LEACHING, DEGRADATION AND FATE OF ^{14}C-MEXACARBATE IN COLUMNS PACKED WITH FOREST SOILS

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ABSTRACT

Leaching, degradation and fate of ^{14}C-mexacarbate (4-dimethylamino-3,5-xylyl N-methylcarbamate) were studied under simulated field conditions in the laboratory using hand-packed and fortified 30 cm soil columns containing sandy and clay loam forest soil profiles. Flooding and subsequent analysis of the soil horizons and the leachates, following extraction, combustion, liquid scintillation counting, and thin layer chromatography showed the presence of free, loosely bound and tightly bound residues. The bulk of the ^{14}C-material was strongly adsorbed onto the litter layers unless the columns were saturated with 454 g of the labelled mexacarbate in which case the radioactivity moved beyond the column length into the leachate, although most of the radioactivity was still retained in litter layers. Analysis of the sandy and clay loam litters and the corresponding leachates showed carbamate moieties, phenols and other metabolites, indicating that the chemical degraded rapidly. Incubation of the soil columns under aerobiosis for 30 and 45 days showed that the radioactivity was retained in the litter layers in both soil types. The persistence and degradation of the chemical as well as the quantity of metabolites formed were influenced by soil type and duration of incubation. The chemical was completely degraded under 15 d anaerobiosis (moist), and after 30 d aerobic (dry) incubation. Although on the average about 40% of the total applied radioactivity was found in the litter and humus layers, and in the leachates, no carbamate moiety was found in them; only some phenols and other water-soluble metabolites. Incubation of sterile and non-sterile litter samples fortified with ^{14}C-mexacarbate for 45 days produced negligible amounts of $^{14}CO_2$ in sterile samples, whereas the non-sterile sandy and clay loam litters yielded 25.3% and 18.9% $^{14}CO_2$ respectively, showing that soil microbes played an important role in the degradation of the chemical. Analysis of the litter samples after the incubation period confirmed the presence of free, loosely bound and tightly bound residues. The characteristics of the free and loosely bound residues were similar to the aerobic soil-column study conducted earlier. Breakdown of mexacarbate in forest soils is a rapid process and therefore it would in all likelihood be innocuous to the biota at the suggested use pattern of 70 g AI/ha. The metabolic pathway for its degradation in forest soils that is proposed, is consistent with the observed results.

RÉSUMÉ

Nous avons étudié en laboratoire la percolation, la dégradation et le devenir du mexacarbate (N-méthylcarbamate de diméthylamino-4 xylyle-3,5) marqué au ^{14}C, dans des lysimètres de 30 cm emplis à la main de loams forestiers sableux et argileux enrichis de ce produit, où les conditions étaient fidèles à celles du terrain. L'analyse des horizons et des percolats a révélé, après mouillage abondant, extraction, combustion, comptage par scintillation en milieu liquide et chromatographie sur couche mince, la présence de résidus libres, faiblement liés et fortement liés. Le gros des matières marquées était fortement adsorbé sur les constituants des couches de litière, sauf dans les cas où, le sol ayant été saturé avec 454 g de mexacarbate marqué, la radioactivité s'est retrouvée dans les percolats, même si, en grande partie, elle était retenue dans la litière. L'analyse des litières des différents loams et des percolats correspondants a mis en évidence des groupements carbamate, des phénols et d'autres métabolites, signes d'une dégradation chimique rapide. Le maintien des sols en aérobiose durant 30 et 45 jours a montré la rétention de la radioactivité dans la litière des deux loams. La rémanence et la dégradation de la matière chimique ainsi que la quantité des métabolites formés ont varié selon le sol et la durée de l'aérobiose. La dégradation a été complète après 15 j d'anaérobiose postérieurs à 30 j d'aérobiose. En moyenne, 40% de la radioactivité d'origine s'est retrouvée dans la litière, l'humus et les percolats, mais on n'a retrouvé dans ces milieux aucun groupement carbamate,

seulement quelques phénols et d'autres métabolites hydrosolubles. L'incubation, pendant 45 j, d'échantillons stériles et non stériles de litière, enrichis de mexacarbate marqué, s'est, dans le premier cas, accompagnée d'une production négligeable de $^{14}CO_2$, mais, dans le second, elle a donné, pour les loams sableux et argileux, 25,3 et 18,9% de $^{14}CO_2$ respectivement, ce qui met en évidence le rôle de premier plan des microbes du sol dans la dégradation. L'analyse des échantillons de litière, après l'incubation, a confirmé la présence de résidus libres, faiblement liés et fortement liés. Les caractéristiques des deux premiers types de résidus étaient semblables à celles qui avaient été observées en aérobiose dans une étude antérieure en lysimètres. La dégradation du mexacarbate dans les sols forestiers est rapide, et le produit, selon toutes les probabilités, serait inoffensif pour les organismes vivants s'il était utilisé à la dose conseillée de 70 g de matière active à l'hectare. Le cycle métabolique de sa dégradation dans les sols forestiers que nous suggerons est confirme aux resultats.

INTRODUCTION

Mexacarbate (4-dimethylamino-3,5-xylyl N-methylcarbamate), a broad-spectrum insecticide, was first introduced by the Dow Chemical Company under the trade name Zectran® in 1961 (Worthing, 1974). The chemical has potential for forestry use because of such desirable properties as high insecticidal activity (Prebble, 1975), short environmental persistence (Spencer, 1973) and low impact on most non-target species (Diamond et al., 1972). In view of these properties, the chemical is currently undergoing field trials in eastern Canada as a candidate material for large scale spruce budworm *(Choristoneura fumiferana*, Clem.) control operations.

Before a pesticide can be used in Canada, it must be registered under the Pest Control Products Act, which is administered by Agriculture Canada. Under the terms of this act, a pesticide must not have a significant adverse impact on environmental quality or on human health. In order to have such materials registered for forestry use in Canada, it is essential that we have an adequate understanding of their environmental safety. This knowledge is not only essential for registration purposes, but it is also useful in addressing provincial and public concerns relating to the use of such forest management tools. The present study is intended to elucidate the behavior of mexacarbate in forest soils and to aid in the evaluation of its safety in the soil environment.

The persistence and metabolic fate of mexacarbate in animals, plants, insects, water and sediments have been studied and reviewed extensively (Kuhr, 1970; Ryan and Knaak, 1971; Schlagbauer and Schlagbauer, 1972; Meikle, 1973; Kuhr and Dorough, 1976; Khan et al., 1976). Kazano et al. (1972) found that the persistence and metabolism of the chemical in agricultural soils were influenced by the soil type and Laskowski (1972) reported on the accumulation of demethylated, hydrolytic and oxidative products in soils caused by mexacarbate metabolism. Meikle (1973) postulated a variety of degradative pathways for the chemical in soils.

Most of the forest soils in Canada, in contrast with the bulk of agricultural soils, are unmodified virgin soils, rich in organic matter and living organisms. The soil profiles vary according to the nature and extent of microbial and chemical decompositions occurring in them (Armson, 1977). In such complex soil matrices, mobility, persistence and degradation of mexacarbate could be different from those occurring in agricultural soils. An understanding of these phenomena would not only help in the safe and effective use of the chemical in forestry but would also provide data for registration.

Controlled laboratory studies, using soil columns, have provided quantitative and definitive information on the mobility, persistence and metabolic fate of different pest control chemicals in agricultural soils (Weber, 1972; Lichtenstein et al., 1972; Starr and Cunningham, 1975; Hamaker, 1975; Grover, 1977; Sharom et al., 1980; Wild and Mazaheri, 1980; Bowman and Sans, 1982; Harvey, Jr., 1983). However, no data are available on mexacarbate in forestry soils. Therefore, the present study was undertaken with the following objectives.

1. To elute ^{14}C-labelled mexacarbate from fortified soil columns, hand-packed with forest soil profiles, to ascertain its adsorption and downward mobility.

2. To investigate the persistence and metabolic fate of mexacarbate in soil profiles under aerobic and anaerobic (moist) conditions.

3. To obtain a mass balance for the pesticide to account for its disposition.

The study was designed by following the guidelines proposed by the Environmental Protection Agency (EPA) (1981) in the U.S.A. Because of the inevitable differences in the use patterns of pesticides in agriculture and forestry, the experimental design required modifications in some areas to meet forestry needs.

MATERIALS AND METHODS

Soil samples

Two soil samples, a sandy loam and a clay loam, were used in the study. The sandy loam soil was collected from a mixed forest area (ratio of conifer to deciduous was approximately 2:1) north of Sault Ste. Marie (84°05'47" W; 46°44'52" N) and the clay loam, from a mixed forest area of nearly similar composition west of the city (84°26'36" W; 46°30'39" N). In both locations, trenches up to 4.0 m long, 0.6 m wide and 1.6 m deep, were dug to expose the vertical profiles of the soil. The average depth of the horizons from the forest floor, their thickness from the vertical cross-section of the profiles and the notations used for them in Canada (Armson, 1977) are given in Table 1.

The soil samples were collected in early April of 1984, when they were damp due to spring thaw. The sandy and clay loam horizons were collected separately using flat spades to slice them carefully across the exposed soil layers. After removing stones, fallen twigs, etc., each layer was carefully removed from different areas in the trench, pooled, stored in labelled plastic bags and brought to the laboratory for processing. In the laboratory each horizon, after the tiny stones and twigs were removed, was chopped in a Hobart food processor, passed through a 4 mm mesh sieve, mixed thoroughly and stored in sealed plastic bags at 4°C until use. The moisture contents of the samples were determined by drying 10 g duplicates of each sample at 105°C for 16 h in a thermostatic oven (AOAC, 1955). The characteristics and compositions of the processed soil horizons are summarized in Table 2.

Table 1. Notations used for forestry soil horizons, their average depth from forest floor and thickness

Name of horizon	Notation*	Sandy loam		Clay loam	
		Depth from surface (cm)	Thickness (cm)	Depth from surface (cm)	Thickness (cm)
Litter or organic layer	O,L,H,F	0	5	0	3
Humus layer	A	6	15	4	20
Mineral layer	B	21	45	24	45
Unaltered soil	C	66	55	69	50

* Armson (1977).

