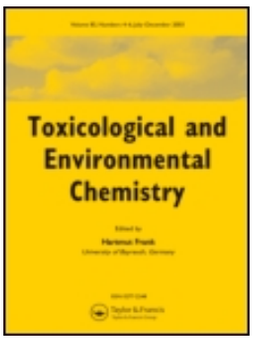

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THE DISSIPATION AND DEGRADATION OF METHOXY-^{14}C MALATHION IN SOIL UNDER TROPICAL CONDITIONS

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^{14}C-malathion[S-1,2-bis(ethoxycarbonyl) ethyl O,O-dimethyl phosphorodithioate] has been studied in soil under tropical field conditions by applying the ^{14}C-malathion pesticide to soil in Polyvinyl chloride (PVC) pipes and monitoring it with elapsed time. In one area, ^{14}C-malathion dissipated with a half-life values of 36.7 days and 41 days in the long rain and short rain seasons respectively. The bound residue of malathion in the soil built up to 51.8% and 73.4% of the initial pesticide dose in the short and long rain seasons, respectively. However, after sometime the bound residue decreased and this has been attributed to biodegradation by micro-organisms in the soil. In another area, ^{14}C-malathion dissipated slowly with a half-life value of 770 days in the dry spell. The bound residue built up in the soil slowly, attaining a value of 5.49 μg/g (35.4%) of the initial pesticide dose after 70 days. The bound residues did not decrease at some stage and this has been attributed to the prevailing dry conditions, which did not promote the biodegradation of the bound residues in the soil by micro-organisms. The metabolites in the soil as determined by TLC and confirmed by GC-MS, showed the presence of malaoxon and the malathion α-mono or β-mono carboxylic acid in addition to the parent compound, malathion.

Keywords: ^{14}C-malathion; half-life under field conditions

INTRODUCTION

The high margin of safety of malathion to mammals and birds, and its selectivity against target insects, make it a good general purpose contact insecticide employed in controlling insects of household, home garden,

* Corresponding author.

stored grains, greenhouse, agriculture, forestry and public health [1]. Malathion is used as a foliar spray on a wide spectrum of crops and as a grain protectant in grain storage but its fate in the soil has not been studied in Kenya. The objective of this study was to investigate the dissipation of ^{14}C-malathion in soil in polyvinyl chloride (PVC) pipes under field conditions.

MATERIALS AND METHODS

^{14}C-malathion[(S-1,2-bis(ethoxycarbonyl)ethyl-O,O-(^{14}C)-dimethyl phosphorodithioate] with Sp. Activity: 5.2 mCi/mmol and radiochemical purity of 98% (by HPLC) was purchased from Sigma Chemical Company, St. Louis Missouri, U.S.A.

Emulsifiable concentrate (50% a.i.) of malathion was purchased from local suppliers. Non-labelled malathion standards of malathion, malaoxon, malathion monocarboxylic acid were obtained from Chester PA, USA. The organic solvents were all pure grade purchased from Sigma Chemical Company. Triton-X in water, 2,5-diphenyloxazole (PPO) and 1,4-bis-2-(5-phenyloxazolyl)-benzene (POPOP) in toluene used in Liquid Scintillation Spectrometry were purchased from Sigma Chemical Company through International Atomic Agency (IAEA).

Liquid Scintillation Counter (Packard Tricarb® 1,000 model) and Biological Material Oxidizer (OX-600 model) both from Canberra Co., U.S.A. TLC Scanner Berthold LB 2760, Berthold UV-254 nm lamp, Gas Chromatogram (Carlo Erba HRGC Fracto Vap 4160; detection by FID) and Double Focused Finnigan MAT 95 Mass Spectrometer were used.

