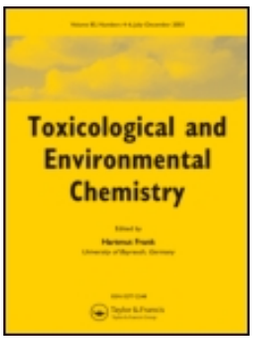

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THE MAJOR ENVIRONMENTAL FACTORS THAT INFLUENCE RAPID DISAPPEARANCE OF PESTICIDES FROM TROPICAL SOILS IN KENYA

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Results of field and laboratory studies on adsorption/desorption, leaching, dissipation, bound residue formation and metabolism of DDT, DDE, lindane, parathion, malathion, dimethoate and carbofuran in tropical soils in various regions in Kenya are summarized in this paper. Based on reported half-lives of dissipation in temperate soils, DDT, DDE and lindane were found to dissipate much more rapidly in tropical soil conditions with half-lives of dissipation of 64.5–245.6, 145 and 5–8 days, respectively. Carbofuran ($t_{1/2}$ = 66–115.5 days), malathion ($t_{1/2}$ = 36.7–770 days), parathion ($t_{1/2}$ = 48 days) and dimethoate ($t_{1/2}$ = 72 days) were also less persistent. The major environmental factors, wind, rainfall, solar radiation intensity and soil moisture content that contributed to this rapid disappearance are presented, explaining also the influence of important soil characteristics such as pH, % organic carbon, texture and microbial activity on pesticide distribution and degradation in soil.

Keywords: Pesticides; Fate; Persistence; Half-lives; Tropical soils

INTRODUCTION

In Kenya, the environmental fate of pesticide residues is an issue that is now receiving more attention than ever before due to international residue limit requirements in food, drinking water supplies as well as in export products

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such as fish, fruits and horticultural produce. Monitoring of pesticide residues in food, water, and horticultural produce will therefore continue to play an important role in export trade especially in this new millennium. This is particularly important because of the increasing use of pesticides in agriculture and public health vector control, mainly evident in the veterinary and horticultural sectors which have been modernized and are using pesticides intensively to increase their yields, as shown by the steadily increasing annual expenditure on imports of various formulations and ingredients of insecticides and acaricides from 1986–1998, in comparison to herbicides and fungicides as shown in Fig. 1.

A lot of concern has been expressed worldwide regarding the fate of pesticide residues in the environment and their effects on non-target organisms [1–3,4–6]. Most pesticide residues reach the soil either through direct application or indirectly through transport by wind and rainfall [7]. Residues are also transported from the point of application to other locations by leaching in soil and by surface runoff and often eventually enter into the aquatic environments where they can have adverse effects on aquatic organisms as well as on humans who depend on these organisms as a source of food. It is estimated that up to 50% of all pesticides applied to

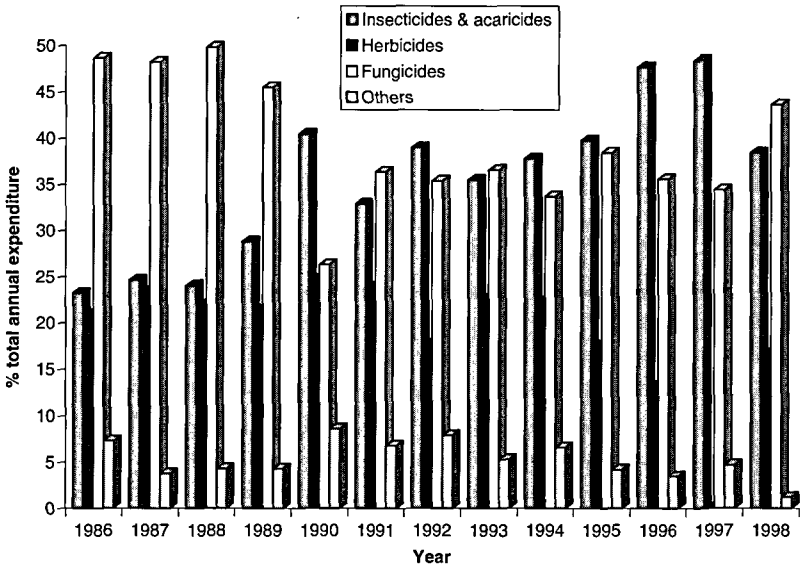

FIGURE 1 The value (in Kshillings) of different groups of pesticides imported into Kenya (1986–1998) expressed as % of total annual expenditure on pesticide imports, showing the increase in import of insecticides and acaricides from 1986–1998. Source of information: Pest Control Products Board of Kenya.

crop foliage reach the soil as spray drift or surface runoff [8,9]. It is therefore important to determine the persistence and metabolism of pesticides in soil in order to understand their fate and potential effects on both terrestrial and aquatic organisms. The rates of dissipation and metabolism of pesticides in soil are dependent on their rates of volatilization and chemical transformation to other metabolites. These rates are enhanced by adsorption/desorption processes in the soil matrix, sunlight intensity, chemical reactions such as hydrolysis and oxidation/reduction reactions, and microbial activity in soil [10–14]. Chemical transformation processes in soil are influenced by soil characteristics such as pH, temperature, clay content, organic matter content, moisture content, presence of micro-organisms and the type of functional groups attached to the pesticide molecules. In addition, external environmental factors such as wind, % relative humidity, soil and air temperatures and rainfall also influence the dissipation of pesticides from the soil [15–18].

Organochlorine pesticides such as the cyclodiene insecticides, heptachlor, aldrin, endrin, dieldrin are the most persistent and were found to persist in field crop soils for long periods of time, with long half-lives of disappearance, ranging between 0.3–2.8 years in temperate soils (see Table VIIIB) [19]. Organochlorine pesticides are only weakly adsorbed to soil matrix, and therefore soil moisture content, surface evaporation as well as their water solubility are very influential in their dissipation from soil. DDT was reported to be most persistent in rich forest soils of Canada with a half-life of 35 years where the forest cover, in addition to the cold temperatures, could not allow any significant loss by evaporation or wind [20,21]. However, lindane has comparatively very low persistence even in temperate soils due to its weak adsorption to soil which results from its small molar volume, high vapour pressure and high water solubility, all favouring its loss by volatilization [10,22].

Most organophosphorous pesticides have been found to rarely persist into the next 2nd year after application, even in temperate soils [10]. For these pesticides, soil characteristics play a very influential role in their degradation and dissipation. Parathion, for example, has a short half-life of between 2–4 weeks in temperate soils, whereas some of the most persistent organophosphates such as chlorvenvinphos and carbophenothion have soil half-lives of about 12 and 24 weeks, respectively [20]. Carbamate insecticides are moderately persistent in soil with half-lives of up to a few weeks except the systemic methyl carbamates such as carbaryl and carbofuran which have higher half-lives ranging between 18–378 days in temperate soil conditions [23,24].

From previous studies done in temperate soils, the disappearance of pesticides from soil under field conditions was found to fit closely into first order kinetics model showing a typical biphasic pattern with an initial rapid phase of disappearance experienced immediately after application when the pesticide was still on the soil surface, followed by a second phase when the dissipation rate was much slower or almost constant in some cases and the pesticide residues tended to become more tightly bound to the soil matrix [10,12,20,25]. The same pattern of dissipation has also been found to apply to pesticide behaviour in tropical soil conditions [22,26–28]. The first rapid phase of dissipation of pesticides however appears to be very significant in tropical soils where high temperatures, intense solar radiation, wind and soil moisture retention ability contribute to very rapid volatilization eventually reducing the overall half-lives of disappearance considerably. This first phase is also influenced greatly by rainfall if it comes immediately after application of the pesticide. It is due to this rapid initial volatilization that pesticides are often applied in higher amounts than the recomended doses by farmers in these tropical regions in order to achieve the desired effectiveness.

Half-lives of dissipation of the persistent organochlorine compounds were found to be shorter in tropical soils [7,22,24,29,30]. This rapid dissipation from soil was attributed to their high volatilization rates that were favoured by more adverse climatic conditions that prevail in the tropics such as high temperatures, intense solar radiation all year round, and higher levels of microbial activity. These findings led to a new interest in these compounds and in 1988, the International Atomic Energy Agency (IAEA) initiated an internationally coordinated research programme involving several tropical countries from South East Asia, South America and Africa, to investigate their persistence and behaviour in tropical soil conditions [30]. It was considered that for similar reasons, even the organophosphates and carbamates would have shorter half-lives in tropical soils in comparison to those reported in temperate soils. Most studies were therefore done on DDT, lindane, endosulfan and some of the less persistent ones such as parathion and carbofuran. The results obtained from these different tropical countries were very comparable (see Table VIIIA). The experimental procedures and methods of analysis used were similar, making it possible to compare data from all the countries involved. Laboratory intercomparison exercises were also done. We present in the following sections the results that we obtained from both field and laboratory investigations on persistence and degradation of DDT, DDE, lindane, parathion, malathion, dimethoate and carbofuran in tropical soils in various regions in Kenya under this

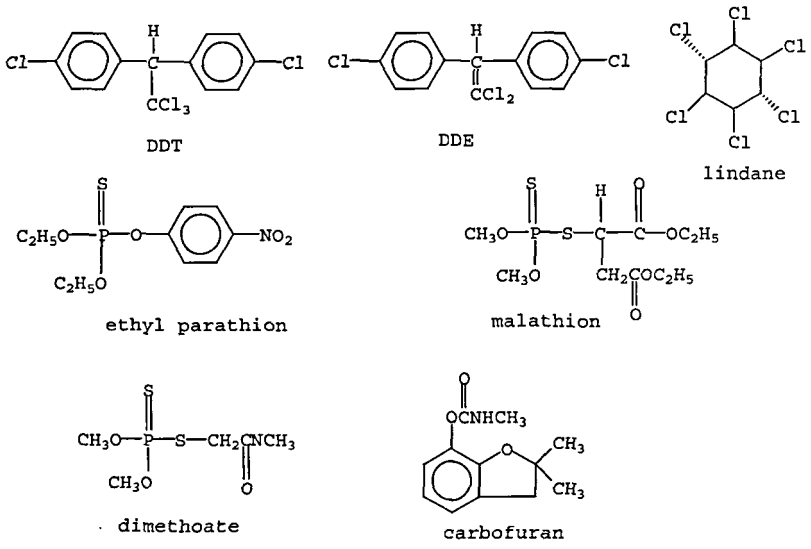

FIGURE 2 The structures of the pesticides studied in our field and laboratory experiments.