Table 2. Characteristics and compositions of forest soil horizons used in the study

Horizon	pH	Average moisture content (%)	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)
		Clay loam				
Litter	4.20	35	15.3	43.9	42.3	13.8
Humus	4.18	27	6.3	39.0	48.8	12.2
Mineral	4.48	22	2.8	62.7	28.7	8.6
Unaltered soil	5.52	14	0.7	66.5	28.7	4.8
		Sandy loam				
Litter	4.36	28	7.0	52.5	35.0	12.5
Humus	5.41	19	3.7	57.7	30.0	12.3
Mineral	4.86	17	0.9	29.4	54.6	16.0
Unaltered soil	5.33	15	0.1	95.0	2.5	2.5

Reagents

Radioactive mexacarbate labelled with ^{14}C in the 1-position of the benzene ring was supplied by the Union Carbide Agricultural Products Company. The specific activity was 20.3 mCi/mmol. Purity was 99.5%, with traces of unidentifiable impurities as evidenced by thin layer chromatography (TLC). Freshly prepared stock solution of the material in methanol was diluted according to the requirements of the experiment. All standard solutions were stored at 1°C in tightly sealed volumetric flasks covered with aluminum foil to prevent possible photodegradation.

The non-radioactive authentic compounds (mexacarbate and its potential degradation products listed in Table 3) were also supplied by Union Carbide. The purity of these compounds was nearly 99%, as evidenced by TLC.

All organic solvents were either pesticide-grade or distilled in glass. The inorganic reagents were of analytical grade and supplied by Fisher. Anhydrous Na_2SO_4 was heated overnight at 260°C prior to use. Aluminum oxide (Activity State I) for column chromatography was supplied by Merck.

Apparatus

A Sorvall Omni-Mixer was used for the extraction of mexacarbate and its metabolites from soil samples. Gas-liquid chromatographic (GLC) analyses were performed with a Hewlett-Packard HP 5710A NP-FID gas chromatograph. Reversed-phase high performance liquid chromatographic (HPLC) analyses were done using a Hewlett-Packard 1084B model instrument equipped with a UV detector (λ = 190-600 nm), micro-processor and an electronic integrator (HP 79850B). Thin-

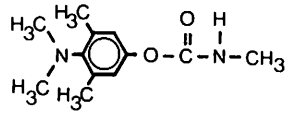
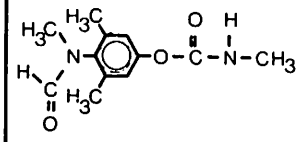
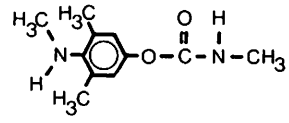
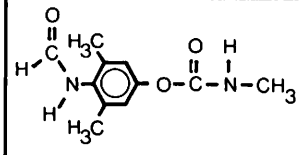
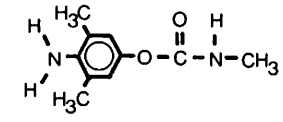
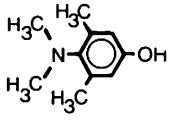
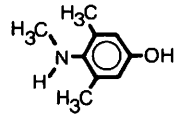
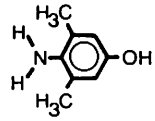
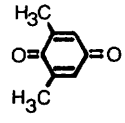
No.	CHEMICAL STRUCTURE	NAME (IUPAC USAGE)	ABBR.
1		4-Dimethylamino-3,5-xylyl N-methylcarbamate	M.
2		4-Methylformamido-3,5-xylyl N-methylcarbamate	MFM
3		4-Methylamino-3,5-xylyl N-methylcarbamate	MAM
4		4-Formamido-3,5-xylyl N-methylcarbamate	FAM
5		4-Amino-3,5-xylyl N-methylcarbamate	AM
6		4-Dimethylamino-3,5-xylenol	DMAX
7		4-Methylamino-3,5-xylenol	MAX
8		4-Amino-3,5-xylenol	AX
9		3,5-Dimethylpara-quinone	DMPQ

Table 3. Mexacarbate and some of its common metabolites used in the study

layer chromatography (TLC) with diethyl ether:hexane:ethanol; 77:20:3 (v/v) as the solvent system, was done by using pre-coated high performance (HP) silica gel plates containing a 254 nm fluorescent indicator (HP-7011-4, 10 cm x 10 cm - 200 µm thickness) supplied by J.T. Baker (Cat. No. C5451-162) and using the technique described by Sundaram et al. (1980). Radiocarbon contents in organo- and aqueous-soluble fractions from soils were determined with a Beckman LS9000 liquid scintillation counter (LSC) with built-in automatic external standardization to determine counting efficiency. Total and unextractable soil residues were combusted in a United Technologies Packard Model No. 306 sample oxidizer prior to LSC. Radioactive spots were detected by radioautography by placing developed TLC plates under X-ray film (Kodak X-Omat AR Film: XAR-2; 8" x 10") and holding them at -20°C for several hours, depending on the radioactivity. The spots from TLC plates were scraped free from the glass support and solvent extracted for LSC.

Soil column preparation

For studying the downward movement of mexacarbate and its fate under aerobic and anaerobic conditions in forest soil profiles, the method described by Weber (1972) was followed to simulate field conditions.

Fifty-cm-long soil columns were cut from 5.6 cm (i.d.) polyvinyl chloride (PVC) tubing of 0.5 cm thickness. A 30-cm length of the column served to hold the hand-packed simulated soil profile and the remainder was used as a reservoir for water during flooding of the column. Each column was lined inside with Cole-Parmer's "Protective Overlay" consisting of a layer of Teflon FEP® film on a vinyl backing to prevent adsorption of the chemical and its breakdown products onto the PVC column. The bottom end of the column was fitted with a metal screen (2 mm mesh) with a thin mat of glass wool over it (Fig. 1).

The thickness of the horizons in each soil column were adjusted as follows after considering the depth of each horizon in the natural soil profile.

Horizon	Depth (cm)	Weight of soil required (g)	
		Sandy loam	Clay loam
Litter (O,L,H,F)	10	200	250
Humus (A)	10	230	230
Mineral (B)	5	138	138
Unaltered soil (C)	5	154	154

The soil samples were allowed to thaw prior to packing. Each column was held vertically on a Thermolyne Maximix®. The soil sample from C horizon was added first with a spoon in small but equal amounts. After each addition the column was agitated on the mixer for uniform settling of soil particles. The soil layer was then gently pressed with a rubber plunger to attain uniform packing and to avoid channels which could cause mass flow of fluid in the soil column. This was repeated until the depths of all the four layers were completed. All the other columns were also packed in a similar manner.

Fortification, leaching and metabolic fate of mexacarbate in soil columns

The mobility of mexacarbate in the soil columns (sandy and clay loams) and its fate under aerobic (dry) and anaerobic (moist) conditions were studied in duplicate using the following concentration levels of the ^{14}C-material.

1. Mobility in soil columns:

   (a) Control
   (b) 5 µg of ^{14}C-mexacarbate
   (c) 15 µg of ^{14}C-mexacarbate
   (d) 25 µg of ^{14}C-mexacarbate
   (e) 40 µg of ^{14}C-mexacarbate
   (f) 57 µg of ^{14}C-mexacarbate
   (g) 227 µg of ^{14}C-mexacarbate
   (h) 454 µg of ^{14}C-mexacarbate

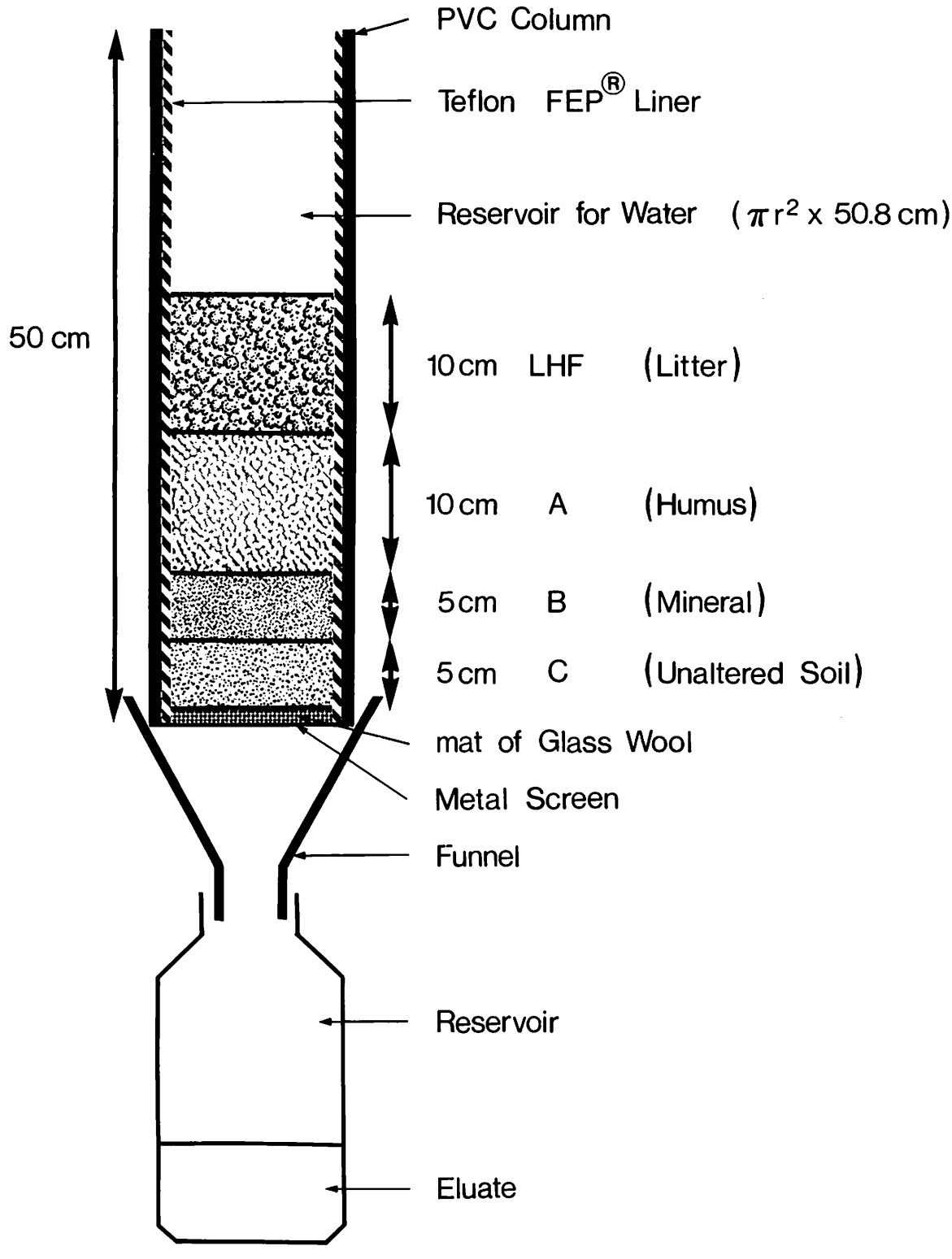


Fig. 1. Soil column for leaching studies.