Sample Treatment and Sampling Procedure

In the Kisii area at an altitude of 1778 M, latitude of 0°41′S and longitude of 34° 48′E, a plot measuring 20 m × 20 m was prepared. A total of 30 PVC pipes each of length 45 cm and internal diameter of 6 cm were driven into the soil with 3 cm left protruding above the soil surface to prevent loss of soil due to surface run-off. After one week, 2.43 μCi of methoxy-^{14}C malathion and 15.375 mg of non-labelled malathion in n-hexane was applied to soil in the pipe while in the second application, 1.5 μCi of methoxy-^{14}C malathion and 15.432 mg of non-labelled malathion was applied. In the Nairobi field station at an altitude of 1815 M, latitude of 01° 18′S and longitude of 36°45′E, 1.8 μCi of the methoxy-^{14}C malathion and 15.415 mg of non-labelled

malathion in *n*-hexane was applied to the topsoil in each PVC pipe. The initial pesticide concentration applied to soil in each PVC pipe was 15.53 μg/g.

Soil samples from the pipes in triplicates were air-dried in a hood, mixed and ground in a mortar with a pestle. A sub-sample of 50 g was taken in thimbles and exhaustively extracted in Soxhlet extractors with 200 ml of pure methanol for four hours.

Analytical Methods

The concentrated extract (replicates of three) was cleaned by passing it through a glass column of internal diameter of 20 mm packed with 2 g of celite at the base followed by 0.8 g of activated carbon dispersed in 3.2 g of celite and topped with glass wool. The extract was eluted with pure methanol. The eluted extract was concentrated to 10 ml from which 1 ml of the extract was taken, mixed with 5 ml of the cocktail (PPO and POPOP in toluene) and radioassayed in liquid scintillation counter to determine the extractable residues in the soil. External standardisation method was used for quench correction of the readings of liquid scintillation counter. The extracted soil sample was air-dried in a hood. A sub-sample of 1,500 mg (replicas of three) was taken in porcelain boats and combusted in a biological materials oxidiser. The $^{14}CO_2$ released was trapped by Harvey ^{14}C-cocktail. The trapped $^{14}CO_2$ was mixed with the cocktail (PPO and POPOP in toluene) and radioassayed to determine the bound residues in the soil samples.

The methanol extracts were concentrated to dryness and re-dissolved in ethyl acetate. The extracts in ethyl acetate were concentrated again to dryness by blowing nitrogen gas through them. The residues were dissolved in 10 μl of *N*-methyl *N*-trimethylsilyl-trifluoracetamide (MSTFA), $F_3CC(O)N(CH_3)Si(CH_3)_3$ reagent, as a derivatizing agent. The extracts were analysed for metabolites by TLC, autoradiography and confirmed by GC-MS.

Leaching Experiments in the Laboratory

Leaching of malathion in three soils with different characteristics was done in the laboratory. The soil samples were homogenised and sieved through a 2-mm pore sieve. The sieved soil samples were packed in glass columns with internal diameter of 27 mm to the height of 420 mm with glass wool plug at the bottom. Each soil column was saturated with 0.01 M calcium chloride

($CaCl_2$) solution by passing the solution through it by capillary for 12 hours. The column was then allowed to drain freely overnight with the 0.01 M $CaCl_2$ solution. The dry mass of the soil in each column was 300 g. Malathion of 22.14 mg with initial radioactivity of 0.303 μCi was applied from the top of the soil column and washed with 0.01 M $CaCl_2$ solution at the rate of 7.3 ml per hour for 48 hours. After 48 hours the volume of the leachate was measured and analysed for radioactivity. The soil column was carefully removed and sub-divided into 0–7 cm, 7–14 cm, 14–21 cm, 21–28 cm, 28–35 cm, and 35–42 sections for the determination of radioactivity. The volume of the leachate was analysed by adding 2-ml aliquots to 10 ml of Triton-X cocktail and radioassayed. The extractable residues in various sections of the soil column were determined by extracting the soil in the Soxhlet extractor with 150 ml of dichloromethane. One ml aliquot of the dichloromethane extract was mixed with 5 ml of the cocktail (PPO and POPOP in toluene) and radioassayed. The extracted soil was air-dried and combusted to determine the bound residues.

