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DEGRADATION OF DDT UNDER WET HUMID AND DRY SUBHUMID AGRO-ECOSYSTEMS IN NIGERIA.

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Abstract

Degradation and dissipation of DDT (Dichloro-diphenyl-trichloro-ethane) were investigated at two locations, viz, Ilorin in the subhumid Guinea Savanna and Ile-Ife in the wet humid Rain Forest Zones of Nigeria. These were monitored in soil within plastic cylinders (25cm x 10cm diameter), spaced 1.5m x 1.5m and driven into the soil leaving 3cm above the ground level in order to prevent run off losses. Extractable and bound residues of DDT were determined using Thin Layer Chromatography (TLC) and Gas Liquid Chromatography (GLC).

The results showed that the pattern of dissipation of DDT were biphasic at the two locations. The rapid and slow phases of degradation occured during the first 3 weeks and the 4th week to the end of the experiment respectively. While extractable residues decreased, bound residues increased with time at both locations up to the end of the experiments. The rates of dissipation during the rapid phase and throughout the whole period were higher at Ile-Ife with half-lives of 38 and 370 days than at Ilorin with half-lives of 41 and 388 days respectively. However, there was greater transformation of DDT into less toxic products, viz. dichloro-diphenyl-ethane (DDE) and dichloro-diphenyl-dichloro-ethane (DDD) at Ilorin than at Ile-Ife. Hence, DDT was found more persistent at Ile-Ife. The trend emphasised the importance of soil factors especially the presence of sorption sites due to organic matter and clay in determining the persistence of DDT. The binding of DDT and its degradation products to exchange sites could have deleterious effects on long-term soil fertility and productivity.

INTRODUCTION

In a bid to achieve food self-sufficiency in developing countries, more land intensive agriculture which requires the use of pesticides is being practiced. Dichloro-diphenyl-trichloro-ethane (DDT) is still widely used in the developing tropical countries to control pests of agricultural and health importance because it is a cheap and effective broadspectrum pesticide. This pesticide has, however been banned in the developed countries because of its persistence in soil (Nash and Woolson, 1967; Matsumura, 1975; Bayer and Gish, 1980) and deleterious effects on non-target organisms (Atlas *et al.*, 1978; Perfect, 1960). The

leaching and/or erosion of pesticides into bodies of water could also be a health hazard. Some workers believe that DDT may not be as persistent in tropical as in temperate soils because of high temperature and rainfall regimes. Working under laboratory conditions, Olayinka *et al.* (1997) showed that the degradation of C-DDT took place at mesophilic temperatures with optimum at about 35°C. Both microbial mineralization and volatilization were found to be important processes in the loss of DDT carbon from the soil system. There is a need to assess the factors that might be affecting the persistence of DDT under field conditions. This study became necessary in order to characterise the behaviour of DDT under two agroclimatic conditions in Nigeria.

MATERIALS AND METHODS

Field Studies

The field studies were conducted on flat land at the University of Ilorin, Ilorin and Obafemi Awolowo University, Ile-Ife in the subhumid Guinea Savanna and wet humid Rainforest zones of Nigeria in 1991 and 1992 respectively. The soil properties and summary of weather data are shown in Table 1.

Experimental Procedures

The experimental sites were weeded manually and the trash was removed. Plastic clyinders measuring 25cm x 10cm in diameter, spaced 1.5m x 1.5m were driven into the soil leaving 3cm above the ground level in order to prevent runoff loses. Two weeks later, the portion of soil in each cylinder was amended with 10mg DDT in 10ml n-hexane. The cylinders were kept weed-free throughout the 48 weeks of experimentation. Three cylinders were randomly sampled at the start of the experiment (zero time), extracted and taken as 100% of the treatment dose. Thereafter, sampling was done weekly for the first month, forthnightly for the next 2 months, monthly for the next month, and bi-monthly for the next 8 months. At each sampling occasion, three cylinders were randomly selected, dug out and the soil removed for the determination of extractable, bound and total residues.

