range of 3.4–24.6%. The intercept in eq 1 (36.58) may be taken as the theoretical value for HCH sorption when no organic matter is present. This compares well with the mean value for the pooled data for sorption of the three isomers of HCH by oxidized soils (28%). The change in slope at an organic matter level of 3.4% could be due to "organic masking" as reported earlier for parathion (Wahid and Sethunathan, 1978).

Organic matter is the most important single factor governing the sorption of pesticides in soils (Weed and

Weber, 1974). The importance of soil organic matter in sorption of α, β, and γ isomers of HCH follows from the drastic reduction in the sorption capacity of the soils following treatment with H_2O_2 (Table I). In the absence of organic matter, the role of other soil constituents, e.g., clay content and/or free iron oxide, in the sorption process becomes pronounced, at least with regard to the β and γ isomers. Thus sorption of γ-HCH was correlated significantly with clay content ($r = 0.63*$) and free iron oxide ($r = 0.64*$) and that of β-HCH with free iron oxide ($r = 0.718**$). No significant correlation existed between α-HCH sorption and clay content and free iron oxide. Lotse et al. (1968) implicated both organic matter and clay in γ-HCH sorption. According to our study, free iron oxide is perhaps more important than clay in the sorption of β and γ isomers of HCH in soils containing very low organic matter.

Sorption Isotherms. Mills and Biggar (1969) found that sorption of β- and γ-HCH from water and hexane in soil materials such as peaty muck, calcium bentonite and calcium venado clay and silica gel followed Freundlich adsorption isotherm. The three isomers used here obeyed Freundlich adsorption isotherm in all four soils tested (Figure 2) in the following form:

$$x/m = KC^{1/n}$$

or

$$\log x/m = \log K + 1/n \log C$$

where x/m = micrograms of pesticide sorbed/gram of soil, K = the distribution coefficient representing micrograms of pesticide sorbed/gram of soil 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.

In the present study, the amounts of different isomers available for sorption per gram of soil were in the ranges of 0–2.5 μg for the α isomer and 0–3.0 μg for the β and γ isomers. The Freundlich constant K obtained by extrapolation (Table III) was generally higher for α- than β- or γ-HCH. Variations in K for different isomers for the same soil were also found. For example, with soil 13 a value of 31.62 for K was obtained for the γ isomer and a value of 79.43 for the β isomer; the values were reversed with soil 14 for these two isomers. Thus, large variations in sorption can occur at higher pesticide concentrations as compared to insignificant variation at low concentration (Table I). The K values increased with increase in organic matter content of the soil irrespective of the isomer used,
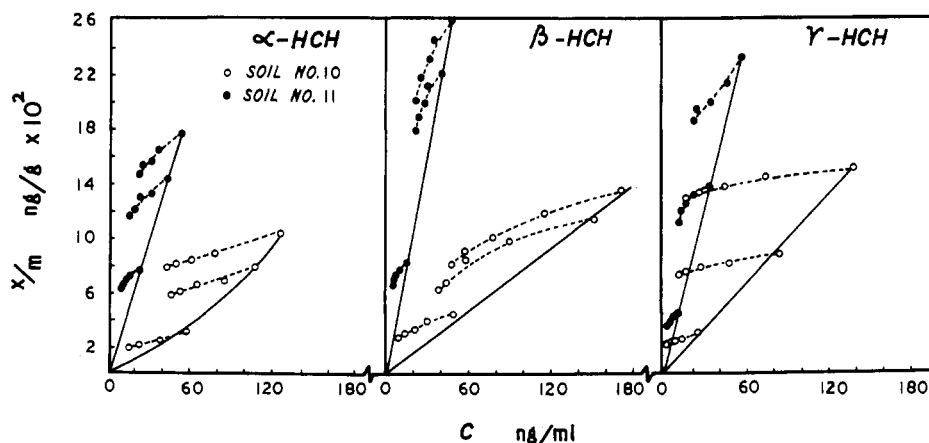

Figure 3. Sorption (—) and desorption (- -) isotherms of α, β, and γ isomers of HCH in soils.

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Table III. Freundlich Isotherm Constants for HCH Isomers

HCH isomer	soil no.	K	1/n
α	10	28.18	1.60
	11	52.48	1.26
	13	70.79	0.94
	14	501.20	1.16
β	10	5.13	0.82
	11	39.81	1.20
	13	79.43	0.80
	14	158.50	0.80
γ	10	8.91	0.90
	11	25.12	0.80
	13	31.62	0.80
	14	446.70	1.10

Table IV. Desorption of HCH Isomers from Soils

soil no.	% HCH desorbed					
	α-HCH		β-HCH		γ-HCH	
	a	b	a	b	a	b
10	50	100	60	86	41	92
11	28	92	33	47	28	61
13	17	74	14	53	18	59
14	6	77	5	51	6	58

^{a} Natural soil. ^{b} H_2O_2-oxidized soils.

while no regular pattern was evident for $1/n$ values. In general, $1/n$ values were higher with α-HCH than with the other two isomers.

Desorption. Desorption of HCH isomers from four soils was studied after sorption at three different concentrations; but data for only two soils are included in Figure 3. Desorption of all isomers from all soils was virtually negligible. Sorption and desorption isotherms did not overlap ("hysteresis"). In the experiment on desorption from four soils before and after oxidation with H_2O_2, in natural soils, an inverse relationship was found between soil organic matter content and desorption of the pesticide, with least desorption from soil 14 of highest organic matter content (24.6%). More desorption of HCH isomers occurred from oxidized soils than from natural soils (Table IV). Isomers differed as to the amount desorbed from oxidized soils although no appreciable differences in sorption and desorption were noticed in natural soils. The

α isomer was desorbed more than the γ and β isomers from all oxidized soils. As in the case of parathion (Wahid and Sethunathan, 1978) the sorption of HCH seemingly takes place on hydrophobic sites.

CONCLUSIONS

Strong sorption of HCH isomers by organic matter rich kari and pokkali soils reduce the availability of pesticides applied to such soils for insecticidal action. Pesticides are used on a large scale in the organic matter rich kari soil of Kuttanad. Surprisingly pesticide applications in this area in terms of rates and intervals are similar to those practiced in other rice-growing tracts with soils of low organic matter content. The tremendous buildup of insect pests in rice in Kuttanad in recent years is perhaps, at least in part, due to the application of soil pesticides at inadequate rates and intervals developed without regard to the sorption characteristics of the soil of this area. Our results emphasize the need for better application schedules for pesticides for soil types with relatively high organic matter content.

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