The recovery rates of ^{14}C-malathion from the spiked soil samples at a concentration of 15.53 μg/g from the two areas were 88.4% and 91.6% for the Kisii and Nairobi soils, respectively. The results were corrected according to these recovery rates. The data were subjected to statistical analysis according to the method of Mactaggart and Farewell [2].

RESULTS AND DISCUSSION

Figures 1 and 2 show the results of dissipation of methoxy-^{14}C labelled malathion from Kisii soil in the short and long rain seasons, respectively. In both seasons the extractable residues initially decreased very fast and then slowly with time. The bound residues initially increased with time and then later decreased in the soil. Both the bound and extractable residues decreased faster during the long rain season than during the short rain season. The loss of the malathion extractable residues from the soil with time was due to leaching by rain, vapourization, binding of the pesticide to the soil and due to biodegradation by micro-organisms. In both seasons, rain was well distributed (Figure 3). The maximum air temperatures were on average above 20 °C while the minimum air temperatures on average were above 10 °C. The wind flow for the entire period of study was high and on average was above 100 km/h. The higher rate of loss of malathion residues from the soil in the long rain season is due to higher rainfall, evaporation rate and wind flow than they were during the short rain season.

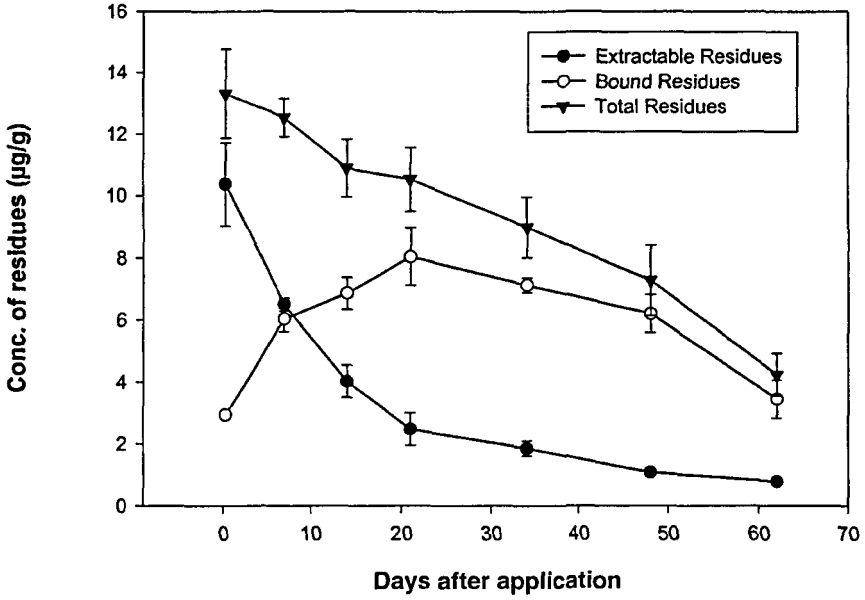

FIGURE 1 Dissipation of malathion from Kisii soil in the short rain season.