2. Metabolic fate:

a) Control
b) 57 µg of ^{14}C-mexacarbate
c) 115 µg of ^{14}C-mexacarbate
d) 227 µg of ^{14}C-mexacarbate
e) 454 µg of ^{14}C-mexacarbate
f) 908 µg of ^{14}C-mexacarbate

The soil column (h) containing 454 µg level, was used to investigate the metabolic fate of the material following column leaching.

The soil columns were placed in an environmental chamber kept at 15°C and 80% relative humidity (RH) with a photoperiod of 16 h light and 8 h darkness, using an artificial lighting system (400W multivapor discharge lamps) to simulate sunlight. A day prior to fortification, each column was flooded with 1.251 L of distilled water to attain consistent moisture levels and to eliminate possible air-locks. On the following day, aliquot quantities of methanolic solution of standard mexacarbate, as listed above, were carefully added with a 1.0 mL graduated pipet, covering as much as possible the entire surface area of each soil column. The mexacarbate added was allowed to equilibrate with the soil for 8 h, and then each column was leached with 1.251 L of distilled water. This was done according to the EPA guidelines by using the volume of water corresponding to 50.8 cm times the cross-sectional area of the column [50.8 cm x 3.14 x (2.8 cm)^2 = 1.251 L]. The time taken to complete the leaching process varied according to the soil type. On the average, the sandy loam took 13 h and the clay loam took about 19 h. Because of the swelling property of the soil colloids (Graham, 1964; Haque, 1975), infiltration of water was slow. The leachates from columns were collected in Teflon® bottles and stored in a freezer prior to extraction and analysis. The soil columns used for the leaching study were capped with aluminum foil and were stored at -20°C until analyzed. The columns used in the metabolic studies under aerobiosis, or moist conditions, were left undisturbed for 30 d in the environmental chamber. One set, containing duplicate columns in each concentration and in each type of soil, was covered with aluminum foil and frozen. The other set was left undisturbed for another 15 d for comparison with the columns maintained under anaerobiosis. After 30 d, the columns used for the anaerobic study were flooded daily with 49.2 mL of water for 15 d, as per the EPA guidelines. The volume of water used during this period was equal to the volume of the soil column (739 cm^3). Upon completion of the experiment, the eluates and the columns were frozen until analysis.

Degradation rates of ^{14}C-labelled mexacarbate in soils (litter layer)

Using the simple flow-through apparatus developed by Goswami and Koch (1976) (Fig. 2), the rate of volatilization and evolution of $^{14}CO_2$ from the fortified chemical in autoclaved and non-autoclaved litter layers were studied under aerobic conditions to carry out a mass balance at the end of the study. This was done to account for the overall disposition of the chemical, including the microbial activity in the soil.

Thirty-gram portions of litter samples (sandy and clay loams) were fortified with 30 µg of methanolic solution of ^{14}C-mexacarbate. After allowing the solvent to evaporate, the soil was mixed thoroughly to distribute the chemical evenly. The apparatus was kept in the same environmental chamber after covering the sides of the soil layer in the Erlenmeyer flask with aluminum foil to prevent any photodegradation. The $^{14}CO_2$ that evolved was absorbed in vials containing Carbo-Sorb® (United Technologies Packard) at intervals of time up to 45 d by flushing the system with air (100 mL/min) for 10 min each time, and counting the activity. The moisture content of the soil was maintained at the same value as that of the litter in the soil columns during the entire period of the study. At the end of the degradation study, the residues in the soil samples in the Erlenmeyer flask were separated and analyzed.

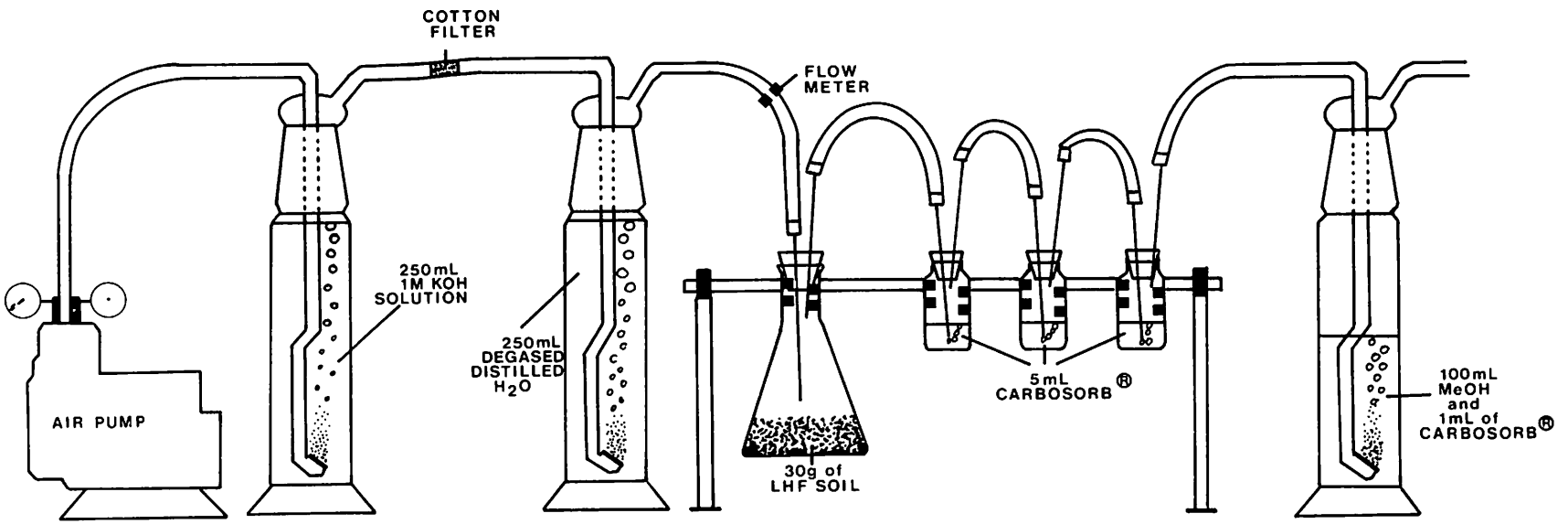


Fig. 2. Apparatus for trapping $^{14}CO_2$ from the degradation of ^{14}C-labelled mexacarbate in soil.

Soil analysis

At the time of analysis, each soil column used in the leaching or metabolic study was allowed to thaw and was then cut longitudinally. The soil horizons from each were separated, transferred individually to glass mortars and mixed well. Ten-gram aliquots in duplicate were used for moisture determination. Fifty-gram aliquots were taken for the extraction using successively water, dichloromethane, aqueous-methanolic HCl (0.1M), and aqueous-methanolic NaOH (0.1M), as described in the flow chart (Table 4). Soil combustion was done in the Packard Oxidizer and the samples were counted in the liquid scintillation counter to separate the radiocarbons into free (F), loosely bound (L) and tightly bound (T) portions. All experiments were carried out in duplicate. Spiked soil samples used in studying the rate of evolution of $^{14}CO_2$ from the ^{14}C-labelled mexacarbate were also analyzed similarly after the experiment was completed.

The organic extracts were concentrated and analyzed by TLC as described by Sundaram et al. (1980) to separate and identify the parent compound and its metabolites. The authentic pure samples acted as the reference standards and the R_f values, obtained for the solvent system used, are given in Table 5. The radioactivity was localized by scraping the silica gel into counting vials and was measured in the liquid scintillation counter with Insta-Gel® (United Technological Packard) universal scintillation cocktail. Aliquots of the aqueous layers (Table 4) were assayed similarly for radioactivity using the above scintillation solution. Except for TLC analysis of the aqueous extracts with CH_2Cl_2, no attempts were made to characterize water-soluble radioactivity. The unextractable tightly bound radioactivity (Table 4) in different soil layers was determined after 0.30 g aliquots of the soil residues were subjected to combustion in the Packard Oxidizer, the $^{14}CO_2$ was absorbed in Carbo-Sorb®, and the activity was counted in the LSC.

In situations where high concentrations of the parent compound were used for fortification, mexacarbate and its possible metabolites were examined by GLC and HPLC; but in most cases the materials were found to be non-chromatographable. The use of microcolumn (10 cm x 0.8 cm i.d. Pasteur pipet) cleanup with Al_2O_3 as the adsorbant, and ethyl acetate (10 mL) as the eluant, helped to minimize tailing of spots and interferences in TLC.

RESULTS AND DISCUSSION

Mobility and distribution of mexacarbate in soil columns

The extent of mobility and distribution of mexacarbate and its degradation products through sandy and clay loam soil columns at fortification levels ranging from 5 μg to 454 μg are given in Tables 6 and 7. The results are expressed as the percent of applied radioactivity recovered from each soil horizon, based on oven-dry (AOAC, 1955) soil weights. The minimum detection limit (MDL) in the LSC was found to be about 200 dpm, i.e., twice the background level for 1 g of dry soil. All samples were counted for at least 10 min. The minimum detection limit for the overall procedure, in terms of μg of fortified material per g of oven-dry soil, was calculated using the conversion factor 0.2 x 10^6 dpm per μg of ^{14}C-material. It was found to be 0.001 μg or 1 ng of the applied material per g of oven-dry soil.

