

MOBILITY OF DEFLUBENZURON IN TWO TYPES
OF FOREST SOILS

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ABSTRACT

Diflubenzuron (DFB) [1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl) urea] and two formulations, Dimilin WP-25, and Dimilin SC-48 were applied separately at 17.23, 51.69 and 155.07 μ g of active ingredient (A.I.) (corresponding to 70, 210 and 630 g A.I./ha) to the top layers of columns (30 cm x 5.6 cm i.d.) packed with sandy and clay loam forest soils. Water (1.25l L) equivalent to 50.8 cm of precipitation was leached through each column. The columns were segmented into 5 unequal segments and the DFB residues in soils were extracted and analyzed by high performance liquid chromatography (HPLC). At 70 g A.I./ha, the DFB was immobile and nearly all the residues were found within 2.5 cm of the column. Mobility of DFB did not increase with dosage. Even at 630 g A.I./ha, only about 9% of the technical DFB moved below the 2.5 cm level in sandy loam. Corresponding values for Dimilin SC-48 and Dimilin WP-25 were only 7% and 4%. Mobility of DFB in clay loam was lower than in sandy loam. No residues were found below the 10 cm level or in the leachates in either soil type at all dosage levels. In addition to soil type, mobility of DFB was also influenced by the additives present in the formulation and decreased in the order: Dimilin® WP-25 < Dimilin® SC-48 < DFB® (tech.).

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INTRODUCTION

Diflubenzuron (DFB) [1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl) urea] insecticide is a chitin synthesis inhibitor (Post et al. 1974) introduced commercially by Duphar, B.V. Holland under the trade name Dimilin® in 1976 (Rabenort et al. 1978). The use of this chemical for pest control in agriculture and horticulture crops and for the control of flies, mosquitoes and other nuisance insects has increased rapidly because of its selectivity and effectiveness against a wide range of pests (Anon. 1985). It has low toxicity to higher animals and is relatively non-hazardous to honeybees and predatory insects (Worthing and Walker 1983). However, DFB is relatively toxic to chitin-synthesizing aquatic arthropods (Cunningham 1976; Ali and Mulla 1978a and b; Lacey and Mulla 1978; Apperson et al. 1978; Costlow 1979; Colwell and Schaefer 1980; Nimmo et al. 1980; Gulka et al. 1980; Tester and Costlow 1981; Hansen and Garton 1982; Weis and Ma 1987). The EC₅₀ values for cladocerans, one of the most sensitive groups of crustaceans, have been reported to be in the range of 0.5 to 15 ppb (Miura and Takahashi 1974; Julin and Sanders 1978; Nimmo et al. 1980; Tester and Costlow 1981; Hansen and Garton 1982).

Recent field trials have shown that DFB has considerable promise for use against various forest pests (Retnakaran and Wright 1987). Before a pesticide can be used in Canada, it must be registered under the Pest Control Products Act (PCPA), which is administered by Agriculture Canada. One of the requirements in the Act is to generate and provide reliable data to the regulators of the PCPA on the mobility of the chemical in forest soils in order to assess its potential for ground-water contamination (Anon. 1987). Because of DFB toxicity to aquatic arthropods and fish, such data are essential to assess the possible hazards to the aquatic environment. To date, no information has been available in literature on the mobility of this chemical in forestry soils. Our objective was to study the downward movement of technical and formulated DFB in two types of forestry soils under laboratory conditions using hand-packed soil columns.

MATERIALS AND METHODS

Reagents

Diflubenzuron (purity 97.6%, m.p. 227-231°C), Dimilin WP-25 (a water dispersable powder containing 25 g of DFB/100 g) and Dimilin SC-48 (a suspension concentrate containing 48 g of DFB/100 g) were provided by Duphar B.V., Weesp, Holland. Florisil® (PR grade, 60-100 mesh calcined at 650°C by the manufacturer - Floridin Co., Pittsburgh, PA) was heated at 150°C overnight, after repeated washing with anhydrous methanol and diethyl ether, then deactivated by adding 5.5 mL of distilled water to 100 g of activated Florisil, mixed thoroughly in a rotary mixer and stored in sealed air-tight bottles. Sodium sulfate (Fisher-reagent grade anhydrous, granular) was extracted successively with hexane and ethyl acetate to remove organic impurities, dried and

heated for 8 h at 300°C prior to use. All solvents were HPLC (high-performance liquid chromatography) grade, received from J.T. Baker and tested prior to use for their spectral purity. They were filtered through appropriate Millipore® filters and degassed before use.

Soil Samples

Two types of forest soils (a sandy loam and a clay loam) were used in the study. Each type of soil was collected from two different locations within a mixed mature forest area near Timmins, Ont. The near grid reference for the sandy and clay loam sites were respectively 81°37'55"W, 48°35'03"N and 81°38'54"W, 48°35'03"N. Prior to sampling, stones, fallen twigs and undecayed leafy materials were removed from the sites. About twenty 30 cm deep soil cores were collected randomly from each site using a 9.2 cm diam. tube auger. Soil cores of each soil type were pooled and brought to the laboratory where they were screened (4 mm), macerated in a Hobart chopper for uniform consistency, stored in plastic bags and placed in an environmental chamber at 4°C in a moist condition until initiation of the study. Some common physical properties of the soils are given in Table 1.