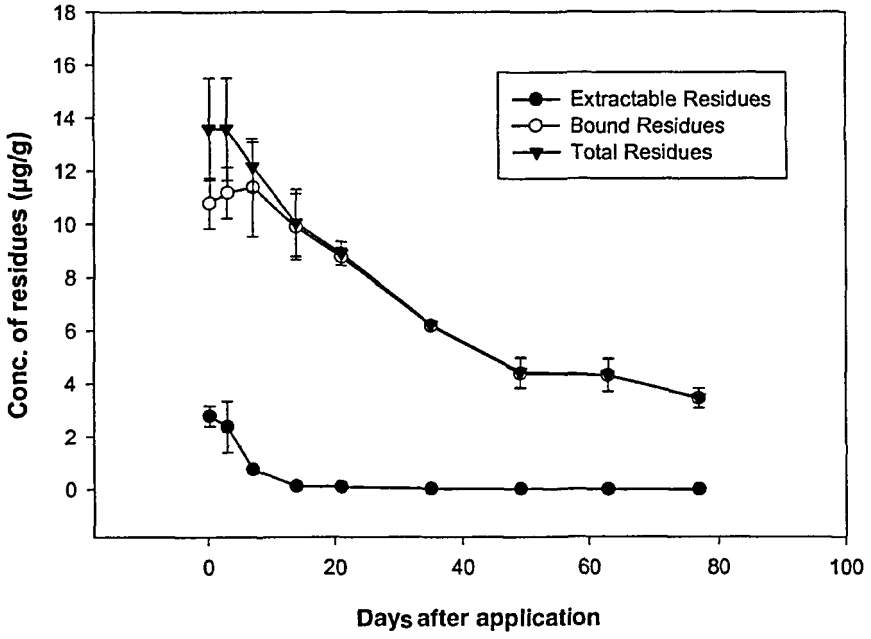

FIGURE 2 Dissipation of malathion from Kisii soil in the long rain season.

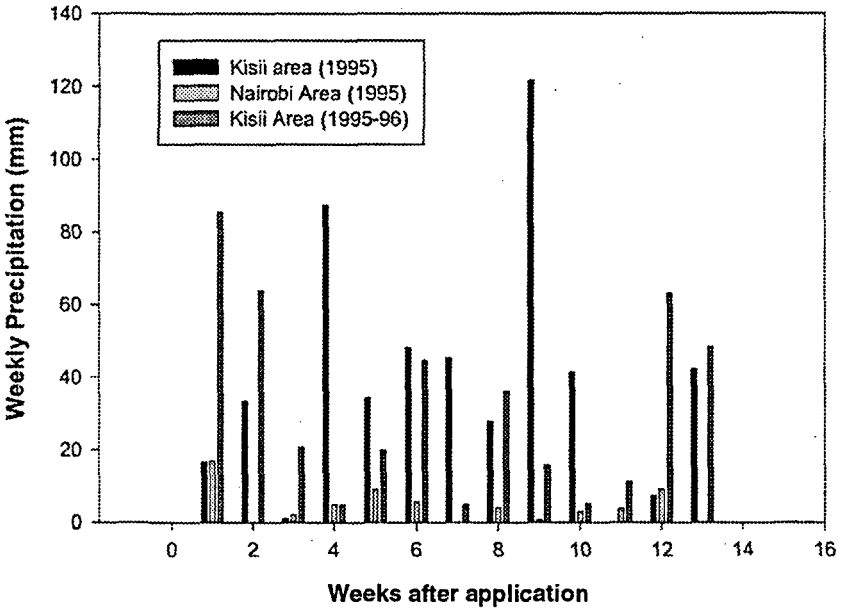

FIGURE 3 Rainfall distribution pattern during the field studies.

When the bound residues started decreasing in the soil, there was no accompanying increase in the extractable residues in the soil as shown in both Figures 1 and 2. The study shows that the bound residues did not revert to the extractable residues. The decrease in the bound residues in the soil was well correlated with the $^{14}CO_2$ emitted from the 2nd and 3rd ^{14}C-labelled in the mercaptosuccinate of malathion in an experiment conducted in a greenhouse [3]. This study shows that micro-organisms can access bound residues of malathion in the soil. It is reported from other studies in the literature that, once the pesticide residues are bound to the soil, bound residues of some pesticides may be protected from biological and chemical degradation and for the others, they may undergo faster degradation [4]. The pesticide residue getting bound to the soil enhanced the persistence of the pesticide in soil. Total residues of malathion dissipated faster in the long rain season than in the short rain season.

On semi-logarithm transformation of the data for malathion residues in the soil for both seasons, there was good correlation between the log of concentration of the residues with time (Figures 4 and 5). The first order kinetics model for the data gives half-life values of 41 and 36.7 days for the total malathion residues in the soil in the short rain and long rain seasons respectively, in the Kisii soil.