The results presented in Tables 6 and 7 are the mean of two soil columns for each concentration with S.D. (±) < 10% of the mean. The data indicate that up to the 25 μg level of fortification, most radiocarbon moieties did not usually move downward in the columns beyond the 10 cm litter layer. At 227 μg level, the radioactivity moved down to the humus and mineral layers in sandy loam but only to the humus layer in clay loam. At the 454 μg level, the radioactivity moved farther down the 30 cm soil column to include all four soil horizons. The leachates obtained from sandy and clay loams contained respectively, 10.41 and 5.83% of the radioactivity, indicating that adsorption of the chemical in the lipophilic

TABLE 4

Separation procedures for the metabolites of mexacarbate in soil

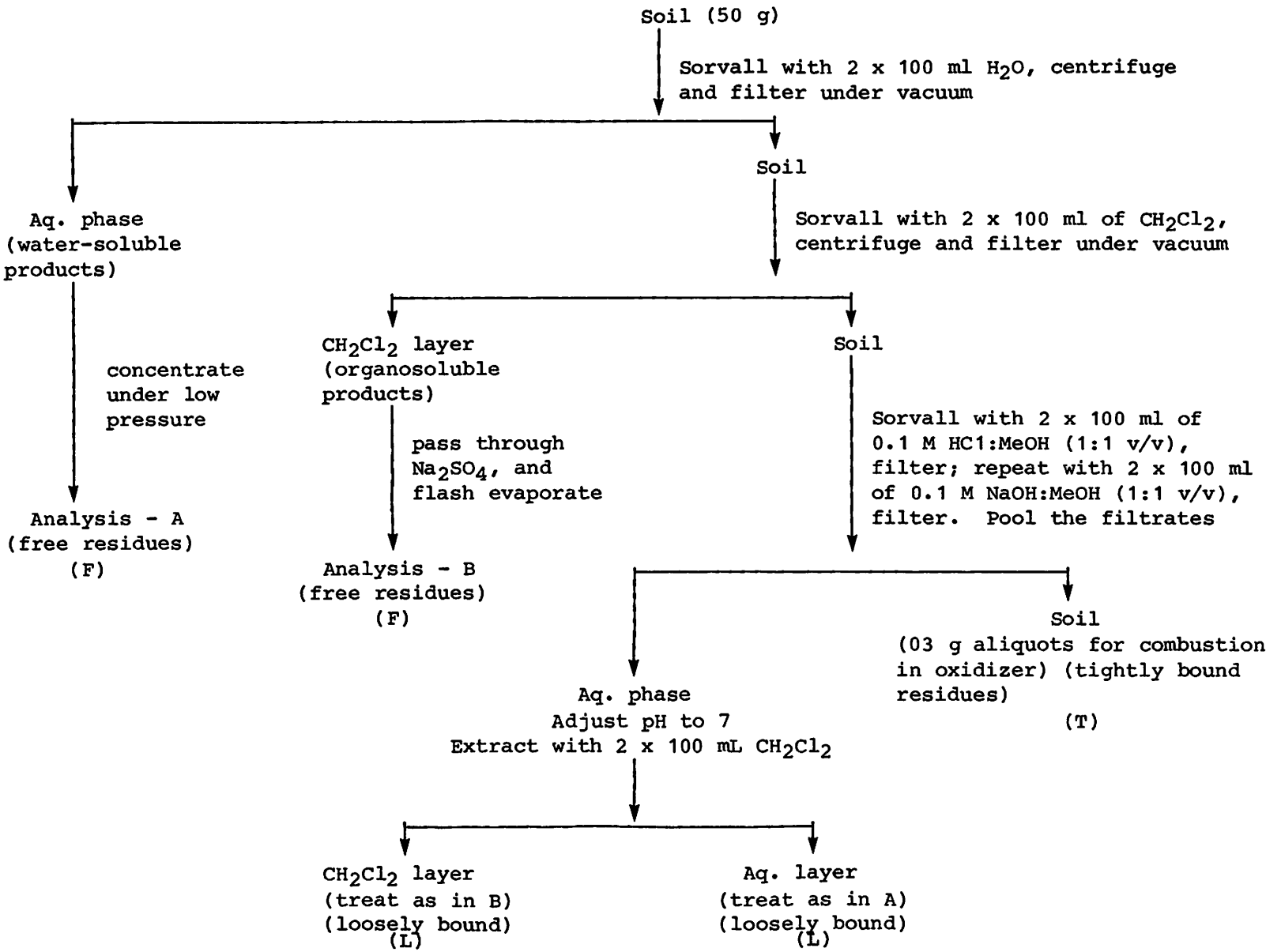


Table 5. R_f values of authentic compounds in thin layer chromatography

Name of the compound (IUPAC usage)	Abbr.	R_f (Ether:hexane:ethanol - 77:20:3 v/v%)
4-Dimethylamino-3,5-xylyl N-methylcarbamate	M	0.65
4-Methylformamido-3,5-xylyl N-methylcarbamate	MFM	0.26
4-Methylamino-3,5-xylyl N-methylcarbamate	MAM	0.36
4-Formamido-3,5-xylyl N-methylcarbamate	FAM	0.12
4-Amino-3,5-xylyl N-methylcarbamate	AM	0.31
4-Dimethylamino-3,5-xylenol	DMAX	0.78
4-Methylamino-3,5-xylenol	MAX	0.39
4-Amino-3,5-xylenol	AX	0.40
3,5-Dimethylparaquinone	DMPQ	0.80

sites of the soil matrice is higher in clay loam as than in the sandy loam (Swanson et al., 1954; Geissbuhler, 1969; Helling, 1971; Farmer and Aochi, 1974; Weed and Weber, 1974). Consequently, the rate of release and downward movement of the material in the clay loam is also low. Hamaker et al. (1966) showed a qualitative inverse relationship between adsorption and leaching.

Generally, the organo- and water-soluble free residues were slightly higher (36.61%) in the sandy loam litter compared to the clay loam (33.00%). On the other hand, loosely bound (HCl/CH_3OH and $NaOH/CH_3OH$ extractable) and tightly bound residues were higher in the clay loam litter (10.54% and 45.19%) compared to the sandy loam (5.04% and 36.05%). Similar trends were also observed in the radioactivity of leachates. Adsorption appears to be lower in sandy loam than in clay loam (Geissbuhler, 1969). It is known (Edwards, 1972) that clay loams have a much larger internal surface area than sandy soils, and this could be the reason for the greater amounts being retained. Several investigators (Hill et al., 1955; Eshel and Warren, 1967; Gray and Weierich, 1968) have also shown the inverse relationship between adsorption and movement of organic chemicals by water through soil.

The radioactive compounds identified by TLC from the pooled organo- and water-soluble (free residues) and loosely bound fractions from the litter layers of both types of soils at the 454 µg fortification level and of the leachates are given in Table 8. Although the pattern of fragments

Table 6. Mobility and distribution of mexacarbate in sandy loam soil columns

Fortification level of ^{14}C-mexacarbate* (µg)	Percent distribution and recovery of radioactivity**													
	Soil horizon													
	Litter			Humus			Mineral			Unaltered soil				
	F+	L+	T+	F	L	T	F	L	T	F	L	T	Leachate	Total
5	35.48	4.10	40.38	ND++	ND	ND	ND	ND	ND	ND	ND	ND	ND	79.96
15	36.71	5.27	41.01	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	82.99
25	37.98	4.51	36.96	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	79.45
40	41.38	6.48	40.73	0.11	ND	0.24	ND	ND	ND	ND	ND	ND	ND	88.94
57	36.53	5.95	35.06	3.42	2.08	3.26	ND	ND	ND	ND	ND	ND	ND	86.30
227	36.44	4.29	30.61	6.23	2.86	5.13	1.54	0.09	1.18	ND	ND	ND	ND	88.37
454	31.72	4.66	27.62	4.71	1.13	5.24	0.70	0.14	0.99	0.19	0.04	0.44	10.41	87.99
Average	36.61	5.04	36.05											84.86

* 1 µg = 0.2 x 10^6 dpm.

** Radioactivity (dpm) applied to the oven-dry soil is referred to as 100%. The values represent the mean of duplicate determinations with S.D. (±) <10% of the mean.

+ The letters F, L and T refer to free, loosely bound and tightly bound residues in soil.

++ ND = not detectable; detection limit is the radioactivity corresponding to 0.001 µg or 1 ng of the applied ^{14}C-materials per g of oven-dry soil.

Table 7. Mobility and distribution of mexacarbate in clay loam soil columns

Fortification level of ^{14}C-mexacarbate* (µg)	Percent distribution and recovery of radioactivity**													
	Soil horizon													
	Litter			Humus			Mineral			Unaltered soil				
	F+	L+	T+	F	L	T	F	L	T	F	L	T	Leachate	Total
5	34.34	11.16	42.91	ND++	ND	ND	ND	ND	ND	ND	ND	ND	ND	88.41
15	34.40	11.38	45.51	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	91.29
25	35.01	11.73	47.70	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	94.44
40	33.28	10.47	46.28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	90.03
57	33.22	11.48	47.73	0.11	0.14	0.52	ND	ND	ND	ND	ND	ND	ND	93.20
227	30.63	9.73	44.79	2.01	0.88	4.13	ND	ND	ND	ND	ND	ND	ND	92.17
454	30.11	7.86	41.41	2.13	0.79	4.23	0.27	0.43	0.71	0.11	0.32	0.46	5.83	93.66
Average	33.00	10.54	45.19											91.89

See footnotes in Table 6.