Table 1. Physical properties of soils used in mobility studies under laboratory conditions

Texture	pH	Organic matter (%)	CEC (me/100 g)	Particle size classes (%)		
				Clay	Silt	Sand
Sandy loam	5.6	5.4	21	6	38	56
Clay loam	5.1	11.7	49	16	46	38

Soil Column Preparation

The soil column leaching apparatus consisted of polyvinyl chloride (PVC) tubing 5.6 cm i.d. x 6.1 cm o.d. x 40 cm long, lined inside with Cole-Parmer's "protective overlay" which consisted of a layer of Teflon FEP® film on vinyl backing to prevent adsorption of the chemical 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. Each column was held vertically on a Thermolyne Maximix®. The soil was added in small amounts using a spoon. 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 (bulk density 1.20 g/cm³) and to avoid channels which would cause mass flow of fluid. The process was repeated until the soil was packed to a depth of 30 cm. The filling procedure was similar to that of Guenzi and Beard (1967) and Weber (1972). The top of each soil

column was covered with a circle (trimmed to fit) of Whatman® No. 1 filter paper to prevent channelling when adding water to the column. Each column was clamped near the top on a Fisher Flexaframe® stand and rested on a glass funnel, suspended on a ring stand. A 1-litre Teflon® bottle was placed beneath each funnel for collecting eluates. A 1.5 L separatory funnel was suspended over the top of each column with the aid of a ring stand to apply water.

Sixty columns were set up: 27 columns for each soil type (sandy loam and clay loam) and six columns as untreated control. The 27 columns were divided into three groups. Each group would be tested in triplicate with 17.23 µg, 51.69 µg and 155.07 µg of the active ingredient (A.I.) present in each of technical DFB, Dimilin WP-25 and Dimilin SC-48. Since the surface area of each column is 24.62 cm², these treatment levels would give respectively the corresponding field dosages of 70 g A.I./ha, 210 g A.I./ha and 630 g A.I./ha.

The stands containing the soil column assemblies 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 (400 W multivapor discharge lamps) to simulate sunlight. Prior to DFB application, all columns were conditioned by leaching with 2 x 1.25 L of distilled water at the flow rate of approximately 1.5 mL/min and maintaining about a 3-cm level of water above the soil surface.

Treatment Procedures

For the treatment of soils, stock solutions of technical DFB in methanol (40.61 mg/100 mL), Dimilin WP-25 in water (280 mg/100 mL) and Dimilin SC-48 in water (140 mg/100 mL) were prepared. Aliquots of the stock solutions were further diluted with water so that 1 mL of the resulting solution would contain 17.23 µg of DFB.

Prior to fortification of the columns with DFB, the filter paper discs covering the soil columns were removed. Columns meant to receive 70 g A.I./ha were treated with 1 mL of the diluted solution containing 17.23 µg of DFB mixed with 9 mL of water. Using a graduated pipet, the solution was applied uniformly covering the entire surface (24.62 cm²) of the column. Similarly, columns designated to receive dosages of 210 and 630 g A.I./ha were fortified with 3 mL of the 17.23 µg/mL stock solution diluted with 7 mL of water and 9 mL of the stock solution mixed with 1 mL of water, respectively.

After fortification, the columns were allowed to equilibrate for 1 h, then a new filter paper disc was placed on the soil surface of each column. The columns were then eluted with 1.25 L of distilled water according to the guidelines of PCPA (Anon. 1987) and EPA (Anon. 1981) using the same flow rate as in column equilibration. The volume of water used corresponded to the representative average annual rain fall (50.8 cm) times the cross-sectional area of the column (50.8 cm x 3.14 x

$(2.8 \text{ cm})^2 = 1.251 \text{ L}$]. The average time taken to complete the leaching process in sandy loam soil columns was 3.5 h whereas in clay loam, the water movement was slow and it took on average 6 h, perhaps due to swelling of soil colloids (Graham 1964, Haque 1975). The leachates from columns were collected in Teflon bottles and stored in a freezer prior to extraction and analysis. The soil columns were capped with aluminum foil and were stored at -20°C until analysis.

Analysis of Diflubenzuron

At the time of analysis, each soil column was allowed to thaw and then the filter paper disc at the top, the glass wool mat and metal screen at the bottom of the column were removed. The column was carefully cut open longitudinally using a circular saw. After removing the Teflon sheet cover, the soil core was placed on a clean aluminum sheet and segmented sequentially, using clean sharp knives, from bottom to top into five unequal segments -two 10 cm increments from bottom, followed by one 5 cm increment and then the two 2.5 cm increments. The segments were separated, transferred individually to glass mortars and mixed well. Ten-gram aliquots in duplicate were used for moisture determination (AOAC 1955). Thirty-gram aliquots (done in duplicate per segment per column) of soil and 200 mL leachate (done in duplicate per column) were taken for the extraction and analysis of DFB.