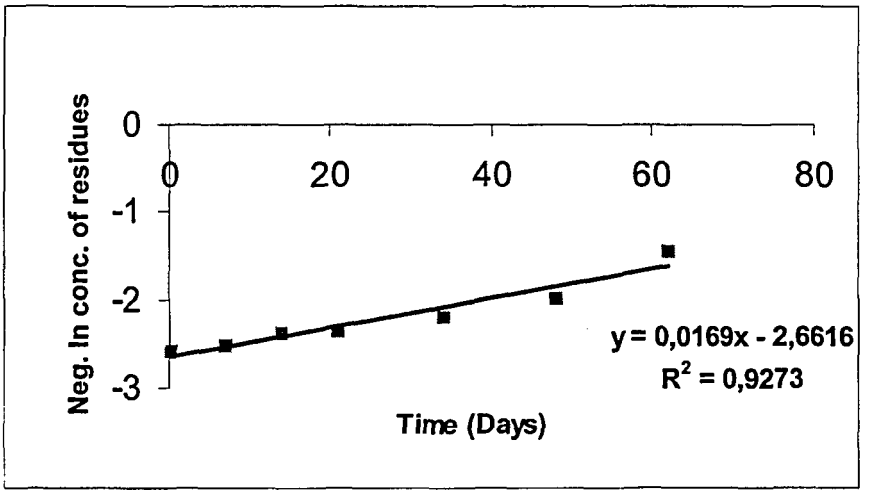

FIGURE 4 Linear regression curve for dissipation of malathion from Kisii soil in the long rain season.

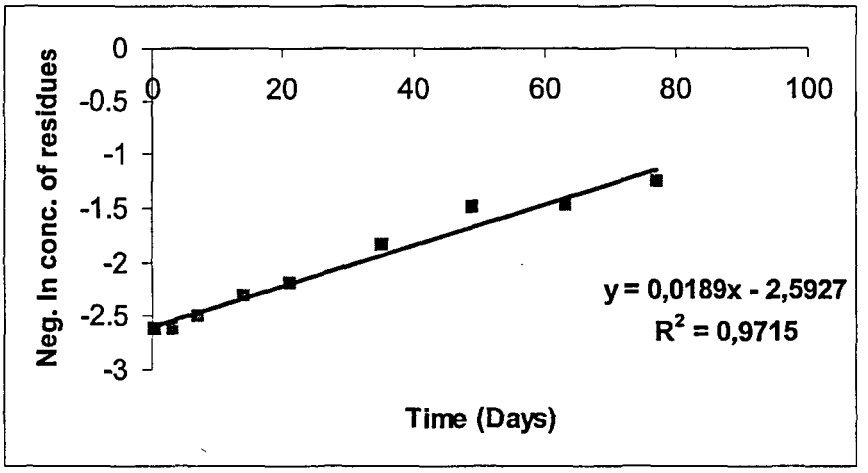

FIGURE 5 Linear regression curve for the dissipation of malathion from Kisii soil in the short rain season.

Figure 6 shows the dissipation of ^{14}C-malathion residues from soil in Nairobi area in the dry season. The dissipation curve for the extractable residues is characterised by two phases, an initial fast rate of dissipation and later, slow rate of dissipation. The bound residues in the soil initially built up fast and then slowly. This study did not show that the bound residues