IAEA research programme (Fig. 2). The conclusions made from these results are presented and the influence of the major environmental factors and other mechanisms that contribute to the rapid disappearance of pesticides from tropical soils are also discussed.

EXPERIMENTAL PROCEDURE

The field experiments were conducted in four different agricultural regions in Kenya: Nairobi plot, located in Nairobi (altitude: 1660 m), with red silt loam agricultural soil, Kisii Plot (altitude: 1788 m) located in the rich western highlands region of Kenya, Mtwapa plot (altitude: 21 m, sandy soil) located 30 kilometres away from the Indian Ocean coast in Kilifi district, Mombasa plot (sea level, sandy soil) in a coastal area near Diani Beach (50 m away from the sea) along the Indian Ocean coast and Ahero plot (altitude: 850 m), located within a paddy rice scheme with lowland heavy sandy soils in Kano plains, 50 km from Lake Victoria. For each experiment, a suitable plot was chosen in an open field marked for exclusive use of low ^{14}C-radioactivity pesticides. Soil samples were taken from these areas for analysis. The weather data collected during the period of the experiment were obtained from the Meteorological Department, Dagoreti, Nairobi. The soil characteristics and weather data are given in Tables I

TABLE I Summary of the weather data in Nairobi, Mtwapa and Ahero during the DDT, parathion, DDE and carbofuran field studies

Weather element	*Nairobi*	*Ahero*	*Mtwapa*
% relative humidity (range)	45–70	50–75	–
Max air temp °C (range)	20–26	26–33	26–28
Min air temp °C (range)	12–15	20–33	24–26
Wind speed kph (range)	70–185	125–200	–
Sunshine hours	10	10	10
Average rainfall mm/day	3.81	2.93	3.04
Soil temperatures °C (range)	18–23	23–28	27–37

Note: Data obtained from the Meteorological Department, Dagoreti, Nairobi.

TABLE II Summary of the weather data in Kisii and Nairobi during malathion and dimethoate field studies

Weather element	*Kisii (dry season)*	*Kisii (rainy season)*	*Nairobi (dry season)*
% relative humidity (range)	45–75	40–68 (av. 60)	73–90 (av. 85)
Max air temp °C (range)	25–30	22–28 (av. 26)	20–25 (av.22)
Min air temp °C (range)	24–25	< 10	18–22 (av. 20)
Wind speed kph (range)	55–200	50–250 (av.130)	50–100 (av. 72)
Sunshine hours	10	10	10
Average rainfall mm/day	33.3	45.8	5.9
Soil temperatures °C (range)	22–25 (av. 24)	21–25 (av. 24)	20–22 (av. 21)
Evaporation rate mm/day	1–5 (av. 4)	2–6 (av. 5)	2–3 (av. 2)

Note: Data obtained from the Meteorological Department, Dagoreti, Nairobi.

and II and Figs. 3a and 3b in the results section. The experiments were conducted for 292 days (DDT, Mtwapa), 172 days (DDT, Nairobi), 189 days (DDE, Nairobi), 72 days (parathion, Nairobi), 111 days (carbofuran, Ahero), 77 days (malathion, Kisii), 70 days (malathion, Nairobi), 62 days (malathion, Greenhouse) and 29 days (dimethoate, Greenhouse).

Analytical Equipment and Chemicals

Radioactivity was quantified in a Tri-Carb 1000TR liquid scintillation counter and a Canberra Packard 2500 TR. Bound residues in soil were determined by combustion in a Packard 307 Biological and an Ox-600 Harvey Biological Oxidizers. The metabolites recovered from the soil samples were determined in a Hewlett Packard GLC, Model 437 with FID and 335 Automatic Integrator; carrier gas: N_2 at 1.5 ml/min; Column: HP-5 crosslinked with 5% phenylmethyl silicone (25 m × 0.2 mm × 0.5 µl film thickness); Column temperature: 80°C for 1 min, then 20°C/min upto 260°C (hold for 20 min)

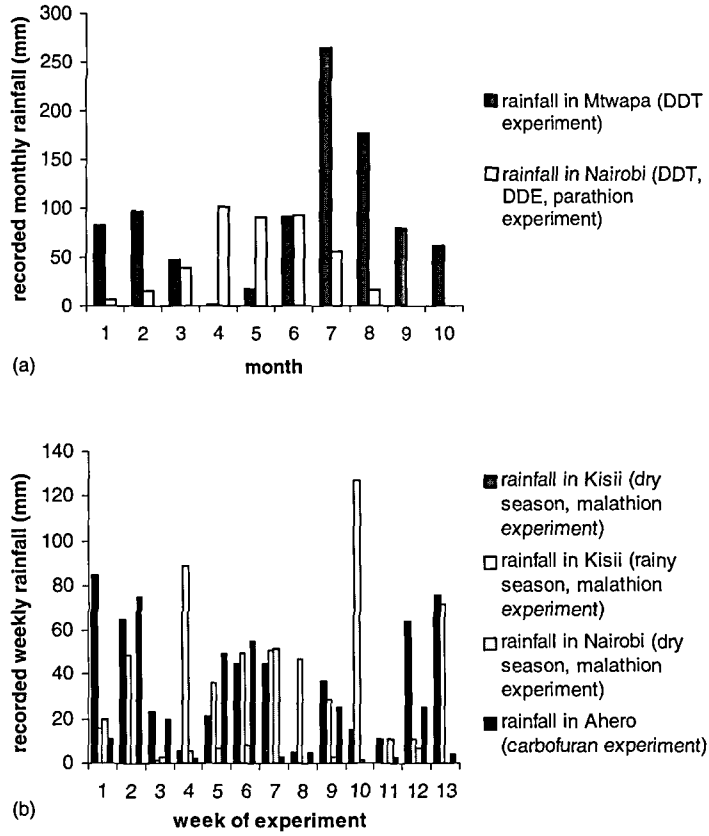

FIGURE 3 (a) Total monthly rainfall in Mtwapa and Nairobi during DDT, DDE and parathion field experiments (data obtained from the Meteorological Department, Dagoreti, Nairobi). (b) Recorded weekly rainfall in Kisii, Nairobi and Ahero during malathion and carbofuran field experiments (data obtained from the Meteorological Department, Dagoreti, Nairobi).

for DDT and DDE. Other GC used for malathion and dimethoate were a Perkin Elmer GC Model 8500 with EC detector; Detector temperature: 350°C, oven temperature 200°C; isothermal conditions for 50 min; carrier gas: white N_2 at 75 ml/min, and a Carlo Erba HRGC1 GC Fracto Vap 4160 with FID detector, respectively. HPLC analysis of carbofuran and its metabolites was done on a Hewlett Packard with ODS column fitted to Berthold Two Channel UV-radiodetector LB510 and automatic fraction collector; solvent: acetonitrile/water (7/3, vol) at 1.2 ml/min. DDT metabolites were confirmed in GC-MS, Hewlett Packard 5985 B Quadrapole, RTE-VI data system; Mass spectral libraries Wiley and NBS; GC column: 15 m DB

1 fused silica capillary column, 0.25 µl film, splitless mode; detector temperature: 300°C; temperature profile: 160°C (2 min hold), ramp to 280°C at 10°C/min; carrier gas: helium (1 ml/min); MS: EI scan 40–500 Da and malathion and dimethoate in a double focused Finnigan MAT 95 Spectrometer GC-MS [15–18]. Metabolites were also analysed by TLC using a Berthold LB 2760 and a LB 2832 Linear Analyzer scanners, respectively. Uniformly all-ring labeled ^{14}C- p,p'-DDT and ^{14}C-p,p'-DDE, ^{14}C-lindane, ^{14}C-parathion (phenyl ring labelled) as well as pure non-labelled metabolite standards were obtained from the NEN Research Products and Aldrich Chemical Company, Inc. USA, ^{14}C-Carbofuran (benzofuranyl-ring labelled) and non-labelled metabolite standards from International Isotopes, Munich, ^{14}C-malathion (methoxy labelled) and ^{14}C-dimethoate (methoxy labelled) and their metabolite standards from Sigma, St Louis, Missouri. A mixture of PPO and dimethyl POPOP in toluene was used as liquid scintillation counting solvent while Hydroluma cocktail was used for aqueous samples.

Application of Pesticides, Sampling and Analysis

The field plots, all measuring approximately 7 × 12 m, were prepared by digging deep and harrowing to remove all weeds and stones. For every plot, fifty hard PVC cylindrical pipes of lengths 15 cm and 10.4 cm diameters (for DDT, DDE, lindane) and lengths 55 cm and 6.6 cm diameters (for parathion, malathion and carbofuran) were cut to size and driven vertically into the prepared soil (1 m apart) in every plot, leaving 2–3 cm protruding above the soil surface to prevent losses due to surface runoff in case the rains fell soon after pesticide application. The lengths of the pipes were chosen so as to ensure that no pesticide residues that leached into the soil were left in the bottom ground during sampling, making it possible to study only losses due to volatilization and chemical degradation [30,31]. It had been established previously that DDT (and its residues such as DDD and DDE) and lindane do not leach beyond 10 cm in the soil whereas organophosphates and carbamates required 55 cm pipes to avoid losses through leaching [30,32]. The use of these standard lengths also made it possible to compare our results with those of other groups from other countries involved in the programme. The plots were then left undisturbed for one week after which a mixture of known amounts of ^{14}C-labelled and non-labelled pesticide dissolved in 10 ml *n*-hexane was added to the soil surface in each cylinder carefully using micropipettes to a concentration of 10 ppm for Nairobi DDT, DDE, parathion experiments, 20 ppm for Ahero carbofuran experiments,

3.77 ppm for Mtwapa DDT experiment, and 15.53 ppm for malathion and dimethoate experiments, respectively. Immediately after application of the pesticide to the soil, the soil surface was covered lightly with a small amount of soil to prevent direct exposure. PVC cylinders of soil samples were then carefully removed in duplicates, periodically, placed in polythene bags and taken for analysis of the residues in the laboratory in the Department of Chemistry, University of Nairobi. Samples of soil from Mombasa, Kisii, Mtwapa and Ahero were transported to Nairobi by bus overnight immediately after removing the pipes containing the soil, carefully packed in polythene bags. The amount of residues in the soil samples were determined by Soxhlet extraction, biological tissue combustion, and by liquid scintillation counting. This was done by Soxhlet extraction of 50 g sub samples of air-dried soil samples (in triplicate) with 200 ml methanol for 4 h. Aliquots of 1 ml (in triplicate) were taken from the extracts for analysis to quantify the amount of radioactivity by liquid scintillation spectrometry. The remaining extracts were reduced to 10 ml and used for TLC, GC and HPLC analysis after clean up as described [15–18,22,27,28,30–34]. The moisture contents of the soil samples were determined by heating 5 g samples in an oven at 105°C overnight and determining the difference in weight. The adsorption/desorption and leaching characteristics of malathion, dimethoate and carbofuran were also studied in the laboratory using known methods [35,36]. The extent of mineralization and degradation of carbofuran by microorganisms in dry and submerged soils in biometer flasks as well as the influence of UV light on volatilization of DDT from soil were also investigated under laboratory conditions [27,30]. Soxhlet extracted soil samples were combusted in the Oxidizers for determination of bound residues [15–18,22,27,28,30–40]. For Greenhouse studies, conditions were controlled to simulate tropical conditions (light illumunation: 5×250 W for 11 h daily, temperature range: 10–26°C, 0% relative humidity).