Extraction of Pesticide Residues:

To extract pesticide residues, 50g sub-samples of amended soil were taken through 10 cycles of soxhlet extraction with methanol over 3 hours. The bound residue was extracted thus:

Bound residues were determined in methanol-extracted samples by wet combustion technique. Fifty millilitres (50ml) of 0.5N H_2SO_4 was added to the sample in a 500ml conical flask and left for 48 hours. One hundred millilitres (100ml) of methanol was then added and extraction was carried out four times with 50ml n-hexane. The hexane layer was transferred to a separating funnel, washed four times with distilled water to remove traces of acid, dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to 5ml and applied to preparative TLC plate developed in 5:1 n-hexane-acetone.

The silica-gel on the developed plate with retention factor (RF)0.6 - 0.9 was carefully scrapped and re-dissolved in 20ml hexane. After centrifuging, the hexane was decanted

and the silica-gel was again washed with hexane twice. The three portions of hexane were combined and the volume reduced to 1ml out of which 1ul was applied to the GLC.

Determination of concentrations and types of pesticide residues:

The metabolites of DDT extracted were determined by TLC and GLC using Varian 1200 with 63Ni ECD and Varian Aerograph linear recorder under the following conditions: column, stainless steel (2m x 4mm) packed with chromosorb 80/100 mesh coated with 1% OV-17; carrier gas, N_2 30ml/min; column temperature, 190°C; injector and detector temperatures, 20°C; chart speed, 10mm/min. Identification in the TLC was by comparison of RF with those of authentic standards obtained from the Pesticide Research Centre, Michigan State University, East Lansing, U.S.A. In the GLC, the types, and quantities of residues in extracts were determined by matching sample peaks with the peaks of standard DDT, DDE and DDD.

RESULTS AND DISCUSSION

Soil and Weather Conditions:

The soil physical and chemical properties and the weather conditions during the 48-week periods of the experiments at Ilorin and Ile-Ife are presented in Table 1. The soil at Ilorin classified as Oxic Haplustalf is a sandy loam while that at Ile-Ife, an Oxic Paleustalf is a sandy clay loam. With the higher contents of organic carbon, NO_3-N, available P and exchangeable Ca, the soil at Ile-Ife was more fertile than that at Ilorin. The weather at Ile-Ife was more humid (29.1°C, 61.4% R.H. and 800mm mean annual temperature, relative humidity and rainfall respectively) than that at Ilorin (27.1°C, 54.6% R. H. and 16mm mean annual rainfall). Despite the lower mean annual temperature of 27.1°C at Ile-Ife, a higher rate of evaporation and volatilization would be expected at Ilorin because of the lower relative humidity and longer length of the dry season.

Degradation and dissipation of C-DDT

The extractable, bound and total residues of C-DDT expressed at % of the initial DDT concentration applied throughout a period of 48 weeks at Ilorin and Ile-Ife are shown in Figures 1 and 2. At both sites, the extractable C-DDT decreased rapidly during the first 3 weeks to 66.1% and 65.2% respectively and gradually thereafter up to the end of the experiments. During this period, the concentrations of bound residues increased to 3.2% at both Ilorin and Ile-Ife, but thereafter increased gradually to 7.8% at the end of the experiments (Figures 1 and 2). These findings indicate that the binding of DDT to the soil and its dissipation were biphasic. The binding therefore involved both rapid and slow reactions at the sorption sites. Because these soils are known to lack the more reactive 2:1 expanding layer clay minerals (Jungerious and Levelt, 1964; Gallez et al., 1975), the rapid sorption site could be attributed to soil organic matter. The slow binding sites would be due to the clay minerals which are less reactive than organic matter. Organic matter and clay have been found to be sites for binding pesticides in soil (Harris, 1967; Briggs, 1984, Madhun *et al.*, 1986). Microbial activity tends to be intense during the first four weeks after addition of organic materials to soil (Olayinka and Adebayo, 1984). Hence, as found under laboratory conditions (Olayinka *et al.*, 1997), this trend indicates a role for soil microorganisms in the transformation of DDT.

Table 1: Some soil properties and weather conditions at Ilorin and Ile-Ife.