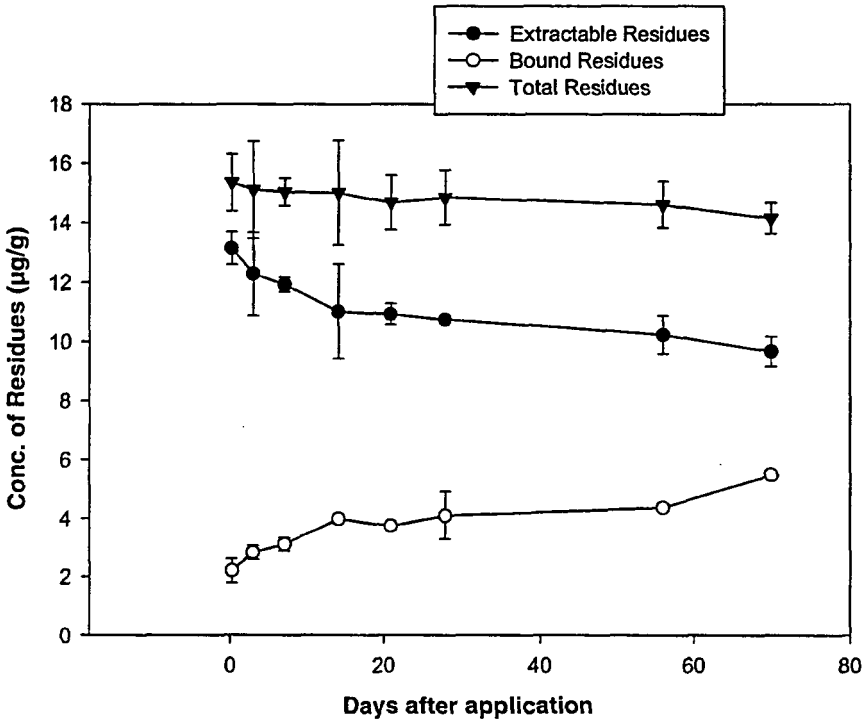

FIGURE 6 Dissipation of malathion from soil in Nairobi area in the dry season.

decreased at some stage. Total residues of malathion in the soil dissipated from soil slowly with time. The study was carried out during the dry season. There was very little rainfall (Figure 3) and leaching of the pesticide from the topsoil was not a major process in accelerating the loss of malathion residues from the soil. The evaporation rate and wind flow values were low. The prevailing weather conditions did not speed up the loss of malathion residues from the soil. Low precipitation led to dry conditions in the soil, which did not favour microbial degradation of the bound residues in the soil. This observation is consistent with studies reported in the literature on degradation of malathion and some organochlorines in flooded and non-flooded soil conditions [5].

The balance between the extent of adsorption of pesticide residues in the soil and the degree of the pesticide leaching by rain determines the rate of dissipation of a pesticide from soil. The dissipation rate of total malathion residues from Nairobi soil has been determined from first order kinetics model (Figure 7) and a half-life value of 770 days has been estimated. The

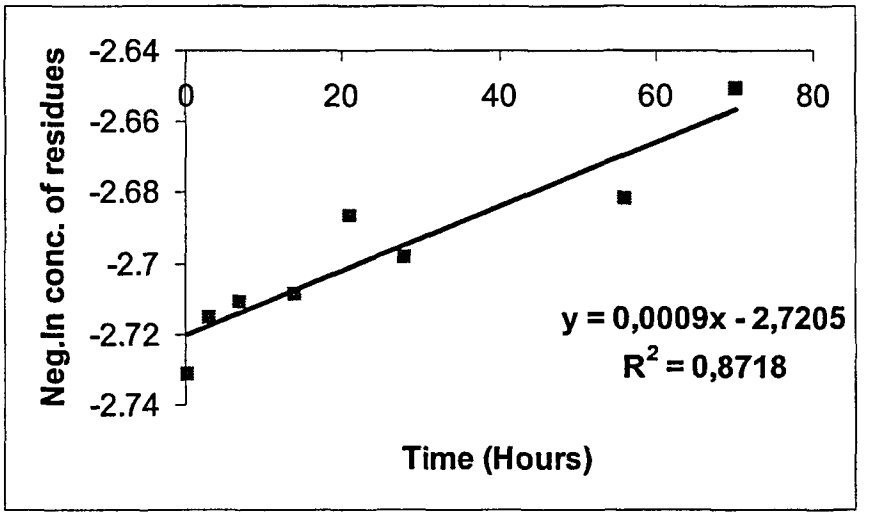

FIGURE 7 Linear regression curve for the dissipation of malathion from Nairobi soil in the dry season.

high half-life value is consistent with the behaviour of the malathion residues in the soil under dry conditions.