RESULTS AND DISCUSSION

Tables I–III and Figs. 3a and 3b show the weather data summary for all the locations of the field experiments. The Mombasa weather data are not included because they were similar to those for Mtwapa. Mtwapa and Ahero are lowlands near large water masses often experiencing higher % relative humidities and temperatures than the other locations. Kisii received much more rainfall than all the other sites during these

TABLE III Characteristics of the soil samples taken from the field locations (expressed as %)

Soil sample	*% moisture*	*pH*	*Mn*	*K*	*Na*	*Ca*	*P*	*%C*	*% sand*	*% silt*	*% clay*	*texture*
Kisii	12	4.9	2.0	1.8	1.0	5.5	32.5	1.68	14	20	66	clay
Nairobi	8.4	6.1	14.5	2.2	0.8	6.2	18	1.22	30	28	42	silty clay
Ahero	5.3	7.0	nd	nd	nd	nd	nd	1.08	38	25	37	sandy clay
Mtwapa	0.6	6.5	nd	nd	nd	nd	nd	0.54	90	2	8	sandy
Mombasa	2.8	8.5	nd	nd	nd	nd	nd	0.85	90	2	8	sandy
GSF Sandy	0.7	6.0	nd	nd	nd	nd	nd	0.7	97	3.2	5.1	sandy
Bayreuth	0.7	6.5	0.28	2.7	3.6	45	17.4	0.89	nd	nd	nd	sandy

Note: nd denotes 'not determined'. Nairobi, Ahero and GSF sandy soils were analysed by Bayerische Hauptversuchsantalt für Landwirtschaft der Technische Universität, München, the Mombasa soil by National Agricultural Laboratories (NAL), Kabete, Nairobi; Kisii and Bayreuth soils by the Department of Plant Physiology, Bayreuth Universität, Bayreuth, Germany.

experiments. The windspeeds were high in all locations possibly because of high temperatures. These tropical weather conditions are more adverse compared to those experienced in temperate regions. The soil characteristics given in Table III show differences in soil moisture content, % organic carbon, % sand and % clay which can contribute to differences in degradation and volatilization rates of pesticides in the various soils.

The results obtained from the experiments showed very rapid dissipation from soil for all the pesticides studied. There was significant metabolism and chemical degradation in soil. Some of these results have already been published individually but previously we were not able to integrate all the data to compare and show the magnitude of influence of tropical climatic factors and soil characteristics on rapid disappearance of the pesticides in tropical soil conditions. All the results obtained from both laboratory and field studies during the period between 1990–1998 are compared and discussed under the following sections.

1. Nature and Chemical Composition of Pesticides Studied

The pesticides used in our studies represented organochlorines, organophosphates and carbamate classes of pesticides and therefore had different chemical structures and different physico-chemical properties. The main physico-chemical properties that were likely to influence their behaviour and fate in soil include their water solubility, vapour pressure, log K_{ow}, melting point (mp) and boiling point (bp) which are given in Table IV. Gas exchange across the air–water/soil interphases (i.e. volatilization) is controlled by Henry's Law constant (H_L), which is the ratio of vapour pressure of the pesticide and its water solubility. Vapour pressure and water solubility of pesticides, therefore, directly determine their volatilization

TABLE IV The physico-chemical properties of the pesticides studied

	DDT	*DDE*	*Lindane*	*Parathion*	*Malathion*	*Dimethoate*	*Carbofuran*
MW/g/mol	354.5	318.0	219	291.3	330.4	229.3	221.3
Water solubility mg/L	0.0012	Low	7.0	24	145	25,000	700
Vapour pressure mbar	1.7 $\times 10^{-7}$	–	1.7 $\times 10^{-4}$	7.4 $\times 10^{-4}$	1.6 $\times 10^{-4}$	5.1 $\times 10^{-6}$	2.6 $\times 10^{-5}$
Log $K_{o/w}$	4.98	5.69	5.23	–	2.36	0.78	–
mp °C	108.5	89	112	6.1	2.85	52	147
Bp °C	–	–	–	–	156.5	107	–

Note: Data were obtained from various sources [15–18].

rates from soil. Their rates of volatilization from soil were also influenced by the size of their molecules, molecular shape, their pKa values and polarity though these properties are not included in the table. Lindane has a high concentration of chlorine atoms and its size is relatively smaller compared to the other organochlorines making it much more soluble in water than DDT and DDE (almost 7000 times more soluble). This high water solubility and small size was expected to make it more easily volatilized from soils with high moisture content, despite its lower volatility (high vapour pressure) compared to that of DDT and DDE. However, the solubilities of the organochlorine insectides were lower than those of malathion, parathion, dimethoate and carbofuran. Whereas the vapour pressure would be a major factor controlling volatilization for DDT and DDE, moisture content of soil would be very significant in the volatilization of the more soluble lindane, malathion, dimethoate and carbofuran. In addition to the characteristic groups that are responsible for their insecticidal properties, other various functional groups such as Cl (in DDT, lindane, DDE), –C=O and –COOH (in malathion, dimethoate, carbofuran), –NH (dimethoate, carbofuran), S- (parathion, malathion, dimethoate) and NO_2 (parathion), attached to the aliphatic or aromatic groups were likely to affect their interaction with soil colloids, soil organic carbon and microorganisms which could then influence their adsorption/desorption, volatilization as well as various chemical degradation reactions in soil such as hydrolysis, oxidation/reduction, catalysis, free radical formations and photolysis. The three organophosphorous pesticides and carbofuran studied are known to be easily hydrolysed and more easily biodegradable by microorganisms in soil than DDT, DDE and lindane. For example, the various types of functional groups in malathion, parathion, dimethoate and carbofuran make it possible for them to easily interact with soil matrix and undergo hydrolysis in soil [1,2,39–42].

The structural variability of these organophosphorous compounds is reflected in their wide range of physico-chemical properties and also in the considerable diversity of mechanisms through which they can be attacked by enzymes. The varying physico-chemical properties include different vapour pressures at a given temperature, different water solubilities and their structural chemical properties. They are all relatively more soluble in water and are easily hydrolysed. Carbofuran is comparatively non-persistent in soil and closely related in biological action and resistance development to the organophosphorous pesticides [2,39,40]. It is fairly soluble in water and is also easily hydrolysed. Carbofuran is used in Kenya in the form of 5% (a.i.) Furadan for control of soil dwelling, foliar feeding insects and mites at seed furrow and in rice paddy fields [16]. It is adsorbed and rapidly metabolised in soil giving a large number of metabolites which were identified in our experiments. Lately in Kenya, the commercial market is dominated by the organophosphates and carbamates while most of the organochlorines such as DDT have now been banned [17,41,42].

2. Adsorption/Desorption of Carbofuran, Malathion and Dimethoate in Different Soil Samples from Different Regions in Kenya

In our experiments, we determined the adsorption, desorption and leaching characteristics of carbofuran, malathion and dimethoate because they are known to become strongly adsorbed to the soil matrix. The adsorption and desorption of these pesticides were determined according to the EEC methods [35]. These three pesticides have characteristic functional groups that enhanced their adsorption to the soil matrix. The amino and carbonyl groups in carbofuran and dimethoate can participate in hydrogen bonding with other O- or N-atoms present in soil colloids. Generally, pesticides with functional groups such as NHCOR and NHR in their molecular structure tend to show higher adsorption to soil [43–45]. The amino groups in parathion, carbofuran and dimethoate could also adsorb to soil colloids as cations, after getting protonated depending on soil pH and their individual pKa values. The presence of a large moiety such as the benzene ring, with mobile π electrons, in carbofuran molecule influences its polarization and therefore would increase the strength of the adsorption bonds [45–55].