SOIL PROPERTIES AND WEATHER DATA	ILORIN	ILE-IFE
Particle Size Analysis	73% sand, 12% silt, 15% clay	65% sand, 19% silt, 16% clay
Textural Class	Sandy loam	Sandy Clay loam
Soil Taxonomy	Oxic Haplustalf	Oxic Paleustalf
Organic Carbon	1.09%	1.50%
pH (0.01M $CaCl_2$)	5.2	5.4
NO_3-N	13.1 $mgkg^{-1}$	16.0$mgkg^{-1}$
Available P (Bray 1)	6.3 $mgkg^{-1}$	8.5$mgkg^{-1}$
Exchangeable Ca, K,	5.63, 0.51 0.57	6.85, 0.50, 0.47
Mg, Na	0.52 $cmol\ kg^{-1}$	0.55$cmol\ kg^{-1}$
CEC	7.23 $cmol\ kg^{-1}$	8.37 $cmol\ kg^{-1}$
Range and Mean monthly temperature	24-31°C; 27.1°C	26-34°C; 29.1°C
Range and mean monthly relative humidity (R.H.)	33-81%; 54.6%	40-78%; 61.4%
Range and mean monthly rainfall	14-56mm; 16mm	50-2000mm; 800mm
Number of wet months	6 months	10 months.

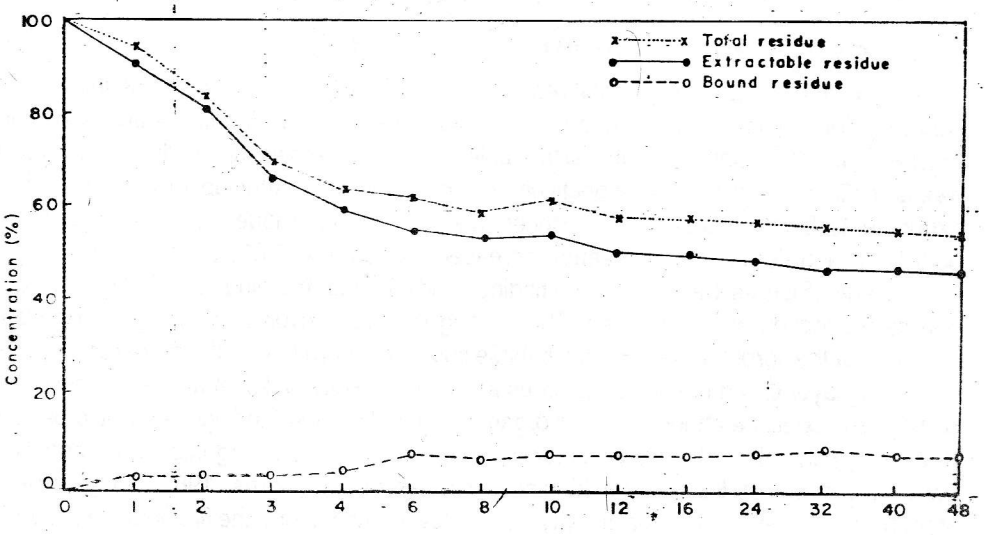

Figure 1: Extractable, bound and total residues as percent of initial concentration of DDT applied at Ilorin site.

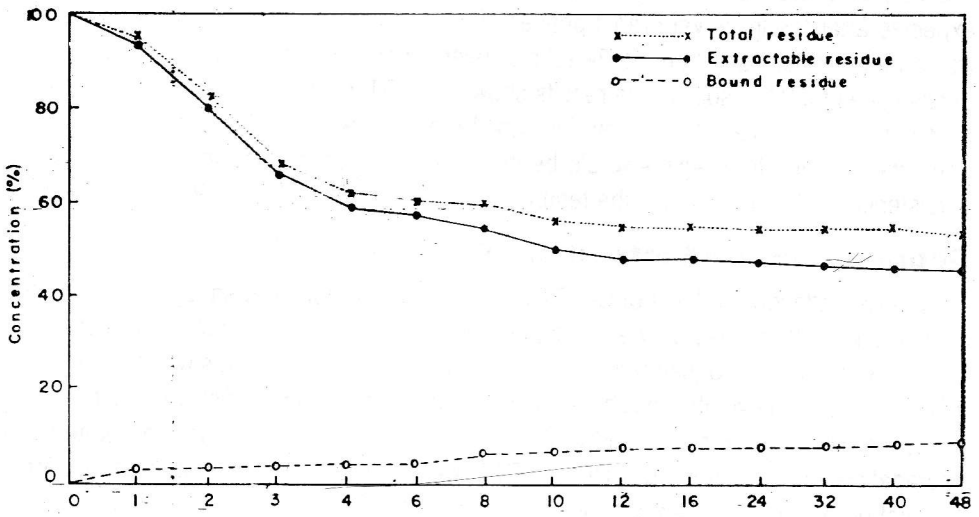

Figure 2: Extractable, bound and total residues as percent of initial concentration of DDT applied at Ile-Ife site.