Figure 8 shows results of leaching of malathion from three soils with different characteristics. Malathion leached most from Mombasa soil with the least carbon content (0.54%). The highest amount of malathion was retained in the Kisii soil with the highest carbon content (1.68%). Malathion being an insecticide with average lipophilicity (log $Ko/w = 2.36$) will be bound to soil with high organic carbon content. The insecticide is also expected to bind to the clay minerals of the soil through the carboxyl functional group. Studies have reported that malathion is adsorbed in each homoion clay saturated with Na^+, Ca^{2+}, Cu^{2+}, Fe^{3+} or Al^{3+} by hydrogen bonding between the carbonyl oxygen atoms and hydration water shells of the cation [6]. Chopra and Arora [7] have reported the formation of co-ordination complexes with $FeCl_3$, $ZnCl_2$, $CuCl_2$ and $MnCl_3$ by malathion in the soil.

The TLC separation using ethyl acetate: petroleum ether (4:1) solvent mixture gave spots with R_f values at 0.55 for malathion, 0.20 for malaoxon and 0.203 for malathion carboxylic mono-acid. The compounds were confirmed by GC-MS. Formation of maoloxon, which is an oxygen analogue of malathion is formed as a result of photo-oxidation of malathion by UV-light at the wavelength of 2537Å [8]. Malathion mono carboxylic acid is formed by hydrolysis reactions, bacterial and fungal degradation of

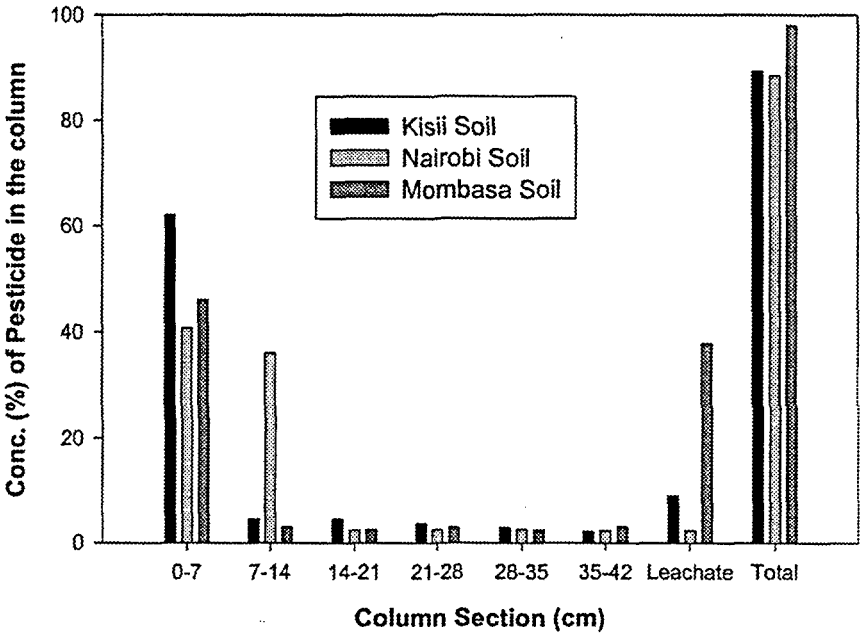

FIGURE 8 Leaching of malathion through the soil column.

malathion in the soil [9]. *N*-methyl *N*-trimethyl silyl-trifluoratamide, $[F_3CC(O)N(CH_3)Si(CH_3)_3]$ was meant to convert free acids to the trimethyl-silyl (TMS) derivatives. The conversion of the free acids to TMS derivatives is represented by the equation:

$$R\text{-}CH_3\text{-}COOH + F_3CC(O)N(CH_3)Si(CH_3)_3 \longrightarrow R\text{-}CH_3\text{-}C(O)O\text{-}Si(CH_3)_3$$

The GC-MS spectrometry confirmed the metabolites detected by the TLC and showed the presence of additional metabolites, diethyl mercaptosuccinate, O,O-dimethyl phosphorodithioate and the malaoxon mono carboxylic acid. The carboxylic acids were detected as TMS derivatives.