Table 8. Average levels of extractable radiocarbon from the litter layers of sandy and clay loam soils and the column leachates at the fortification level of 454 µg of ^{14}C-mexacarbate

Fraction	Sandy loam		Clay loam	
	Compounds with R_f values	Radioactivity isolated by TLC† (%)	Compounds with R_f values	Radioactivity isolated by TLC†† (%)
Free and loosely bound	Carbamates: MFM (0.26), MAM (0.36), AM (0.31) and M (0.65)	18	Carbamates: MFM (0.26), MAM (0.36), AM (0.31) and M (0.65)	24
	Phenols: AX (0.40) and DMAX (0.78)	7	Phenols: AX (0.40) and DMAX (0.78)	6
	Others: U1* (0.10), U2 (0.48), U3 (0.55) and U4 (0.81)	10	Others: U1 (0.10), U2 (0.48), U3 (0.55), U4 (0.81) and U5 (0.86)	7
Leachate	Carbamates: MFM (0.26)	1	Carbamates: MFM (0.26), MAM (0.36) and AM (0.31)	1
	Phenols: AX (0.40) and DMAX (0.78)	4	Phenols: AX (0.40) and DMAX (0.78)	1
	Others: U1 (0.10) U2 (0.48) and U4 (0.81)	5	Others: U1 (0.10), U2 (0.48) and U3 (0.55)	3

* U = unidentifiable 1, 2, 3, etc.
† Average values of radioactivities recorded in Table 6.
†† Average values of radioactivities recorded in Table 7.

formed was the same in both types of litter and leachate, the nature and quantity of moieties formed were different. More hydroxylated and polar compounds were found in litter and leachate of the sandy loam compared to those in the clay loam. The liquid scintillation counting of the eluted TLC spots of the carbamate fractions (Table 8) of both types of litter layers contained detectable levels of intact carbamate moieties. The data in Table 8 indicate that the pathway of mexacarbate degradation in sandy and clay loam soils was about the same when the flooding was done under similar experimental conditions.

The radioassay of the soil columns (Tables 6 and 7) clearly demonstrated that mexacarbate and its metabolites were strongly linked to the litter, possibly through several types of soil-insecticide (mexacarbate) bonds (Harris, 1966; Hamaker and Thompson, 1972; Green, 1974; Stevenson, 1982), and hardly moved through the soil beyond the 30 cm length of the column, unless overloaded with a very high level of the insecticide (454 µg), causing mass flow down the column. The solubility of mexacarbate in water is only about 100 ppm at 25°C (Marquardt, 1964) and its poor leachability is attributable to its strong adsorption onto the soil matrices. This is in agreement with the observations of Bailey and White (1964) who found an inverse relationship between leachability and water-solubility. The leachates contained a higher percent of phenolic and unidentifiable compounds as metabolites compared to the parent material. In view of the results obtained, it is highly unlikely that mexacarbate will be leached deep into the soil layers by percolating water.

In a recent aerial spray trial in New Brunswick using a water-based formulation of mexacarbate at the operational dosage rate of 70 g AI/ha, the maximum deposit obtained on the forest floor was only 9.4% (Sundaram and Nott, 1985). At this rate of deposition, the maximum level of mexacarbate on the top surface area (24.64 cm^2) of the soil column would only be 1.6 µg. The maximum deposit obtained with the oil-based formulation, however, was 14.7%, and this would provide a value of 2.5 µg on the top surface of the soil column. The present study has demonstrated that at these fortification levels in the soil column, the chemical would not move beyond the litter horizon of the forest soil profile. Assuming a worst case situation, even if all the sprayed material reached the forest floor, the value would only increase to 17.25 µg, which again is too low for downward movement beyond the litter horizon. The tendency for negligible downward movement coupled with rapid degradation of the chemical to form non-carbamate moieties indicates that it is highly unlikely to be a threat to non-target biota in the aquatic and soil environment.

Fate of mexacarbate in soil columns under aerobic and anaerobic conditions

Distribution of radioactivity in the two types of soil columns dosed with 57 to 908 µg ^{14}C-mexacarbate and incubated under aerobic and anaerobic conditions, is given in Tables 9 to 12. Under aerobic conditions only the litter layer contained radioactivity (Tables 9 and 10), whereas under anaerobic conditions the radioactivity penetrated downward to the humus layers and to the leachates (Tables 11 and 12) of both soil types. The data generally indicate that the concentration of mexacarbate did not influence the relative amounts of free and bound residues formed. Similar observations have been made by others (Fleming and Maines, 1954; Gallaher and Evans, 1961) with organochlorines. Most of the radioactivity was found as "bound residues" in the litter layers of both types of soils under aerobic and anaerobic conditions. No activity was found in the mineral and unaltered soil layers showing that the chemical and its metabolites have a greater affinity for organic surfaces than for mineral surfaces (Scott and Weber, 1967).

In sandy and clay loam soils, radioactivity decreased appreciably with lapse of time due to the degradation of ^{14}C-mexacar-

Table 9. Fate and distribution of mexacarbate under aerobic conditions in sandy loam soil after 30 and 45 days of incubation

Fortification level of ^{14}C-mexacarbate* (μg)	Percent distribution and recovery of radioactivity*												Total
	Soil horizon												
	Litter			Humus			Mineral			Unaltered soil			
	F	L	T	T	L	T	F	L	T	F	L	T	
57	10+ (8)+	15 (12)	38 (36)	ND*	ND	ND	ND	ND	ND	ND	ND	ND	63 (56)
115	15 (13)	23 (18)	37 (34)	ND	ND	ND	ND	ND	ND	ND	ND	ND	75 (65)
227	11 (9)	17 (14)	36 (33)	ND	ND	ND	ND	ND	ND	ND	ND	ND	64 (56)
454	16 (15)	15 (13)	35 (29)	ND	ND	ND	ND	ND	ND	ND	ND	ND	66 (57)
908	15 (14)	19 (15)	34 (29)	ND	ND	ND	ND	ND	ND	ND	ND	ND	68 (58)
Average	13 (12)	18 (14)	36 (32)										67 (58)

* See footnotes in Table 6.

+ Radioactivity values without parenthesis are for 30 d post-application; with parenthesis are for 45 d post-application.

Table 10. Fate and distribution of mexacarbate under aerobic conditions in clay loam soil after 30 and 45 days of incubation

Fortification level of ^{14}C-mexacarbate* (μg)	Percent distribution and recovery of radioactivity*												Total
	Soil horizon												
	Litter			Humus			Mineral			Unaltered soil			
	F	L	T	T	L	T	F	L	T	F	L	T	
57	11+ (9)+	14 (12)	44 (42)	ND*	ND	ND	ND	ND	ND	ND	ND	ND	69 (63)
115	12 (10)	16 (14)	48 (45)	ND	ND	ND	ND	ND	ND	ND	ND	ND	76 (69)
227	11 (9)	12 (10)	46 (43)	ND	ND	ND	ND	ND	ND	ND	ND	ND	69 (62)
454	8 (6)	15 (13)	51 (48)	ND	ND	ND	ND	ND	ND	ND	ND	ND	74 (67)
908	11 (9)	15 (13)	47 (46)	ND	ND	ND	ND	ND	ND	ND	ND	ND	73 (68)
Average	11 (9)	14 (12)	47 (45)										72 (66)

* See footnotes in Table 6.

\+ Radioactivity values without parenthesis are for 30 d post-application; with parenthesis are for 45 d post-application.

Table 11. Fate and distribution of mexacarbate under anaerobic (moist) conditions for 15 days in sandy loam soil columns following aerobic incubation for 30 days

Fortification level of ^{14}C-mexacarbate* (μg)	Percent distribution and recovery of radioactivity													
	Soil horizon													
	Litter			Humus			Mineral			Unaltered soil				
	F	L	T	F	L	T	F	L	T	F	L	T	Leachate	Total
57	5	4	21	1	1	1	ND	ND	ND	ND	ND	ND	2	35
115	4	6	19	1	2	1	ND	ND	ND	ND	ND	ND	1	34
227	4	6	20	1	3	2	ND	ND	ND	ND	ND	ND	1	37
454	6	7	19	1	2	2	ND	ND	ND	ND	ND	ND	2	39
908	4	4	17	1	3	2	ND	ND	ND	ND	ND	ND	2	33
Average	5	5	19	1	2	2							2	36

* See footnotes in Table 6.

Table 12. Fate and distribution of mexacarbate under anaerobic (moist) conditions for 15 days in clay loam soil columns following aerobic incubation for 30 days

Fortification level of ^{14}C-mexacarbate* (μg)	Percent distribution and recovery of radioactivity													
	Soil horizon													
	Litter			Humus			Mineral			Unaltered soil				
	F	L	T	F	L	T	F	L	T	F	L	T	Leachate	Total
57	2	6	25	1	2	4	ND	ND	ND	ND	ND	ND	2	42
115	3	6	27	1	2	6	ND	ND	ND	ND	ND	ND	1	46
227	2	4	24	1	2	3	ND	ND	ND	ND	ND	ND	3	39
454	4	6	25	1	3	3	ND	ND	ND	ND	ND	ND	2	44
908	3	5	24	2	3	3	ND	ND	ND	ND	ND	ND	3	43
Average	3	5	25	1	2	4							2	43

* See footnotes in Table 6.

Table 13. Average levels of extractable radiocarbon from litter layers of sandy and clay loam soils and the column leachates after different intervals of aerobic (dry) and anaerobic (moist) incubations.