Pesticide adsorption in soil follows Freundlich Adsorption equation $x/m = KC^{1/n}$, where C = pesticide concentration in solution at equilibrium, K = Freundlich Adsorption constant and x/m = ratio of pesticide to

TABLE V Freundlich Adsorption constants obtained from adsorption tests for various soil samples

Soil samples source	*Carbofuran*		*Malathion*		*Dimethoate*	
	K_f	*1/n*	K_f	*1/n*	K_f	*1/n*
Ahero	1.7	1.0				
Nairobi	1.5	1.0				
Kisii			1.7	0.70	1.7	0.77
Bayreuth			1.8	0.81	1.1	0.89
			K_f (des)	1/*n* (des)	K_f (des)	1/n (des)
Kisii			1.9	0.64	1.9	1.21
Bayreuth			1.7	0.72	2.6	1.04

Note: The determination was performed according to the EEC method (EEC Directive 79/831, Annex 5, 1988), at 0.05, 0.1, 0.2, 0.5, 1, and 5 ppm concentrations, respectively, of mixtures of ^{14}C-labelled pesticides and normal standard pesticides; des = desorption.

adsorbent (soil) mass. This equation was used in the form $x/m = \log K + 1/n \log C$ to calculate the Freundlich adsorption/desorption constants, K and $1/n$ as intercept and gradient, respectively, of the curve x/m versus log C (see Table V). From our results, we obtained different values of K and $1/n$ for various pesticides in soil samples taken from the different locations where the field experiments were performed (see Table V). All the adsorption data fitted well into the Freundlich adsorption isotherm equation. The difference in adsorption behaviour of carbofuran, malathion and dimethoate in different soils could be explained as adsorption was found to be higher in soil samples containing more organic carbon content (i.e. Kisii, Nairobi, Ahero) than in sandy soils such as those from Mtwapa and Bayreuth. However, dimethoate showed an exception in this behaviour as it was slightly more adsorbed to Bayreuth soil than to Kisii soil sample. Its adsorption was mainly affected by the clay minerals unlike those of carbofuran and malathion that were more influenced by soil organic matter. Carbofuran adsorbed strongly to both Nairobi and Ahero soil samples showing negligible difference in its adsorption in the two soil samples. The soil characteristics of the two soil samples were fairly similar although the red Chiromo soil had silty clay texture while the dark Ahero soil had a sandy clay texture. The adsorption of malathion was higher in Kisii soil than in the Bayreuth sandy soil. This was expected due to high organic matter content in the Kisii soil sample and indicates that its adsorption was mainly effected through the organic matter functional groups.

Adsorption and desorption characteristics of a pesticide are considered as some of the major processes affecting its interactions with the solid phase in the soil environment and therefore affect its degradation and persistence in

soil. The main constituents of the solid phase of soil include clay minerals, organic matter and the oxides and hydroxides of Aluminium and Silicon. This solid phase usually makes up to 50% of the total soil volume, the other half being filled by soil solution and air. But the major components of soil which are of significance to adsorption are its clay and organic matter [23,47–53,54]. The soil crystal consists of superimposed unit layers of cations with hydroxyl and oxygen surfaces adjacent to each other, leaving a cylindrical hole through which smaller molecules such as water, pesticides and other compounds can pass through. The size of the holes and the presence of the hydroxyl and oxygen groups are important in pesticide adsorption since small pesticide molecules can pass through them, consequently resulting in chemical interactions between pesticide molecules and soil. Water molecules can also enter into the spaces and increase the overall size of the mineral. Some of the amorphous components of clay such as allophane may have large surface areas and be positively charged because of their ability to become heavily hydrated [23].

Colloidal oxides and hydroxides of Al, Si, and Fe also occur as separate phases in soil or as coatings on layer silicates [23]. Soils containing high amounts of oxides and hydroxides may show stronger adsorption to pesticides than normal mineral and organic soils [17]. The types of soil clays and their characteristics are given in Table VI. Soil organic matter also plays an important role in pesticide adsorption as was found in our experiments. It is composed mostly of humic acids (HA), fulvic acids (FA) and humin, predominantly aromatic hydrophilic-polyelectrophilic compounds with different molecular weights and different solubilities in acid base media [23,55]. The functional groups of HA and FA include oxygen containing groups e.g. carboxyls, hydroxyls and carbonyls. Humic substances have higher cation exchange capacity than clays and are rich in free radicals such as H^+ and NO_2^+ which influence chemical reactions of pesticides in soil [52]. Soils also contain non-humic substances which

TABLE VI Different types of soil components and their properties

Soil component	*Cation exchange capacity* (meq/100 g)	*Surface area* (m^2/g)
Kaolinite	3–15	7–30
Montmorillonite	80–150	600–800
Vermiculite	100–150	600–800
Oxides and hydroxides	2–6	100–800
Humic substances	200–400	500–800

Note: Data were obtained from [25].

have definite chemical characteristics such as carbohydrates, proteins, amino acids, fats, waxes and low molecular weight organic acids which are easily attacked by microorganisms [23,56–58]. Carbohydrates constitute 5–20% of all soil organic matter and influences retention of pesticides in soil as the microorganisms prefer to use them as source of energy instead of pesticides. Organic nitrogen makes up 20–50% of total nitrogen bound to surface soils, existing in the form of amino acids and sugars in soil colloids [58–60].

Despite the complexity of soil organic matter composition, it has been observed that only up to an organic matter content of 6%, are both the mineral and organic surfaces together involved in adsorption. At higher organic matter contents, the adsorption will occur mostly on the organic surfaces. This is very significant in rich forest soils but is not the case in most agricultural fields. As shown in Table III, the agricultural soil samples from Kenya had between 0.54% (in Mtwapa)–1.68% organic carbon (in Kisii). This was not so different from the soil sample obtained from Bayreuth (Germany) and from GSF (standard sandy soil) which contained 0.885% and 0.7% organic carbon, respectively. The adsorption of pesticides in all these soils would therefore involve both clay and organic matter components. It is also significant to note that all the soil samples from the three regions in Kenya and from Bayreuth had close pH values ranging between 6.0 and 7.0, except the Kisii soil, which also had the highest organic carbon content of 1.68% and was slightly acidic with a pH value of 4.9. This could indicate higher fulvic acid content in Kisii soil compared to other soils. The differences in soil characteristics corresponded to differences in the adsorption of pesticides as shown by the Freundlich adsorption isotherm constants in Table V. The K_f and $1/n$ values depend on the type of soil and its temperature. Decreased temperature reportedly leads to decreased adsorption, as physical adsorption is a characteristic exothermic process, corresponding to weakening of attractive forces between pesticide molecules as solutes and soil surface and to increase with increasing water solubility of the pesticide [61,62]. Similarly high temperatures are known to increase the vapour pressures of pesticides which in turn favour their desorption. Elevation of temperature also causes loss of water from preferential adsorption sites in soil matrix making these sites available to the pesticide while in absence of available active sites, the pesticide molecules are lost to the atmosphere through volatilization. Adsorption of organophosphorous and carbamate insecticides in different soils have shown a linear correlation in log K_f with log(organic matter content), with the cation exchange capacity of

the soil as well as with the log K_{ow} of the pesticide [62]. Adsorption is also influenced by the parachor, which is a measure of molar volume of a molecule and which is an additive function of pesticide molecular size as shown by Hance *et al.* for aromatic herbicides in soils, where log K = 0.0067 $(P-45N)-065$. In this equation, K = Freundlich constant, P = parachor, N = number of proton- or electron-donating sites on the pesticide molecule which can participate in H-bonding [63].

Mechanisms used to explain pesticide adsorption, their interactions in soil and subsequent loss by volatilization include weak van der Waals forces of attraction resulting from short range dipole–dipole interactions of several kinds, mainly in non-ionic, non-polar pesticides or portions of pesticide molecules, hydrogen bonding: a special dipole–dipole interaction in which the H-atom serves as a bridge between two electronegative atoms, one being held by covalent bond and the other by electrostatic forces, charge transfer mechanisms which involve formation of charge transfer complexes where electrostatic attraction occurs when electrons are transferred from one electron rich donor to an electron deficient acceptor within a short distance of separation, and ion-exchange (e.g. pesticide interactions with the –COOH, –OH groups of the organic matter) and coordination bonding, where pesticide molecules cluster around metal ions as ligands. The last three types of interactions were not expected to influence adsorption of the six pesticides that were studied in our experiments [44,63,64]. DDT and other organochlorines, are for example, more loosely held by soil colloids by weak van der Waals forces and are more easily lost through volatilization compared to the organophosphates and carbamates, where non-polar pesticide molecules adsorb to hydrophobic regions of the soil constituents. Parathion also adsorbs to soil organic matter and humic substances in aqueous systems through this mechanism although its adsorption occurs through both H-bonding and van der Waals forces, the latter being dominant when the soil organic matter content is greater than 2% [56,58, 61–63,65].

Lipids present in organic matter are considered to be the primary sites for non-ionic pesticides in soils and aqueous systems, and the adsorption of pesticides by soil is considered primarily as a matter of partition between organic matter and water. The van der Waals forces explain the relative independence of pesticide adsorption from moisture content in soils with more than 6% organic matter as the existing van der Waals forces become strong enough to prevent desorption by water. Low dissipation rates for DDT in rich agricultural soils in temperate regions due to binding to organic carbon, preventing loss through volatilization and

leaching have been reported [12,20]. This type of adsorption is independent of small changes in pH. Carbofuran and the three organophosphates studied, with C=O, P=O, P=S groups bond to soil by H-bonding between unionized functional groups of the pesticide molecule and functional groups of soil organic matter, such as –SH, –O at pH values below their pKa [23,57]. Therefore, the adsorption of organophhosphorous pesticides to soil is related to both organic matter and clay contents of soils, and occurs through both H-bonding and van der Waals mechanisms. Soil moisture however, affects adsorption of organochlorine, organophosphorous and carbamate insecticides similarly where the hydration status of clay minerals affects the adsorption capacity of these pesticides, decreasing with soil moisture content. For example, in partially hydrated systems where parathion molecules are unable to replace the strongly adsorbed water molecules and parathion adsorption only occurs in water free surfaces [57]. This would tend to increase the rate of loss of parathion from such wet soils.

Our adsorption and desorption results were also supported by those obtained from leaching experiments in which carbofuran was found to leach extensively in sandy GSF (German) standard soil but less in Ahero soil which contained more organic matter (see Tables VIIA and B). A similar trend was seen in the mobility of malathion in soil samples from Mtwapa, Nairobi and Kisii. While the leaching pattern of malathion was closely similar in soil samples from Nairobi and Kisii, it was found to leach more in the sandy soil sample from Mtwapa. Carbofuran which is more water soluble than malathion showed higher mobility in Nairobi soil sample as was expected. There were losses from the soil columns through volatilization during mobility experiments in the laboratory especially in

TABLE VIIA Mobility of malathion in Kisii, Nairobi, and Mtwapa soils (expressed as % total recovered residues in various sections of the column after 48 h)

Column section	*Kisii (malathion)*	*Nairobi (malathion)*	*Mtwapa (malathion)*
0–7 cm	62	40.7	46
7–14 cm	4.7	36	3.2
14–21 cm	4.8	2.4	2.5
21–28 cm	3.9	2.5	3.0
28–35 cm	2.9	2.5	2.3
35–42 cm	2.0	2.2	3.1
Leachate	9.1	2.2	37.8

Note: Leaching experiments were performed using glass columns (2.7 cm diameter, 42 cm long) with a low pressure pump; flow rate 7.3 ml/h for 48 h; 15.53 ppm of mixture of ^{14}C-labelled pesticide and normal standard pesticide and 300 g sieved soil (2 mm mesh) [17].