The fragmentation of TMS derivatives upon electron impact has been investigated [10]. The most important fragmentation in the mass spectra of TMS derivatives of aliphatic alcohols and carboxylic acids has been found to be the formation of M-15 ion [10]. The fragment was detected in the samples with the TMS derivatives. For instance, the TMS derivative of malathion monocarboxylic acid gave peaks at *m/z* 359 and 329. The peak at *m/z* 359 is due to M-15 resulting from the loss of a silylated methyl group and peak at *m/z* 359 is due to M-45 resulting from the loss of three silylated methyl groups. The TMS derivative of malaoxon monocarboxylic acid gave

peaks at *m/z* 343, 318 and 269. The peaks at *m/z* 343 and 318 are due to M-15 and M-30 respectively. In both cases the losses result from one and three silylated methyl groups for M-15 and M-45 respectively. The peak at *m/z* 269 is due to M-89 resulting from the loss of three silylated methyl groups and one molecule of CO_2. The compounds diethyl mercaptosuccinate and O,O-dimethyl phosphorodithioate are likely to form at the pH conditions of the soils, which were 4.9 and 6.1 for the Kisii and Nairobi soils, respectively. The two products are formed simultaneously from hydrolysis of the C—S bond of malathion at acidic pH conditions [11].

CONCLUSIONS

The rate of dissipation of malathion from the soil is very much influenced by rain through its leaching action and the organic content of the soil, which adsorbs the pesticide and shields it from leaching action. Micro-organisms which mineralised the bound methoxy-^{14}C malathion residues to $^{14}CO_2$ appear to thrive in moist conditions in the soil.

Acknowledgements

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References

[1] M.S. Mulla, L.S. Mian and J.A. Kawecki, Distribution, transport, and fate of the insecticides malathion and parathion. *Residue rev.*, **81**, 4–6 (1981).
[2] D.L. Mactaggart and S.O. Farwell, Analytical use of linear regression. Part 1: Regression procedures for calibration and quantitation. *J.AOAC internat.*, **75**, 594–606 (1992).
[3] Z.M. Getenga, J.I.O. Jondiko, S.O. Wandiga and E. Beck, Dissipation behaviour of malathion and dimethoate residues from soil and their uptake by Garden pea (*Pisum sativum*). *Bull. Environ. Contam. Toxicol.*, **64**, 359–367 (2000).
[4] B.S. Lartiges and P.P. Garrigues, Degradation kinetics of organophosphorus and organonitrogen pesticides in different waters under various environmental conditions. *Environ. Sci. Technol.*, **29**, 1246–1254 (1995).
[5] K. Rajukkannu, A. Basha, B. Habeebullah, P. Duraisamy and M. Balasubramanian, Degradation and persistence of DDT, HCH, carbaryl and malathion in soils. *Indian J. Environ. Health*, **27**, 237–243 (1985).
[6] U.K. Shahamat, Pesticides in the soil environments. Elsevier Scietnific Publishing Company, New York (1980).
[7] S.L. Chopra and C.L. Arora, Infrared spectra of the complexes of malaoxon with some anhydrous metal chlorides. *Pestic. Sci.*, **5**, 271–274 (1974).

[8] M.A. El-Dib, I.A. El-elaimy, A. Kotb and S.H. Elowa, Activation of *In Vivo* metabolism of malathion in male *Tilapia nilotica. Bull. Environ. Contam. Toxicol.*, **57**, 667–674 (1996).
[9] F.C. Albany and N.Y.F. Korte, Lectures held at the IUPAC third international congress of Pesticide Chemistry, Helsinki 3–9 July 1974, Georg Thieme Publishers, Stuttgart, **3**, 288–291 (1974).
[10] S. Safe and S. Hutzinger, Organophosphorus pesticides. Mass Spectrometry of pesticides and pollutants, CRC Press, Clevelent, 189 (1976).
[11] K. Inderjeet, R.P. Mathur, S.N. Tandom and P. Dureja, Identification of metabolites of malathion in plant, water and soil by GC-MS. *Biomed. Chromatogr.*, **3**, 352–355 (1997)