	Compounds found in TLC spots and their mean radioactivity					
	Sandy loam			Clay loam		
Fraction	30 d aerobic	45 d aerobic	30 d aerobic + 15 d anaerobic	30 d aerobic	45 d aerobic	30 d aerobic + 15 d anaerobic
Free and loosely bound	Carbamates	Carbamates	Carbamates	Carbamates	Carbamates	Carbamates
	MFM, MAM, AM and M 14	MAM, AM and M 9	Not detectable	MFM, MAM, FAM, AM and M 12	MFM, MAM, AM and M 11	Not detectable
	Phenols	Phenols	Phenols	Phenols	Phenols	Phenols
	DMAX, AX and MAX 12	DMAX, and AX 14	DMAX, and AX 3	DMAX, AX and MAX 11	DMAX, AX and MAX 8	DMAX and AX 5
	Others	Others	Others	Others	Others	Others
	DMPQ* and unidentifiables 3	DMPQ and unidentifiables 3	Unidentifiables 8	Unidentifiables 3	Unidentifiables 3	Unidentifiables 5
Leachate	-	-	Unidentifiable (polar) 2	-	-	Unidentifiable (polar) 2

* R_f value 0.80.

bate. The longer the material remained in the column, the lower was the radioactivity of free, loosely bound and tightly bound residues (Tables 9 and 10), suggesting that the degradation products are unlikely to accumulate in soils. Under aerobic conditions, the average percent values of these for sandy loam soils at 30 and 45 d intervals were 13 and 12, 18 and 14, and 36 and 32 respectively for free, loosely bound and tightly bound radioactivity. Similar values for the clay loam were 11 and 9, 14 and 12, and 47 and 45, indicating that the extent of degradation, and the amount of free and bound residues varied with soil type (Edwards, 1972; Adams, Jr., 1973). The loss of radioactivity was usually less under dry (aerobic) conditions than under moist (anaerobic) conditions, indicating that the degradation of mexacarbate was much less in dry soils compared to moist soils (Harris, 1964; 1972). Degradation occurred much less also in the clay loam, and the total residues were generally higher (72 and 66%) compared to the sandy loam (67 and 58%) during the two study periods (Tables 9 and 10). Similar trends were observed under anaerobic conditions, but the rate of degradation was usually higher in both types of soils, and consequently the average total levels of activity found after 45 d for sandy and clay loam soils including the leachates were 36 and 43% (Tables 11 and 12) respectively compared to the activity of 58 and 66% under aerobic conditions (Tables 9 and 10). A comparison of bound residues in the sandy loam litter layer at 30 and 45 d intervals under moist conditions showed that a slight decrease from 36 to 32% occurred, whereas in the litter layer of clay loam under similar situations, the decrease was insignificant, i.e., from 47 to 45%. Similarly, under anaerobiosis the bound residue levels between sandy and clay loam litters were respectively 19 and 25% (Tables 11 and 12). These findings indicate that the litter matrix in the clay loam has a tendency to form more bound residues than the sandy loam litter (Swanson et al., 1954; Helling, 1971; Farmer and Aochi, 1974; Weed and Weber, 1974).

In both soils, the average activity found in the leachates was only about 2% of the fortification level (Tables 11 and 12), showing the presence of small amounts of water-soluble polar metabolites. Attempts were made to identify the organo- and water-soluble radioactive decomposition products from litter layers of both types of soils by TLC followed by autoradiography and LSC of the eluted silica gel scrapings. Interferences such as spot tailing and spot broadening were encountered during the TLC studies, even after the solvent-partitioning and Al_2O_3 column cleanup of the eluates. The relative amounts of degradation products found in both litter layers of sandy and clay loam soils under aerobiosis were higher than under anaerobiosis (Table 13), perhaps due to degradation and dissipation. Some of the spots were unidentifiable because of overlaps but, generally, compounds with carbamate linkage decreased with time; and after 15 d of anaerobiosis, no compound with carbamate linkage was found (Table 13). Sporadic presence of overlapping spots with R_f values of 0.81 and 0.80 were found in soils under aerobic conditions. The spot with 0.80 corresponded with the quinone DMPQ (Tables 3 and 13) but the spot with R_f value 0.81 was not identified, although it could be its reduction product (3,5-dimethylhydroquinone). The radioautography of the spotted radioactivity on the TLC plates showed that appreciable amounts of polar non-identifiable metabolites were present near the origin (Table 13). The concentrations of these metabolites increased with time, and the increase was more pronounced under anaerobic conditions. Attempts to separate and characterize them by GLC and HPLC techniques were not successful. Similarly, the TLC spotting of solvent (CH_2Cl_2)-extracted leachates from the soils under anaerobiosis also contained detectable levels of unidentifiable polar metabolites only, presumably ring-hydroxylated water-soluble moieties of the phenols, but they were not characterized further. In conclusion, the extractable radiocarbons in sandy loam soil under aerobic conditions (30 d and 45 d) were slightly higher (29 and 26%) than the clay loam soil (26 and 22%) (Table 13), but not significantly different and contained more phenolic type metabolites including the quinone (DMPQ). This indicates that the oxidative and hydrolytic

pathways of degradation for the chemical are more predominant in sandy soils than in clay loams. Relative amounts of degradation products found in individual soil columns also showed that the concentration of the chemical had little influence on its persistence and rate of degradation, as observed by Edwards (1972) with other insecticides. However, the type of soil used, sandy versus clay loam, seems to have affected the rate of degradation, agreeing with the finding of Lichtenstein and Schulz (1960). The organo- and water-soluble radiocarbon and the leachates from both soils under 45 d anaerobic conditions did not contain any identifiable carbamate and phenolic moieties.

Degradation of ^{14}C-mexacarbate in the litter samples of sandy and clay loam soils

The results obtained from the degradation of ^{14}C-mexacarbate in the sterile and non-sterile litters following incubation under aerobiosis for 45 d are given in Tables 14 and 15. Approximately 96 and 99% of the applied radioactivity was recovered intact after 45 d incubation under sterile conditions from sandy and clay loam litters respectively. Only about 4 and 2% respectively, were lost from the sandy and clay loam litters as volatile products. Nearly 29% of the applied radioactivity was found as bound residues in sandy loam, compared to 37% in clay loam. The bulk of the

Table 14. Percent radioactivity evolved as $^{14}CO_2$ under aerobiosis after fortification of sandy and clay loam litters with ^{14}C-mexacarbate at 1.0 ppm level

Time (days)	Sandy loam		Clay loam	
	Autoclaved	Non-autoclaved	Autoclaved	Non-autoclaved
0.0	ND	ND	ND	ND
0.5	ND	2.6 ± 1.0	ND	2.3 ± 0.9
1.0	ND	3.4 ± 0.9	ND	2.7 ± 0.6
2.0	0.3 ± 0.2	5.2 ± 1.3	ND	3.8 ± 0.7
3.0	0.3 ± 0.3	6.6 ± 1.5	0.1 ± 0.1	5.1 ± 1.1
5.0	0.5 ± 0.3	7.6 ± 1.4	0.3 ± 0.2	6.2 ± 1.3
7.0	0.7 ± 0.4	12.6 ± 1.7	0.5 ± 0.4	7.2 ± 1.9
10.0	0.9 ± 0.6	15.7 ± 1.8	0.7 ± 0.3	9.8 ± 1.8
13.0	1.3 ± 0.5	18.0 ± 1.6	0.8 ± 0.3	12.2 ± 1.4
16.0	1.9 ± 0.6	20.2 ± 1.8	0.9 ± 0.6	14.0 ± 1.8
20.0	2.2 ± 0.8	21.5 ± 2.0	1.1 ± 0.7	15.3 ± 1.1
25.0	2.7 ± 0.8	23.8 ± 2.1	1.2 ± 0.6	17.1 ± 1.1
30.0	3.0 ± 1.2	25.1 ± 1.8	1.3 ± 0.5	18.4 ± 1.8
35.0	3.3 ± 0.8	25.2 ± 2.4	1.4 ± 0.6	18.7 ± 2.4
40.0	3.6 ± 0.9	25.2 ± 2.7	1.6 ± 0.5	18.8 ± 2.6
45.0	3.8 ± 1.2	25.3 ± 2.9	1.8 ± 0.3	18.9 ± 2.5

Table 15. Average levels of accountable (TLC) radiocarbon after 45 days of incubation in sterile and non-sterile sandy and clay loams litters fortified with 1.0 ppm of ^{14}C-mexacarbate

	Sandy loam litter				Clay loam litter			
Fraction	Compounds* (sterile litter)	% of initial activity	Compounds (non-sterile litter)	% of initial activity	Compounds (sterile litter)	% of initial activity	Compounds (non-sterile litter)	% of initial activity
Free and loosely bound	M (0.65)	46	M (0.65)	1	M (0.65)	50	M (0.65)	5
	MFM (0.26)	2	MFM (0.26)	1	MFM (0.26)	1	MFM (0.26)	1
	MAM (0.36)	5	MAM (0.36)	5	MAM (0.36)	3	MAM (0.36)	8
	AM (0.31)	2	FAM (0.12)	1	AM (0.31)	1	FAM (0.12)	1
	DMAX (0.78)	7	AM (0.31)	1	DMAX (0.78)	2	AM (0.31)	2
	Unidenti-fiable (0.55, 0.81)	1	DMAX (0.78)	6	Unidenti-fiable (0.48, 0.55, 0.81)	3	DMAX (0.78)	7
			MAX (0.39)	1			MAX (0.39)	1
			AX (0.40)	1			AX (0.40)	1
			Unidenti-fiable (0.48, 0.55, 0.80, 0.81)	8			Unidenti-fiable (0.48, 0.55, 0.81)	12
Bound	-	29	-	41	-	37	-	45
Volatiles+		4		25		2		19
Total		96		91		99		99

* R_f values of compounds are given in parenthesis.

+ $^{14}CO_2$ + others.

radioactivity present in the free residues was intact mexacarbate with detectable (by TLC) levels of MFM, MAM, AM and DMAX, showing that in the sterile litter layer of soils, breakdown of the insecticide was low. In the non-sterile litter layer of sandy loam soil, free, loosely bound and tightly bound radioactivities were respectively 14, 10 and 41%. About 25% of material disappeared as volatile CO_2 by the end of the experimental period. Similarly, in the clay loam litter, 10, 22 and 45% were present as free, loosely bound and tightly bound residues, respectively. Only 19% of the material was lost as CO_2, thus accounting for 99% of the fortified material, compared to 91% in the former case. From the data in Table 14, it is apparent that the degradation of the chemical in non-sterile soil was faster than in sterile soil. The breakdown of the material was non-linear, and gradually slowed with time. Most of the volatile degradation products appeared to be in the form of $^{14}CO_2$.