TABLE VIIB Mobility of carbofuran in Ahero, Nairobi and GSF soil (expressed as % total recovered residues in various sections of the column after 48 h)

Column section	*Ahero (carbofuran)*	*Nairobi (carbofuran)*	*GSF (carbofuran)*
0–5 cm	3.95	5.6	0.52
5–10 cm	2.78	10.5	0.34
10–15 cm	6.01	10.5	0.38
15–20 cm	12.51	12.2	0.65
20–25 cm	15.83	13.3	2.24
25–27 cm	19.54	4.38	4.02
Leachate	33	29	60

Note: Laeching experiments were performed using glass columns (4.6 cm diameter, 27 cm long) with a low pressure pump; flowrate 7 ml/h for 48 h, 9.20 ppm of mixture of ^{14}C-labelled pesticide and normal pesticide standard and 550 g sieved soil (2 mm mesh) [16].

sandy soil where the adsorption of the pesticide was low. From field experiments in submerged soils at Ahero Rice Irrigation Scheme it was found that most of the carbofuran residues remained on the soil surface due to its high solubility in water during the 111 days of dissipation study. This indicated the possibility of carbofuran contamination especially in the nearby river that received water from the irrigation canals flowing through the farm. However, in the same field location, under dry soil conditions, carbofuran was found to leach quite extensively.

Helling *et al.* has conveniently ranked different pesticides according to their relative ease of mobility in soil [65]. In their ranking, class I (immobile) pesticides include lindane, parathion, dieldrin, DDT and aldrin and class V (very mobile) pesticides include herbicides such as dicamba and dalapon. Others fall in between, i.e. class II such as propanil, diazinon, azinphos methyl < class III such as 2,4,5-T, atrazine, arachlor < class IV such as picloram and 2,4-D. With a few exceptions, the ranking is similar to the increasing order of mobility: organochlorines (least mobile) < organophosphorous and carbamate pesticides < herbicides such as phenyl ureas with characteristic functional group Ph-NO_2 and s-triazines (with functional group Ph-NH_2, being most mobile). In our experiments, we observed that the mobility of the pesticides was greatly dependent upon the soil characteristics although malathion and carbofuran showed different mobilities in the same soil.

3. Diffusion of Pesticides in Soil

All the pesticides that we studied had very high vapour pressures and were expected to diffuse easily in the soil matrix. Moisture content can increase

diffusion considerably as has been shown previously in lindane where no diffusion occurred in dry silt loam soils but occured very rapidly with increasing water content reaching a maximum at 4% soil water content [66]. Soil temperature affects the diffusion coefficient and the vapour density of pesticides in soil, and an overall increase in temperature results in an increase in diffusion [67–70]. In our experiments, the soil temperatures were very high (i.e. range: 23–28°C in Nairobi soil, and 27–37°C in Mtwapa soil) and were expected to influence the diffusion of these pesticides in soil. Decrease in diffusion coefficient has been shown for atrazine, propazine and simazine when the temperature decreases from 25° to 5°C. Increase in bulk density results in decrease in diffusion coefficient as compaction reduces the porosity of the soil matrix thus reducing vapour phase movement [71]. Thick soils with little organic matter and high clay content such as that in Ahero were expected to allow less diffusion compared to Kisii and Nairobi soils.

Leaching in soil is dependent on the direction and rate of water flow and on adsorption characteristics of the pesticide in soil [72]. Heavy rainfall as experienced in Kisii would have resulted in losses by leaching but PVC lengths were made to presumably contain all the leached residues. In flooded soils at Ahero, leaching was expected during the experiment as was shown by high concentrations of carbofuran recovered from the leachate in the laboratory leaching experiments. However, this was not the case from the experiments although laboratory experiments were conducted with short glass pipes (27 cm). Consequently, external factors such as variation in field characteristics, such as air flow rate, amount of soil moisture, surface evaporation also affect leaching and distribution of pesticides in water as carrier. An inverse relationship between adsorption and movement of pesticides by water through soil has been reported [70]. Apart from diffusion, leaching and surface evaporation, moving soil particles act as carriers of pesticides both in the soil environment and in the atmosphere [23,62,66,73]. Wind can move soil particles to great distances carrying adsorbed pesticides over long distances some of which can be recovered from rainwater associated with dust. The amount of pesticide moved by erosion due to runoff and wind therefore depends on the amount of pesticide adsorbed by the transporting medium. However, in our experiments these direct physical transport mechanisms were expected to be negligible allowing for evaluation of losses through diffusion and eventual volatilization. However, the winds were strong, as shown by the high recorded speeds, and the surface evaporation was high and were therefore expected to influence dissipation from soil in our field experiments.

4. Volatilization of Pesticides from Soil in Various Regions of Kenya

In our field experiments we obtained half-lives of dissipation for DDT, DDE, lindane, parathion, malathion, dimethoate and carbofuran pesticides from soil under field conditions. These are summarized in Table VIIIA. These half-lives of dissipation ($t_{1/2}$) were calculated from the equation $t_{1/2} = 0.693/k$, where k is the gradient of the ln [% total recovered residues (extractable + bound)] after time t, versus time t (days), based on first order reaction kinetics. The losses through volatilization were very high for all pesticides under our field conditions. The half-lives of dissipation obtained for DDT and DDE were comparable to those reported from other tropical countries where similar procedures and methods were used. However, these half-lives are much lower compared to those reported from temperate studies. Data reported from temperate soils gave half-lives of 2.8 years in UK and USA and 11.7 years and 35 years in Canadian field and forest rich soils, respectively, for DDT [10,74]. Other researchers in Nigeria and Taiwan also reported very low half-lives of disappearance of DDT in tropical soils. Perfect (1980) reported that only 2% of total soil applied DDT was left in the soil after 4 years in field studies in Nigeria, while Talekar *et al.* (1977) reported a 20% decline in DDT residue concentration levels six weeks after the pesticide was incorporated into the soil in studies done in Taiwan soils [7,29]. The half-lives of dissipation obtained from our field data for parathion ($t_{1/2} = 48$ days) and carbofuran ($t_{1/2} = 66$ days in submerged soil, $t_{1/2} = 96.3$ days in non-submerged soil and $t_{1/2} = 115.5$ days for technical Furadan in non-submerged soil) were also lower than the highest values reported in temperate soils, although falling within the ranges (see Table VIIIB). This supports the fact that the adsorption of these two pesticides was influenced by both soil organic matter and clay contents.

In our studies we found that soil moisture content played a very significant role in the volatilization process. While the adsorption behaviour was mainly dependent on the type of pesticide and soil organic matter content, volatilization was found to be more dependent on pesticide solubility, volatility (as shown by vapour pressure) and soil moisture content. DDT volatilized more rapidly from Nairobi soil than in Mtwapa soil which is sandy despite high temperatures often experienced at the coast. This can be explained by the higher organic matter content and high moisture content in Nairobi soil. This soil retained high moisture for a long time which contributed to losses through surface evaporation and volatilization. The higher moisture content in Mombasa soil also resulted in higher losses of DDT by

volatilization than in Mtwapa soil even though the soil characteristics and weather data were similar for the two locations. The Mombasa plot was located 50 m from the sea shore and was able to maintain higher average moisture content of 2.9% throughout the experimental period compared to that of 0.6% for Mtwapa soil whose plot was located 30 km from the sea shore. The wind breeze from the sea could also contribute to rapid loss by increasing the rate of evaporation from the surface.

Parathion and malathion were found to dissipate faster than DDT in Nairobi soil as expected, while lindane appeared to be very volatile in both Nairobi and Mombasa soils, giving short half lives of dissipation of 8 and 5 days, respectively, in the two soils under field conditions. Lindane, like other organochlorine insecticides, is held to soil colloids by weak van der Waals forces. However due to its small size, high water solubility, which is comparable to those of the organophosphate pesticides, and high vapour pressures, it was lost more easily from the soil through volatilization than the other organochlorine insectides. A striking result was shown by malathion dissipation in Nairobi and Kisii soils, respectively. In Nairobi soil, malathion half-life of dissipation was quite high at a value of 770 days. This study was done during the dry season and the amount of rainfall received was very little and therefore the soil moisture content was also lower than that in Kisii soil. However results from Kisii soil gave a half-life of 36.7 days only, in the field study conducted during the rainy season. This difference in malathion dissipation rates in the two locations can be explained by the higher organic carbon, higher moisture content and therefore higher rate of evaporation in the Kisii field soil. During the dry season, the rate of loss through volatilization was slightly lower, giving a half-life of 48 days in Kisii soil.

During our experiments, the winds were relatively strong ranging between 10.8–18.0 kph. Although these wind speeds were found to be unusually high, it was suggested that high temperatures increase the kinetic energies of air and in absence of barriers, the winds could be very strong in tropical regions. This was one of the factors that contributed to rapid losses through volatilization. For example, a considerable increase in volatilization has been reported for dieldrin by increasing airflow rate (at 100% relative humidity) over wet soil (10% soil moisture) [72]. Sometimes the degradation products are more volatile than the parent pesticide and this can affect the overall dissipation rate. Methods of application of the pesticides which involved surface application could also influence volatilization rates at initial stages of the experiments [73,75]. Due to the importance of soil moisture content in dissipation of

TABLE VIIIA Half-lives of dissipation (in days) of various pesticides from tropical soils in Kenya (based on % recovered ^{14}C-residues with time)

Location	*DDT*	*DDE*	*Lindane*	*Malathion*	*Parathion*	*Dimethoate*	*Carbofuran*
Nairobi	64–110	145	8	770	48	–	–
Mtwapa	346.5	–	–	–	–	–	–
Mombasa	88	–	5	–	–	–	–
Kisii	–	–	–	36.7–41	–	77	–
Ahero	–	–	–	–	–	–	66–115.5
Tanzania[a]	174–335	233	–	–	–	–	–
Nigeria[b]	490	–	–	–	–	–	–
Pakistan[c]	133	171	–	–	–	–	–
India[d]	103	–	30–45	–	–	–	–
Taiwan[e]	42 (20%)	–	–	–	–	–	–
Hawaii[f]	265	–	–	–	–	–	–
Brazil[g]	114	152	–	–	–	–	–
Philippines[h]	151	210	–	–	–	–	–
Greenhouse[i]	–	–	–	17	–	72	–

Note: [a]*J. Env. Sci. Health* (1994), **B2**(1), 65–72; [b]Second IAEA RCM on Radiotracer studies of the behaviour of DDT in tropical environments, Nov 8–11, 1991, Jakarta, Indonesia; [c]*J. Env. Sci. Health* (1994), **B29**(1), 1–17, 177–185; [d]*J. Env. Sci. Health* (1994), **B29**(1), 73–87; [e]Takelar *et al.* [29]; [f]*J. Env. Sci. Health* (1994), **B29**(1), 103–121; [g]*J. Env. Sci. Health* (1994), **B29**(1), 121–123; [h]*J. Env. Sci. Health* (1994), **B29**(1), 21–37; [i]Getenga, PhD thesis [17].