At the end of the 3rd week of field exposure, the total residues at Ilorin and Ile-Ife constituted 70% and 68.4% meaning that 30% and 31.6% respectively of the applied DDT had dissipated, probably through such processes as leaching, erosion, microbial mineralization and volatilization. Because of the experimental precautions earlier stated and the fact that DDT has low solubility of about 2ppb (Matsumura, 1975), microbial mineralization and volatilizatioin would be the main sources of dissipation. Because the amounts of bound residues increased with time, the relative contribution of volatilization to

the dissipation of applied DDT would tend to decrease with time. This is in line with the observation of Olayinka *et al.* (1997) under laboratory conditions. While the extractable residues decreased to 47.1% and 45.5%, the amounts dissipated were equivalent to 45.1 and 47.8% at the end of 48 weeks at Ilorin and Ile-Ife, respectively.

The half-lives for C-DDT dissipation at Ilorin and Ile-Ife for 0-3 weeks, 4-48 weeks and 0-48 weeks were 41,1391 and 388 days, 38, 1412 and 370 days respectively. Hence, DDT dissipated somewhat faster at Ile-Ife than Ilorin during the first three weeks and on the average throughout the 48 weeks of incubation. A more spectacular difference in dissipation rates was expected considering the contrasts in the weather conditions in Ilorin and Ile-Ife. However, Yeadon and Perfect (1981) reported similar dissipation rates for DDT in Nigeria. The very slow rates of DDT dissipation at both sites between the 4th and 48th weeks were expected after the initial very rapid phases of dissipation. The half-live during this period would be more relevant than the 3weeks or overall half -lives to the determination of the persistence of DDT in soil. These results show that DDT is not as persistent in these soils as in temperate soils as reported by Nash and Woolson (1967) and Bayer and Gish (1980). The lower temperature regime would be the main factor accounting for the phenomenal persistence of DDT reported in the temperate zone (Olayinka *et al.*, 1997).

Degradation Products of C-DDT

The degradation products of C-DDT applied to sandy loam and sandy clay loam soils at Ilorin and Ile-Ife respectively and the patterns of release of such products are shown in Figures 3 and 4. The concentrations of the major degradation products which were found to be dichloro-diphenyl-ethylene chloride (DDE) and dichloro-diphenyl-dichloro-ethane (DDD) increased with time up to the end of the 48th week of experimentation. The patterns of degradation and dissipation of DDE and DDD were found to be similar at both locations. The first product of DDT degradation DDE was first detected at the end of the 3rd week at Ilorin and Ile-Ife. While the products of DDE degradation, DDD was detected at the end of the 1st week at Ilorin, it was not detected until the end of the 6th week at Ile-Ife. The lag in the transformation of DDE to DDD at Ile-Ife might be due to the higher contents of organic matter and clay which would have increased the energy of binding in the soil. This could be supported by the fact that while undegraded DDT and its degradation products made up 19.1% and 28% of the extractable residues at Ilorin at the end of the 48th week, corresponding values at Ile-Ife were 27.1% and 17.5% respectively (Figures 3 and 4). Hence, the two degradation products constituted 59% and 38% of the extractable residues at the end of the experiments at Ilorin and Ile-Ife respectively. Organic matter and clay are known to be active sites for binding pesticides in soils (Briggs, 1984; Harris, 1967; Madhun *et al.*, 1986). Although the rate of dissipation of DDT was higher ($t^1/_2$ = 296 days) at Ile-Ife than at Ilorin ($t^1/_2$ = 309 days), undegraded DDT was more persistence at Ile-Ife.