The identifiable products after TLC and LSC of the scrapings of the free and loosely bound fractions of non-sterile sandy loam litter layer showed the presence of M 1%, other carbamates (MFM, MAM, FAM and AM) 8%, phenols (DMAX, MAX and AX) 8% and unidentifiable products about 8% (Table 15). In the nonsterile clay loam litter, the type of moieties found were the same except that the relative amounts of the products found were higher than in the sandy loam litter. The intact carbamates were slightly greater, and so were the phenolic moieties. Probably, as observed by Sethunathan (1973) in some organochlorines, reductive reactions rather than oxidative ones played a major role in the degradation of mexacarbate in clay loam litter. We can conclude from the data that mexacarbate in forest soils degraded primarily by microbial action, although some chemical (Roberts et al., 1978) and photolytic (Crosby et al. 1965; Silk and Unger 1973) degradations could have occurred. Kazano et al. (1972) observed that the quantity of metabolites formed during degradation depends on the type of litter used. Since sterile litter samples showed an increased evolution of radioactivity with time (Table 14), it is very likely that, in addition to microbial degradation, a very small percent of the fortified ^{14}C-mexacarbate would also have been lost by volatilization.

Microbial degradation increased gradually with time for the first seven to ten days and then tapered off, reaching a stationary state after 30 d. This may be due to adsorption of the chemical onto litter matrices thereby decreasing its bioavailability, or to the inability of the chemical to induce the necessary enzyme changes required by the microorganisms to utilize the pesticide carbon effectively for enriching the microbial pool (Hiltbold, 1974). It is known (Weber et al., 1968; 1969; Adams, Jr., 1973) that adsorption of a basic pesticide such as mexacarbate is pH dependent, and increases with decreasing pH; and that bioactivity is inversely related to adsorption. The litter samples used in the present degradation studies were acidic (pH range 4.20 to 4.36, Table 2). The nonlinear decrease in bioactivity of mexacarbate with time appears to be due to its low bioavailability because of adsorption to acidic litters by ionic and physical bonds (Weber, 1970) rather than its failure to proliferate soil microbes.

It appears that the breakdown of mexacarbate in the litter samples of both soils follow the exponential decay equation (1):

$$Y = A + B\, e^{-Cd} \qquad (1)$$

where Y = the amount of mexacarbate in μg at different days 'd' after treatment; A = the residual concentrations of the material at the end of the experiment; B = the coefficient for the term e^{-Cd}; and C = the rate constant for the exponential decay. Since Y and A are known from the experimental data, equation (2) can be used to obtain B and C for the decay curve (Fig. 3a) of both soils:

$$\log (Y - A) = \log B - \frac{C}{2.303} d \qquad (2)$$

The half-life ($T_{\frac{1}{2}}$), the number of days required for the degradation portion of the residues to reach 50% of the initial values, is inversely related to the rate constant C by the equation (3):

$$T_{\frac{1}{2}} = \frac{\ln 2}{C} \qquad (3)$$

It can be seen from the decay curves (Fig. 3a) that the rate of degradation of mexacarbate is different in the two types of litters. The rate appeared to be faster in the sandy loam litter, with a $T_{\frac{1}{2}}$ value of about 7.38 d, than in the clay loam where the $T_{\frac{1}{2}}$ value was about 7.74 d (although for biological systems such slight variations in $T_{\frac{1}{2}}$ may not be significant). Similar small differences in the rate constant C between the sandy loam litter ($C = 940 \times 10^{-4}$/day) and clay loam litter ($C = 896 \times 10^{-4}$/day) were also observed, confirming that the degradation rates of mexacarbate in the two matrices studied varied slightly.

The rate of breakdown of mexacarbate in the two litters was also represented in terms of the $^{14}CO_2$ evolved (Fig. 3b). It can be seen that the evolution of CO_2 increased with time, and followed the Poisson Function. Non-linear regression analysis and least squares approximation techniques were employed to determine the coefficients E, F and G in equation (4):

$$P = E + F\ (1 - e^{-Gd}) \qquad (4)$$

where P = percentage radioactivity evolved at different days 'd'; E is the final maximum percent obtained at the end of the experiment (45 d); F is the coefficient for the term $(1 - e^{-Gd})$ and G represents the rate of CO_2 evolution. It is evident from Fig. 3b, that CO_2 evolution was faster during the first seven days and therefore higher overall in the litter of sandy loam than in clay loam. The G values are higher for sandy loam litter than for the clay loam, confirming the increased rate of loss of the chemical from the former matrix. This finding is in agreement with the rate of decrease of the chemical in the two types of litters. Edwards (1972) and Hamaker (1972) summarized some of the similar kinetic treatments available for studying the breakdown of insecticides in soils.

Degradation pathways of mexacarbate in forest soils

Apart from the studies made in agricultural soils (Kazano et al., 1972; Benezet and Matsumura, 1974), little has been reported in the literature about the pathways of breakdown of mexacarbate in forest soils. Data generated from other types of soils or from other substrates are not necessarily applicable to forestry soils, because persistence is influenced by soil composition, pH, microbial content, cultural practices, etc. (Graham-Bryce, 1967; Harris, 1964; Edwards, 1972; Hiltbold, 1974; Chapman and Cole, 1982; Rajagopal et al., 1984). These factors do not apply in the same way to forestry as to other soil types. Contrary to this point of view, Meikle (1973) reviewed the available data on the chemical and reported the similarity in its degradation pattern among plants, animals and soils. Hosler, Jr. (1974), Matthews and Faust (1977; 1981) and Roberts et al. (1978) found similar degradation products in water.

In our studies with the soil column leaching (Table 8), metabolic fate under aerobiosis and anaerobiosis (Table 13), and aerobic degradation (Table 15), we found various carbamates, phenols and unidentifiable polar and non-polar products. However, under anaerobic conditions (Table 13), no intact carbamates were identified in either type of soil. The disappearance of mexacarbate in the present study therefore appears to be governed by complicated mechanisms involving oxidative N-demethylation, deamination, hydroxylation, hydrolysis and conjugation to litter matrices (Goring et al., 1975). Similar observations were also made by Meikle (1973) and Roberts et al. (1978). The parent compound is not persistent under anaerobic conditions in either

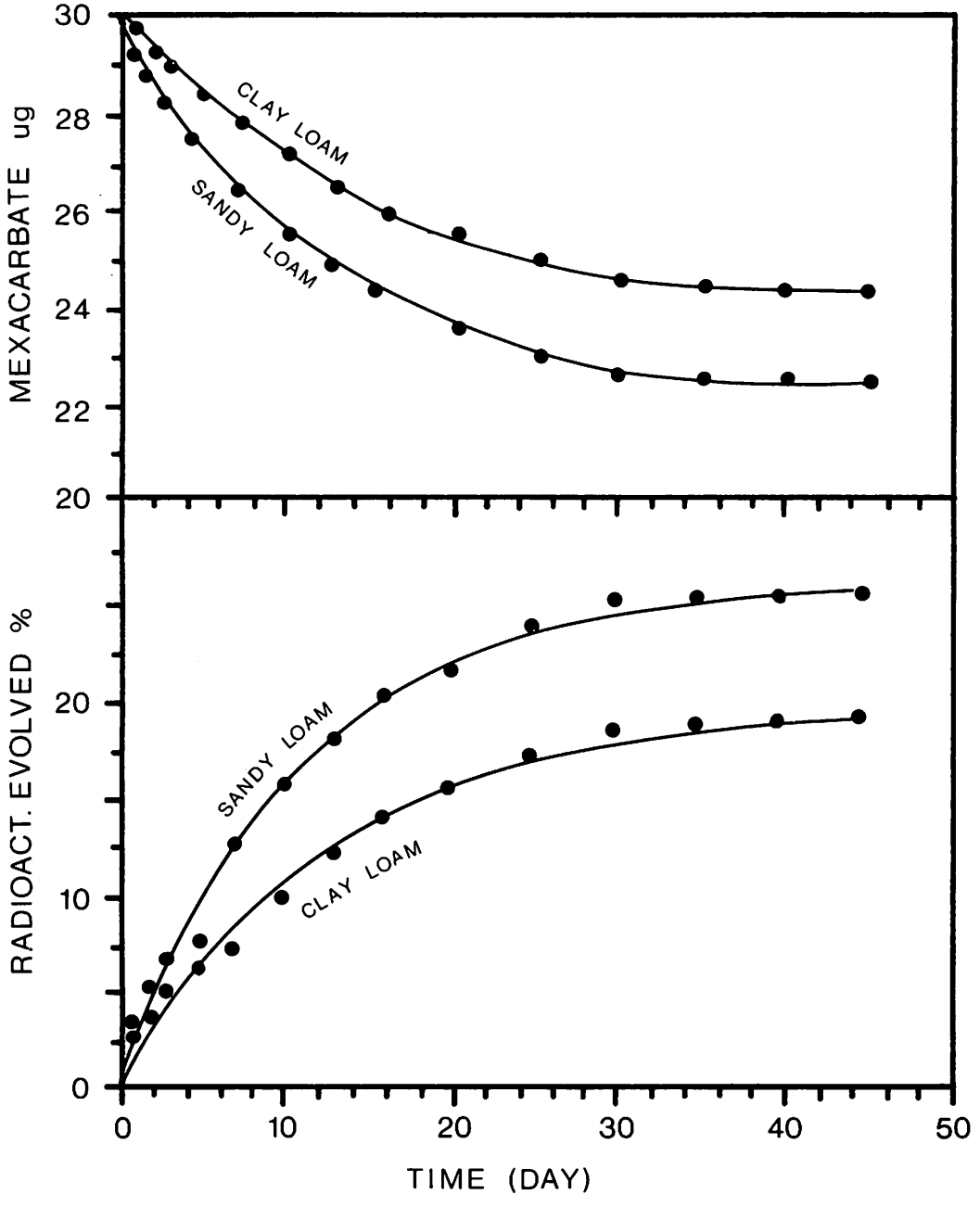


Fig. 3. Mexacarbate degradation in sandy and clay loam forest soils.

type of soil (Table 13). The free and loosely bound fractions, under aerobic conditions, in addition to the parent material, contained other intact carbamate moieties (MFM, MAM and AM). These species, we presume, are formed by N-methyl hydroxylation of the dimethylamino group followed by oxidative decarboxylation, resulting ultimately in the demethylation of the N-dimethyl groups by soil microorganisms (Ryan and Knaak, 1971). Other studies have also shown that mexacarbate is degraded by various substrates to form several oxidative products with the aryl ring and the carbamate moiety intact, emphasizing the non-hydrolytic pathway (Abdel-Wahab and Casida, 1967; Tsukamoto and Casida, 1967; Roberts et al., 1969). The presence of the various unidentifiable metabolites in the present study seems to be due to hydroxylation and oxidation of ring methyls as well as the formation of stable N-hydroxy derivative of the methyl group in the carbamate moiety (Abdel-Wahab and Casida, 1967; Roberts et al., 1969; Kuhr and Dorough, 1976). In addition, ring hydroxylation of methyl carbamate insecticides also occurs (Dorough and Casida, 1964; Williams et al., 1964b; Kuhr and Casida, 1967; Tsukamoto and Casida, 1967; Oonnithan and Casida, 1968; Knaak et al., 1970; Knaak, 1971; Paulson et al., 1972). However no attempt was made to isolate and characterize these metabolites.