TABLE VIIIB Reported half-lives of dissipation of some common pesticides in temperate soils

Pesticide	*Half-lives*
DDT	2.8 years (range 2–16 depending on location)
Heptachlor	0.8 years
Lindane	1.2 years
Aldrin	0.3 years
Dieldrin	2.5 years
Parathion	5–24 weeks
Chlorvenvinphos	12 weeks
Carbophenthion	24 weeks
Carbofuran	18–378 days

Note: Data from [19].

pesticides we determined the moisture contents of samples of soil from the field experimental plots and those samples used for the determination of adsorption and leaching characteristics. Average values are given in the Table III. The soil temperatures recorded during the field experiments are also given in Tables I–II.

It has been established that volatilization is the major factor responsible for rapid disappearance of pesticides from tropical soils and that the rates of volatilization from soil are closely related to their vapour pressures,

their rates of diffusion to the evaporating, soil characteristics and climatic conditions [70,79]. In previous studies it was found that volatilization is slow in sandy, organic deficient soils but becomes greater in wet and hot soils showing that water solubility, moisture content and soil temperature play important roles in the volatilization process [10,13,46,73,77]. This was confirmed for the organochlorines in our field experiments. In addition, assuming minimal downward mobility (e.g. less frequent rainfall), we would expect the more soluble pesticides to volatilize rapidly from moist soils due to rapid evaporation of water. Greater losses through volatilization occur in low organic carbon soils which adsorb pesticides less strongly [67]. However clay soils play a role in adsorption of organic pesticides (all generally weakly polar in nature) when sufficient water is present to cover the mineral surface. Within a moisture range of 1/3 bar suction to approximately monolayer, volatilization is independent of soil water content [72,77]. From our experiments, clay content seemed to influence stronger adsorption of carbofuran and the three organophosphates resulting in half-lives of dissipation which are comparable to those reported in temperate soils (see Table VIIIB).

5. Formation of Bound Residues in Soil under Field Conditions in Kenya

We were able to determine the amounts of residues left in soil after Soxhlet extraction with hot methanol by converting all the bound residues to $^{14}CO_2$ in the oxidizer which was then quantified by liquid scintillation counting (LSC) and expressed as mass equivalents and as percent of total recovered residues. The amount of residues which could not be extracted by Soxhlet was taken as bound residues since due to their strong adsorption to the soil matrix they could not be removed by the solvent [15–18,32,34,76,78,79]. Bound residues of DDT in Nairobi soil increased from 1.3%, 24 h after application, to a plateau level of 5.9% after 64 days. The level then fell to 2.1% after 112 days. The decline in bound residues after 64 days corresponded to the onset of heavy rainfall. Similarly the bound residues of DDT in Mtwapa increased from 2% after 48 h to 5.8% after 168 days, falling to a constant value of 3.5% after 245 days. The formation of bound residues in Mombasa soil was comparatively very low, increasing slightly from 0.16% after 48 days to 0.51% after 81 days, falling again to a low value of 0.21% after 122 days. The constantly high soil moisture content and rapid dissipation of pesticide residues did not support formation of bound residues in this low organic matter Mombasa soil. DDE bound residues in Nairobi soil

increased from 10.4%, 6 h after pesticide application, to 25.4% after 14 days. The level then declined to 13.2% after 70 days, again seemingly corresponding to rainfall pattern. This contributed to high persistence of DDE in soil, compared to DDT.

Parathion bound residue levels increased from 2.4%, 6 h after application, to 24.9% after 56 days. The level then declined to 19.6% after 72 days. During the parathion experiment, however, there was little rainfall. Carbofuran, on the other hand, remained in high concentrations in the form of bound residues, increasing from 10.4% after 24 h to 46.25% after 40 days in non-flooded soil. The level then declined to a constant value of 17.8% after 111 days. The levels of carbofuran bound residues in flooded soil were also high, increasing from 9% after 24 h of application to 40.9% after 40 days, then declined to a constant value of 12.8% after 111 days. Malathion bound residues increased from 2.2% after 48 h to 5.49% 70 days after application in the Nairobi soil. During this period there was little rainfall. In Kisii soil, bound residue formation increased rapidly to 10.8%, two days after application, falling to 3.46%, 77 days later. There was a lot of rainfall during this period. However, it is significant to note that the data for bound residues in our experiments were only important in evaluation of the total residues remaining in soil after losses by volatilization, but not adequate to give any indication of the ultimate fate of bound residues in soil with time extending beyond the experimental periods. This would require monitoring for long periods of time. However, our data showed the expected initial trend for formation of bound residues of DDT, DDE, lindane, carbofuran, malathion and parathion in soil, where DDT and lindane showed less rapid formation of bound residues compared to malathion, dimethoate and carbofuran. DDE behaviour was different from that of other organochlorines showing very rapid formation of bound residues, 10.4% after 24 h and 25.7% after 28 days. This could be due to the presence of a double bond in its molecular structure which may have increased its interaction with soil colloids.

Typical values of bound residues that have been reported in earlier studies range between 20 and 70% of total residues present in soil and consists of the parent chemical and its degradation products [77]. This shows that a significant portion of pesticide applied to the soil remains as persistent residues bound to soil colloids. However, it has now been shown that these bound residues are also bioavailable to organisms and their concentrations in soil decline due to microbial activity as they are taken up by soil microorganisms, plants and soil animals. Some of the bound residues are therefore classified as biounavailable and include

those not taken up by plants, soil animals and microorganisms [70,78,79]. Bound residue formation is therefore important and should be understood in order to do a complete evaluation of the fate of pesticides in soil because it influences pesticide persistence in soil. As time progresses, the bound residues show more resistance to degradation and little bioavailability because of slow incorporation of residues into humic fraction of the soil and/or migration of residues to less accessible binding sites [23,80]. Two main mechanisms involved in bound residue formation have been postulated. These include surface adsorption to soil and covalent bond formation within the soil matrix. The covalent bond formation process is predominant in the binding of degradation products [75,77,81]. Organic matter is largely responsible in the initial binding process but clays which bind some pesticides more firmly than organic matter may also be involved later. As discussed earlier, clay and organic matter (i.e. soil colloids) in particular have very large surface areas and provide millions of square meters of active site surface which can bind pesticide molecules. As time progresses, the bound residues show more resistance to degradation and little evidence of biological activity [78]. This may be due to the slow chemical incorporation of residues into the humic fraction of the soil and/or the result of migration of residues to less accessible binding sites which requires an energy barrier to be overcome [23,80].

From studies done in soils in the temperate regions, different classes of pesticides show different extents of build up in amounts of bound residues. Organochlorines were found to form between 7 and 25% plateau maximum of applied pesticide as bound residues, organophosphates (18–80%), carbamates (32–70%), fungicides such as chlorophenols (45–90%) and herbicides such as ureas (34–90%) [23]. In all our experiments, the formation of bound residues followed a similar pattern of behaviour, showing a gradual build up to peak level and a slow decline with time. This decline seemed to correspond to onset of rainfall which could have accelerated the loosening up of soil matrix and increase in chemical and biological degradation mechanisms. The results of bound residues obtained for all the pesticides under field conditions are summarized in Table IX.

6. Chemical Degradation and Microbial Metabolism of the Pesticides in Tropical Soils

The degradation metabolites of the pesticides recovered from our soil samples are summarized in the following Tables XA, B and C.

TABLE IX The formation of bound residues of various pesticides in different tropical soils

Applied Pesticide	*Bound Residues (%)*
DDT (Nairobi)	1.3 (after 24 h)–5.9 (after 64 days)
DDT (Mtwapa)	2.0 (after 48 h)–5.8 (after 168 days)
DDT (Mombasa)	0.16 (after 48 h)–0.51 (after 81 days)
DDE (Nairobi)	10.4 (after 24 h)–25.7 (after 28 days)
Lindane (Nairobi)	0.3 (after 24 h)–5.7 (after 40 days)
Lindane (Mombasa)	0.19 (after 48 h)–6.0 (after 29 days)
Parathion (Nairobi)	2.4 (after 24 h)–24.9 (after 56 days)
Malathion (Nairobi dry season)	2.2 (after 24 h)–5.49 (after 70 days)
Malathion (Kisii rainy season)	10.8 (after 48 h)–11.4 (after 7 days)
Malathion (Kisii dry season)	2.94 (after 48 h)–8.04 (after 21 days)
Malathion (Green house/Bayreuth)	4.8 (after 1 h)–42 (after 8 days)
Dimethoate (Green house/Bayreuth)	28.5 (after 1 h)–41.3 (after 29 days)
Carbofuran (Ahero, flooded soil)	9.0 (after 48 h)–40.9 (after 40 days)
Carbofuran (Ahero, non-flooded soil)	10.4 (after 48 h)–52.7 (after 18 days)
Furadan (Ahero, non-flooded soil)	9.6 (after 48 h)–48.1 (after 25 days)

Note: The % bound residues were obtained by expressing the amounts of residues determined by combustion of samples of extracted soils, as % of total (extractable + bound) recovered residues. The greenhouse conditions were controlled to simulate tropical conditions (light illumination: 5 x 250 W for 11 h daily, temperature range: 10–26°C, 70% relative humidity). Furadan (5% a.i.) was obtained from Rhone Poulenc, Nairobi.