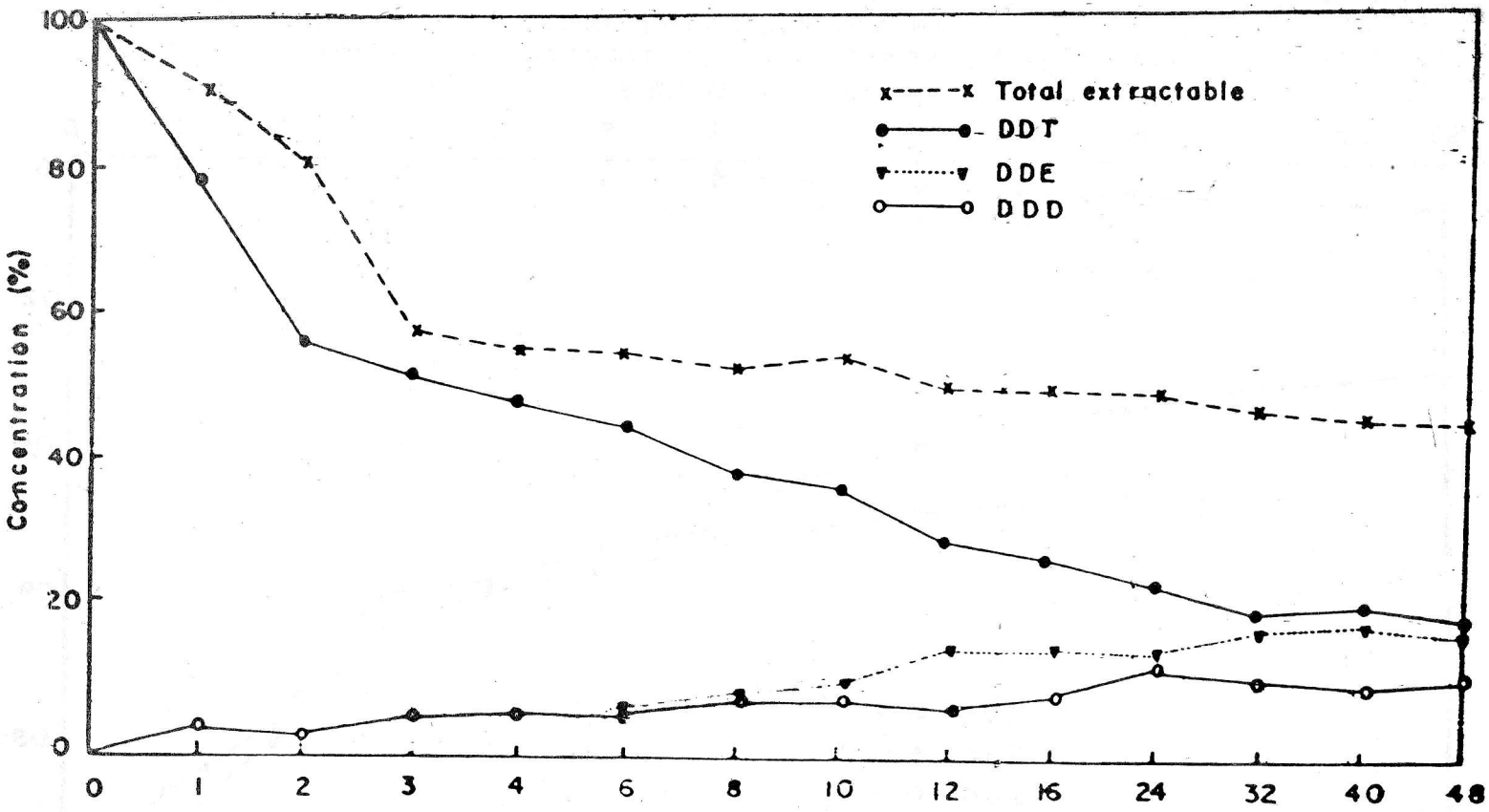

Figure 3: Degradation products of DDT in the top 10cm of a sandy loam in Ilorin expressed as percent of applied dosage.