The presence of phenolic compounds (DMAX, AX and MAX) under aerobic conditions confirms that in addition to the above, hydrolytic removal of the carbamate functional group enzymatically, chemically or by both routes, is also important in the metabolism of mexacarbate (Meikle, 1972). A similar mechanism has been reported for the chemical in soil (Laskowski, 1972; Benezet and Matsumura, 1974), in broccoli plants (Williams et al., 1964a) and in water (Roberts et al., 1978). The amount of these compounds varied according to litter type and experimental conditions. Usually the amounts were lower in the clay loam and under anaerobic conditions. These primary metabolites are present as conjugates (Williams et al., 1964a; Kuhr and Casida, 1967; Meikle, 1973). The xylenols would be linked primarily to humic substances, and to a lesser extent to non-humic substances (carbohydrates, aminoacids, lipids, etc.) in soil, making them water-soluble and biologically inactive (Kazano et al., 1972; Kaufman, 1974; Khur and Dorough, 1976; Stevenson, 1982). Subsequent metabolism of the aminoxylenols appears to be by deamination, followed by hydroxylation due to soil microorganisms forming initially the unidentified transient species, 3,5-dimethyl hydroquinone (R_f 0.81), and the corresponding oxidation product, quinone DMPQ (R_f 0.80), which was sporadically found in sandy loam litter samples (Table 13). Laskowski (1972) reported the formation of hydroquinone in soils. Formation of such hydroquinone derivatives is also common in plants, soils and animals (Williams et al., 1964a, 1964b; Stevenson, 1982). The evolution of $^{14}CO_2$ from ring-labelled ^{14}C-mexacarbate served as a measure of ring cleavage. The results in Table 14 show that 19 to 25% of the applied amount evolved as volatile $^{14}CO_2$ (Laskowski et al., 1983; Lichtenstein et al., 1972). Such degradation by soil microorganisms has been noted earlier with other pesticides (Alexander, 1972; Meikle, 1972; Lannio et al., 1973; Kearney et al., 1967; Starr and Cunningham, 1975; Venkateswarlue and Sethunathan, 1979; Matsumura and Krishna Murti, 1982; Fox, 1983). Although direct precursors of $^{14}CO_2$ have not been characterized, it is apparent that such a ring rupture would yield polar metabolites. The considerable amount of radioactivity, detected near the origin on autoradiograms of thin-layer plates, seems to be due to such metabolites. It was not determined in the present study whether these arose from ring-cleavage or from the intact aryl ring. Similarly, not all the spots on the thin-layer chromatograms were identified because of the low radioactivity as well as overlap among some of the compounds.

From the foregoing observations based on TLC studies and from evidence available to us from other researchers (Meikle, 1973; Roberts et al., 1978), we have postulated a

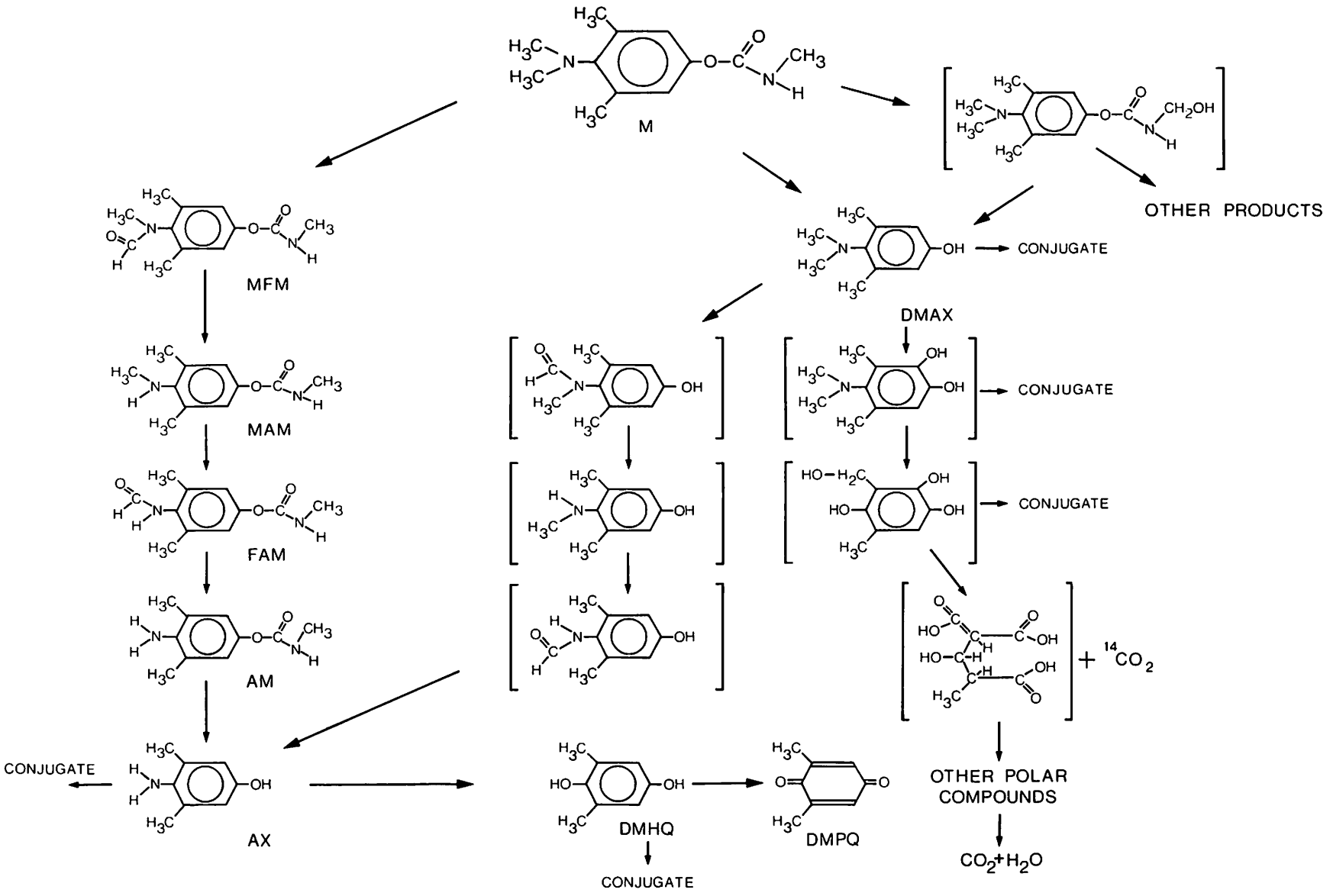


Fig. 4. Possible metabolic pathway of mexacarbate in forest soils

sequence of reactions as shown in Figure 4, for the degradation of mexacarbate in forest soils. It should be pointed out that the proposed metabolic scheme is somewhat speculative because it is based on TLC and radiochemical studies only and does not have further definitive confirmation from mass spectral or nuclear magnetic spectral studies. The point of emphasis is that the degradative pathway in both soils appears to be the same. In the proposed scheme, most of the transient compounds and conjugates are not included unless they serve as necessary intermediates in the overall metabolic process.

As pointed out earlier, during the forest spray operations, the dosage of mexacarbate sprayed is small (70 g AI/ha), and the amount reaching the forest floor is extremely low, ca. 0.1 ppm (Sundaram and Nott, 1985). Under such conditions, the chances of isolating and detecting most of these metabolites would be extremely unlikely. The little that reaches the soil would be degraded rapidly by soil microorganisms, and also by irradiation from sunlight, into innocuous non-carbamate moieties.

CONCLUSIONS

Laboratory studies, conducted under simulated field conditions using hand-packed soil columns, clearly demonstrated that mexacarabate is strongly adsorbed onto soil matrices and seldom leaches downwards to lower layers, unless the soil columns are saturated. This indicates that the chemical is extremely unlikely to reach the water table during any spraying of this chemical over forests at the operational dosage of 70 g AI/ha. Under both aerobic and anaerobic conditions, the chemical degraded rapidly primarily through microbial action, ensuring that it will not pose any persistence problems in the environment. Free and bound insecticide residues decreased rapidly under anaerobic conditions. The principal degradative pathway appears to be oxidative N-demethylation, deamination, hydrolysis, hydroxylation, conjugation and eventually ring-cleavage. Major degradation products, depending upon the experimental conditions, were carbamate moieties, phenols, $^{14}CO_2$ and various other polar and nonpolar unidentifiable compounds. The present data, when extrapolated to field situations, suggest that the amount of sprayed mexacarbate reaching the forest floor would be extremely small and would disappear rapidly without causing any undue concern.

We envision that the procedure used in the study could be standardized to serve as a tool for evaluating pesticide mobility and degradation in forest soils. Knowledge of these aspects is essential not only to understand how a pest control chemical will behave in the biosphere but also for its safe and efficient use.

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