Most chemical degradation reactions of pesticides in soil are mediated through water which acts as a reactant or provides a reaction medium [21,82]. Some of the chemical reactions involved in pesticide degradation in soil include hydrolysis, oxidation/reduction, isomerization and nucleophilic substitution reactions with reactive groups of soil organic matter, and free radical mechanisms [23,51,83]. Some of these reactions are catalysed by clay surfaces, metal oxides and metal ions in soil. The degradation of organophosphorous pesticides such as parathion, malathion and dimethoate proceeds by hydrolysis of the P–*X*A bond, where $X = O$ or S atom and A is the electron attracting moiety of the pesticide molecule. This hydrolysis increases with increasing temperature, soil moisture and low pH conditions. The influence of pH on hydrolysis has been shown at pH range 2–9 in parathion and malathion [81]. Ca-kaolinite clay surfaces exert strong catalytic effects on parathion hydrolysis which is highly moisture dependent as water molecules associated with exchangeable cations participate in the hydrolysis [84]. In the first stage of the reaction, parathion molecules specifically adsorb at saturating cations and are quickly hydrolysed through contact with dissociated hydration water molecules, but slower in second stage where hydrolysis of already bound molecules occurs in the active sites in the soil matrix [69]. The hydrolysis products of parathion, malathion and dimethoate were identified in our soil samples as shown Tables XA, B

TABLE XA Pesticide metabolites identified in soil samples from field and laboratory experiments

Field location and pesticide studied	*Metabolites identified*
Nairobi (DDT)	DDT, DDE, DDD
Nairobi (DDE)	DDE only
Mtwapa (DDT)	DDT, DDE
Nairobi (parathion)	parathion, paraoxon, *p*-nitrophenol, *p*-aminophenol
Nairobi (malathion)	malathion, malaoxon, malathion monocarboxylic acids, isomalathion
Kisii (malathion)	malathion, malaoxon, malathion moncarboxylic acid, isomalathion
Bayreuth/greenhouse (dimethoate)	dimethoate, dimethoxon, methoxy dimethoate, O,O-dimethyl phosphorodithioate
Ahero (carbofuran)	carbofuran, 3-hydroxycarbofuran, 3-ketocarbofuran, 3-hydroxy-7-carbofuran phenol, 3-keto-7-carbofuran phenol
Nairobi (carbofuran)	carbofuran, 3-hydroxycarbofuran, 3-ketocarbofuran, 3-hydroxy-7-carbofuran phenol, 3-keto-7-carbofuran phenol
GSF (carbofuran)	carbofuran, 3-hydroxycarbofuran, 3-ketocarbofuran, 3-hydroxy-7-carbofuran phenol, 3-keto-7-carbofuran phenol

Note: Carbofuran was quantified and identified by HPLC using authentic standards. All the others were identified by GC and DDT (Mtwapa soil) as well as both malathion and dimethoate (Kisii and Nairobi soils) were in addition confirmed by GC-MS.

TABLE XB The metabolites (as % of all metabolites identified) obtained from soil extracts during parathion field studies

Time after soil treatment	*Ethyl parathion*	*Paraoxon*	*p-Nitrophenol*	*p-Aminophenol*
12 h	100	nd	nd	nd
7 days	83.2	11.6	3.6	1.6
14 days	83.5	16.4	nd	nd
21 days	66.3	23.9	6.7	3.0

Note: nd = not detected, analysis by LSC and GC. Identification with authentic standards.

TABLE XC The total metabolite profile (as % of all identified metabolites) obtained from combined column soil extracts and in the leachates after 48 h of exposure

Metabolites	*Ahero soil*	*Nairobi soil*	*GSF sandy soil*
Carbofuran	26.3	51.2	21.3
3-hydroxycarbofuran	6.4	8.5	21.6
3-ketocarbofuran	1.5	13.6	0.4
3-hydroxycarbofuran phenol	34.3	0.8	0.5
3-ketocarbofuran phenol	17.2	22.8	6.5

Note: Analysis by LSC and HPLC, identification by authentic standards, recovery for carbofuran (66% in flooded soil and 94.9% from non-flooded soil).

and C. Carbofuran, like other carbamates, undergoes hydrolysis at the benzylic carbon to give carbofuran phenol, 3-hydroxycarbofuran, 3-keto-carbofuran, 3-ketocarbofuran phenol, both in flooded soils and non-flooded soils and the rate of hydrolysis is found to increase with soil pH [48]. The same hydrolytic metabolites were identified in our soil samples. Pesticides which have low water solubility and are highly retained by the soil matrix tend to resist hydrolysis. For compounds which are susceptible to hydrolysis, chemical hydrolysis is the major factor controlling their persistence in soil rather than adsorption. The pH of the soil affects the ionizability of FA functional groups such as COOH, OH etc., and therefore is an important controlling factor in pesticide hydrolysis.

Oxidation mechanism is important in potentiation of parathion, malathion and dimethoate and the metabolites paraoxon, malaoxon, and dimethoxon that were identified in our soil samples showed that oxidation occurred readily under field conditions at Ahero, Nairobi and Kisii soils and in the Green house experiments. Reduction of DDT to DDD occurred in Nairobi soil (upto a maximum of 4.3% DDD detected after 1 day) but was not detected in Mtwapa soil which indicated that DDD was mainly formed by microbial activity in Nairobi soil due to its higher soil organic carbon and moisture contents. DDT conversion to DDE occurs when DDT diffuses through clay minerals and due to the interaction of DDT with active zones on the surface of homoionic clay minerals during diffusion of the pesticide. This reaction is started by movement of electrons between pesticide molecules and clay complex and is catalysed by sunlight [70]. DDT decomposes more in homoionic Na^+-clay than in corresponding H^+-clay due to higher pH in the sodium system which shifts equilibrium between DDT and DDE towards DDE. This movement of electrons between clay-H_2O molecule protonates the water which then initiates the reaction by abstracting the Cl radical from DDT molecule. A lot of DDE was recovered in soil samples from both Nairobi and Mtwapa field plots. 5.3% DDE (after 1 day), 20% DDE (after 172 days), and 2.81% DDE (after 2 days) and 46.9% DDE (after 292 days) were detected in Nairobi and Mombasa field soil samples, respectively. This shows that DDE was mainly formed by this redox mechanism although conversion to DDE is also known to occur due to microorganisms such as *Streptomyces* [44].

In our experiments, the metabolism of these pesticides in soil were demonstrated both in the field and in laboratory experiments. In the field experiments we were able to identify various metabolites in soil samples that indicated that microbial degradation of the pesticides studied did occur. The metabolites were also quantified to show the extent of these

degradations. Parathion metabolism in Nairobi soil produced paraoxon, *p*-nitrophenol and *p*-aminophenol. As the pesticide moved down into the soil with time and as a result of rainfall, microbial activity seemed to increase and there was a build up of all these metabolites between the 3rd and 42nd day after application (see Table XB). The results showed that parathion was hydrolysed to *p*-nitrophenol and reduced by microorganisms to amino parathion. Under these aerobic conditions, amino parathion was then hydrolysed to *p*-aminophenol. These metabolites have also been reported in other previous studies [39,40,46,53].

Soil samples from both Kisii and Nairobi showed the presence of malaoxon, malathion monocarboxylic acids and isomalathion metabolites in field soil samples. Malaoxon which is formed by oxidation has been reported in other soil studies where oxidation of the S to O atom occurs by mixed function oxidase enzyme systems (MFO) and through photooxidation by UV-light of wavelength 2537 Å [17]. Isomalathion is an isomer of malathion and is formed at elevated temperatures. It is possible also that some of this was formed during extractions in the laboratory. The formation of malathion monocarboxylic acid was possible by action of carboxyl esterases as has been previously reported [17]. The slightly acidic nature of the soil at Kisii could also favour chemical hydrolysis of malathion at the S–C bond in soil to give dimethyl phosphorodithioate and dimethyl malonate although these metabolites were not confirmed by standards [17]. Malathion degradation was observed in Bayreuth soil samples under Greenhouse conditions by trapping $^{14}CO_2$ produced in pots containing both soil and growing garden pea plants. In these studies malathion was labelled at the 2nd and 3rd carbon positions of the diethyl mercapto succinate molecule. Both positions of ^{14}C-labelling gave $^{14}CO_2$ showing that microbial degradation actually occurred at the two positions on the molecule [17].

The microbial degradation of carbofuran in Ahero soil was demonstrated in biometer flasks showing the production of $^{14}CO_2$ from carbofuran in both submerged and non-submerged Ahero soil samples. More $^{14}CO_2$ was produced under anaerobic submerged conditions. In soil columns, used for the determination of carbofuran mobility in Ahero soil, several metabolites were identified including 3-hydroxycarbofuran, 3-ketocarbofuran, 3-hydroxy-7-carbofuran phenol and 3-keto-7-carbofuran phenol in all the soil columns containing soil samples from Ahero, Nairobi and GSF standard soil, after 48 h of application of carbofuran. The results in Table XC show that there was more degradation of carbofuran in both Ahero and Nairobi soils than in the GSF standard sandy soil which was due to the

high organic matter contents in the two soil samples from Kenya. These metabolites were spread throughout the various sections of the soil columns. A lot of 3-hydroxy carbofuran was identified in various sections of soil column in Ahero soil leaching experiment, but equally a lot was also identified in GSF sandy soil column, indicating that chemical hydrolysis rather than microbial hydrolysis, was involved in the GSF sandy soil. Although a lot of 3-keto carbofuran was identified in Nairobi soil column, little was detected in Ahero soil column and almost none in the GSF sandy soil possibly showing the different existing levels of microorganisms in the two soil types. A lot of 3-hydroxy-7-carbofuran phenol was also found in Ahero soil but only traces in Nairobi and GSF sandy soils. There was plenty of 3-keto-7-carbofuran phenol in both Ahero and Nairobi soils but only traces in GSF sandy soils. It is significant to note that the soil samples from Kenya had a lot of microorganisms but no comparisons can be made since the GSF sandy soil was not a true representative of the rich agricultural soils in Germany.