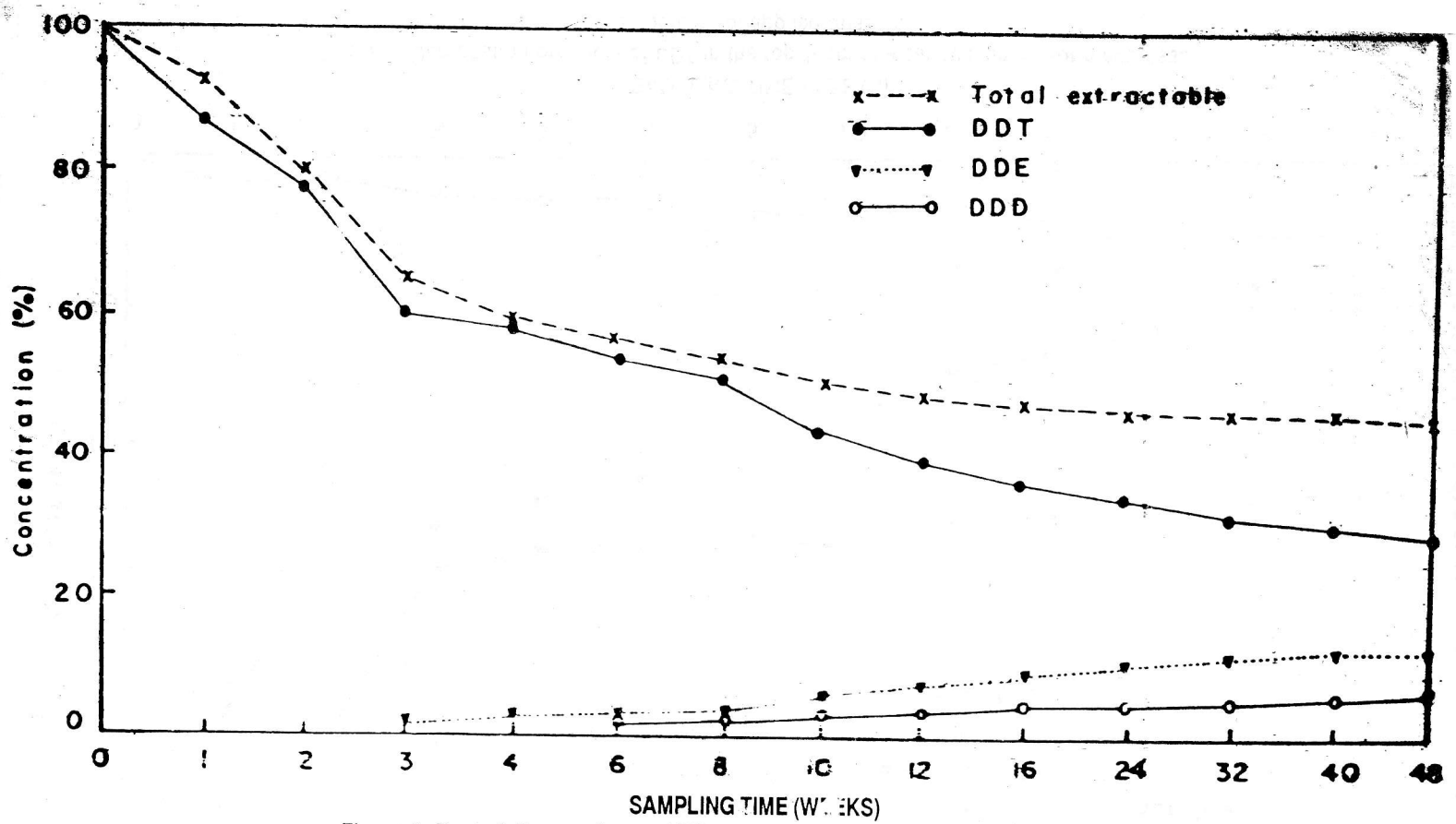

Figure 4: Degradation products of DDT in the top 10cm of a sandy clay loam in Ile-Ife expressed as percent of applied dosage.

CONCLUSIONS

These results indicate that the processes of degradation and dissipation of C-DDT were biphasic under the humid and subhumid climates of Ile-Ife and Ilorin respectively. The rapid phase lasted for about three weeks while the slow phase lasted for the remaining period of the experiments. This pesticide dissipated faster at Ile-Ife ($t^1/_2$ = 370 days) than at Ilorin ($t^1/_2$ = 388 days). However, there was greater transformation of DDT into less toxic products, namely DDE and DDD at Ilorin than Ile-Ife. Hence, DDT was found to be more persistent at Ile-Ife. This trend emphasized the importance of soil factors especially the presence of sorption sites due to organic matter and clay in determining the persistence of DDT. The binding of DDT and its degradation products to exchange sites could have deleterious effects on long-term soil fertility and productivity.

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