The microbial metabolic products such as transformed hydroxylated, epoxide and dealkylated compounds products are often similar to those metabolites formed by chemical degradation mechanisms. Several types of enzymes, bacteria and fungi are involved in pesticide degradation in soil [16,23,51,53,85]. For example, DDT can be converted to DDD by reductive dechlorination under anaerobic conditions by several types of bacteria including, *Pseudomonas* 6 spp, *Xanthomonas* 4 spp, *Erwinia* 4 spp, *Bacillus* 3 spp, *Achromobacter* spp, *Aerobacter aerogenes, Agrobacterium tumefaciens, Clostrodium pasterianum, Corynebacterium michiganese, Kurthia Zopti* [51]. *Streptomyces, Actinomycetes* (*Norcadia*) can also convert DDT to DDE, DDD and small quantities of DDA, dicofol, DDNU and DDOH, while the fungus, *Fusarium oxysporium* also converts DDT and DDE to DDD [82]. In most cases however, it is difficult to detect to any reasonable amounts the metabolites beyond DDE and DDD. DDT is stable in well aerated soils but under reducing anaerobic environments such as by flooding or maintaining oxygen free atmosphere, DDT is dechlorinated to DDD and this degradation is enhanced by the presence of organic matter in the soil [23]. Some of the products of degradation of DDT, such as DDD, DDA, and DDOH, are more water soluble and can be more rapidly lost through diffusion, leaching and volatilization in tropical soils where high temperatures enhance microbial activity [23,51,73]. Cytochrome P450 enzyme extracts from yeast can degrade DDT to DDD while lindane has also been shown to be degraded slowly by bacteria in soil by dehydrochlorination effected by *Bacillus cereus* [84].

This degradation was more rapid under submerged soils than in moist aerated soils and could be inhibited by the antibiotic sodium azide.

Microbial degradation is in addition influenced by soil temperature as shown in rates of DDT degradation where rates of formation of products are optimum at 60°C and no apparent degradation occurs at 20°C [56]. This explains why, in addition to factors previously discussed, the rates of dissipation of these organochlorine pesticides in tropical soils which have high temperatures are consequently high, since some of the degradation metabolites formed are more water soluble and can be removed from the soil matrix by water and lost through volatilization. In contrast, we would expect that degradation of pesticides by microorganisms in temperate soils is only very active in summer when the temperatures favour microbial activity and this occurs only for a short period in a year.

Some microorganisms have been able to produce metabolites from phenoxy alkanoic acids, such as through ring hydroxylations, cleavage of ether and ester linkages, ring cleavage, dehalogenation and S-oxidation of long chain moieties, e.g. *Pseudomonas*, *flavobacterium*, *Achromobacter*, *Arthrobacter*, *Sporocytophaga* and *Corynebacterium*. Although no ring hydroxylation metabolites were found in our soil samples from parathion experiments, cleavage of ether/ester linkages was indicated in parathion, malathion and dimethoate studies by the formation of *p*-nitrophenol, *p*-aminophenol, malathion monocarboxylic acids and dimethoate monocarboxylic acids, respectively. Carbofuran, like other thiocarbamates, may also be attacked by microorganisms at several possible sites and the metabolites identified in our experiments showed that very significant hydrolysis occurred in both aromatic and cyclic alkyl carbon moieties giving 3-hydroxycarbofuran and 3-hydroxy-7-carbofuran phenol. Cleavage of the ester or amide linkages in carbofuran may also have occurred to give carbofuran phenol, 3-keto-7-carbofuran phenol and 3-hydroxy-7-carbofuran phenol, all identified in our soil samples and in the leachate from the leaching experiment. Microbial epoxidation reactions were also indicated by high concentrations of 3-keto- carbofuran, 3-keto-7-carbofuran phenol.

Parathion degradation in soil has been reported to follow two pathways i.e., one involving hydrolysis to *p*-nitrophenol and diethylthiophosphoric acid and the other involving reduction to aminoparathion and although aminoparathion was not determined, *p*-nitrophenol was detected in our soil samples [46,53,56]. The nitrophenol released from parathion degradation can be metabolized by bacteria in flooded soils to give NO_2 and CO_2 as final products. The main pathway of carbofuran metabolism in soils has been reported to be through hydrolysis at carbamate linkage, and the

carbamate moiety is biodegraded to CO_2 and carbofuran phenol formed is rapidly bound to the soil [16,56,87]. The microorganism, *Actinomyces* responsible for converting carbofuran to CO_2 has reportedly been isolated from soils. In flooded non-sterile, anaerobic soil conditions, carbofuran is more rapidly hydrolysed but its hydrolysis products carbofuran phenol and 3-hydroxy carbofuran resist further degradation under anaerobic conditions [16,40,87,88]. Flooding minimizes the amount of O_2. It was suggested in our studies that hydrolysis of carbofuran in flooded soil was mainly chemical, but subsequent degradation of carbofuran phenol metabolite occurred through microorganisms.

7. Photodecomposition of DDT in Nairobi Soil

Photodecomposition experiments were set up on top of the two-storey laboratory to determine the effect of solar radiation (UV) on volatilization of DDT from soil. The results of this study are summarized in Table XI. The $^{14}CO_2$ and ^{14}C-organic volatiles liberated during exposure were trapped and analysed weekly.

In the experiments, we observed the influence of UV light on the degradation of DDT by increasing the rate of mineralization to $^{14}CO_2$ and formation of ^{14}C-organic volatiles of DDT in Nairobi soil sample. Ultraviolet radiation increased the rate of loss of ^{14}C-DDT residues from soil by 16.2%, consisting of 12.2% ^{14}C-organic volatiles and 3.6% mineralization to $^{14}CO_2$. The results of this study are shown in Table XI. DDT was photochemically degraded into more volatile organic compounds and $^{14}CO_2$. Since the penetration of UV light into soil is limited, such photochemical reactions mainly occur near or on the soil surface and the extent of these reactions depend on light intensity and soil characteristics. Solar radiation intensity is high throughout the year in Kenya, which makes

TABLE XI The effect of solar radiation on volatilization of ^{14}C-DDT in Nairobi soil (expressed as % residues recovered after 6 weeks of exposure)

Component analysed	*UV exposed soil*	*Unexposed soil*
Soil	72.9	89.1
^{14}C-Organic volatiles	18.6	6.0
$^{14}CO_2$	8.5	4.9

Note: The experiment was set up using dry soil (1320 g) samples dosed with a mixture of labelled and non-labelled pesticide (38 ppm) in cylindrical quartz tubes capable of filtering in UV radiation. One tube (unexposed soil) was covered with black paper to prevent entry of solar radiation. The ^{14}C-organic volatiles were trapped in polyurethane foam plugs, $^{14}CO_2$ was trapped in 0.1 M NaOH.

photodegradation an important dissipation pathway for pesticides. The experimental results confirm that solar radiation enhanced volatilization and mineralization of DDT in Nairobi soil. Photosensitizers such as organic molecules with benzylic or alkenoic bonds in humic substances often found in natural waters and in soil environments can also absorb solar energy and transfer it to pesticide molecules and consequently effect reactions in compounds that would not normally undergo photochemical transformation on their own [23,86]. These photolysis reactions of pesticides have been found to increase with soil moisture and pH. Polymerization of DDT molecules by UV light has been reported in absence of air as well as its oxidation to dichlorobenzophenone in presence of UV light and air [23,27].

CONCLUSIONS

In our experiments we observed that organochlorine pesticides have much shorter half-lives of disappearance in tropical soils compared to those reported in temperate soils. This is not only significant in terms of effective use of these pesticides but is also important with regard to pesticide regulations which are often based on their persistence and toxicity in organisms. Most of the year, during winter, spring and fall seasons, the temperatures in the temperate regions are very low. During these seasons pesticide degradation in soil and loss through volatilization are minimal. It is therefore possible to account for the long half-lives of dissipation reported from these regions.

Although the residence times in soil are much shorter in tropical soils, it is possible that the volatilized residues still find their way into aquatic environments through aerial transport and rainfall. This may explain why relatively higher amounts of organochlorine pesticides have been detected in water, sediment and fish samples taken from marine environments of tropical and subtropical countries of South East Asia and Africa [41]. Whereas the adsorption, desorption and leaching in soil are, to a large extent, dependent on the nature of the pesticide, the dissipation and degradation of pesticides in soil are mainly influenced by soil moisture content and climatic factors that accelerate evaporation from the soil. In this case the organochlorines have very close half-lives of dissipation in soil in the tropics to those of the well known non-persistent organophosphates and carbamates. Their dissipation under tropical conditions is mainly dependent on soil moisture content, organic matter content, high air and soil temperatures, intense solar radiation and high rates of evaporation throughout the year which

accelerate their degradation and volatilization in soil. Other environmental factors such as strong winds and low % relative humidity which accelerate the rate of evaporation from soil are also involved.

Climatic variations within the same country e.g. rainfall pattern, soil moisture content, presence of wind breaks such as trees can result in large differences in dissipation rates as was shown by malathion which had a half-life of dissipation of 770 days in Nairobi soil during the dry season but only 48 days in Kisii soil where it was applied during the rainy season. Since the soil characteristics were more or less similar, except for the slightly higher organic matter content in Kisii soil, this large difference in half-lives of dissipation can be attributed mainly to the higher rates of evaporation from Kisii soil favoured by its high soil moisture content. The rate of evaporation in Kisii was twice that in Nairobi during the experiments. A similar explanation accounts for a half-life of dissipation of 245 days for DDT in Mtwapa sandy soil with a moisture content of 0.6% and only 97 days in Mombasa sandy soil with a moisture content of 2.8%, even though the soil characteristics and rainfall pattern were on average the same in these locations. The Mombasa plot was located close to the ocean and was relatively wetter compared to Mtwapa plot which was located 30 km away from the ocean. Lindane had an extremely short half-life of dissipation in both Mombasa and Nairobi soils. This is due to its relatively higher water solubility and vapour pressure. Since its molecules are held in soil by weak Van der Waals forces of attraction, they have very little adsorption to soil and stay most of the time in aqueous phase where they are lost through evaporation from the soil surface.

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