Water: The extraction of DFB from each leachate was accomplished by shaking 200 mL thrice, each time with 75 mL of dichloromethane (DCM). After pooling, the DCM layer was dried by passing through a column of Na_2SO_4 , flash evaporated at 35°C to dryness and reconstituted in acetonitrile (ACN). The ACN solution was filtered through a $0.45 \mu\text{m}$ Millipore filter, whereupon its volume was adjusted under dry N_2 and analyzed directly by HPLC without any cleanup.

Extraction efficiencies of DFB from pond waters fortified at 1.0, 0.5 and $0.1 \mu\text{g/L}$ (done in triplicate for each concentration) were respectively $93 \pm 4\%$, $86 \pm 5\%$ and $84 \pm 8\%$. The percent recoveries decreased with the decrease in concentrations of DFB added to the water samples. The minimum quantification limit (MQL) of DFB in natural waters was fixed at $0.05 \mu\text{g/L}$.

Soil: Extraction of DFB in each soil segment was accomplished by refluxing 30 g of soil with 120 mL of $\text{ACN:H}_2\text{O}$ (5:1 v/v) for 30 min. After cooling, the mixture was filtered under gentle aspiration through a Buchner funnel lined with Whatman No. 1 filter paper. The residues were rinsed with $2 \times 10 \text{ mL}$ ACN. The combined extract and the rinses were concentrated under low pressure to remove most of the ACN. The volume of the concentrate was adjusted to 100 mL by adding water and it was partitioned thrice, each time with 50 mL of hexane. The pooled hexane phase, after passing through a column of anhydrous Na_2SO_4 (50 g), was flash evaporated gently at 35°C to dryness and the residue was dissolved in 10 mL of DCM:petroleum ether (PE) (1:9 v/v) for column cleanup.

Column cleanup: Glass column (Fisher 13-678-8 Pasteur Pipet, 15 cm x 8 mm i.d.) was packed from bottom to top with a glass wool plug, 5 cm Florisil, 1 cm Na₂SO₄ and another glass wool plug. The packed column was first prewashed with 20 mL of PE and then 1.0 mL of crude sample extract (1 g substrate = 1.0 mL extract) was transferred quantitatively to the column. The column was eluted successively with 2 mL PE and 2.5 mL acetone (AC):PE (1:9 v/v). The resulting eluates were discarded. The DFB on the chromatographic column was eluted with 2.5 mL AC:PE (1:9 v/v) followed by 5 mL of AC:PE (1:4 v/v). The entire eluant was collected. The cleaned extract was gently flash evaporated at 35°C to dryness, reconstituted in 1 mL of ACN and filtered through a 0.45 µm Millipore filter for HPLC analysis.

Extraction efficiencies of DFB from fortified sandy soil (done in triplicate soon after fortification) at 1.0, 0.5 and 0.1 µg/g (fresh wt.) were respectively 99 ± 7%, 96 ± 5% and 94 ± 9%. Corresponding values for the clay loam were 95 ± 8%, 93 ± 7% and 90 ± 9%. Generally the percent recoveries declined at lower fortification levels. The results reported in this paper are not corrected for extraction efficiency. The minimum quantification limit (MQL) of DFB in both soils was fixed at 0.05 µg/g (fresh wt.) for 20 µL injection. Periodic analyses of aliquots of soils (0-2.5 cm segment) stored at -20°C for up to 40 days, were performed. Residue levels, on average, were decreased to about 18% showing that DFB in the column was either not very stable or not quantitatively extractable after prolonged storage at -20°C. None of the soils in the six control columns showed any HPLC response that corresponded to DFB.

HPLC Analysis

Diflubenzuron residues in the leachates and soil segments were analyzed using a Hewlett-Packard (HP) Model 1090M high performance liquid chromatograph fitted with a DAD detector and an HP 300 computer monitor. The column used was an HP:RP-8 (200 mm x 4.6 mm i.d.) containing methyl octylsilyl-Hypersil® with 10 µm pore size. The instrument parameters are shown in Table 2.

Under the above conditions, the average retention time (R.T.) for a 20 µL injection of 1.0 µg/mL diflubenzuron was 9.45 min with an average peak area of 30 mAU. The deviation in R.T. for each injection was less than 1%.

Detector response was calibrated daily with an analytical standard prepared in ACN. Quantification of the samples was based upon the average peak areas obtained from injections of the cleaned extracts compared to those of the external standard injections injected before and after each sample.

Table 2. HPLC parameters used in the study

Flow rate: 1.0 mL/min
Mobile phase: Solvent A: H₂O
 B: ACN

Oven temperature: 40.0°C
Stop time: 20.0 min

Sample Wavelength: 254 (nm)
Bandwidth: 4

Reference Wavelength: 430 (nm)
Bandwidth: 50

Manual injector (loop size): 20 µL

Mobile phase comp. (v%) for gradient elution

Time (min)	Solvent A	Solvent B
0.00	50	50
12.00	50	50
12.50	0	100
19.50	0	100
20.00	50	50

RESULTS AND DISCUSSION

Distributions of DFB in the sandy and clay loam forest soil columns fortified with 70, 210 and 630 g A.I./ha and eluted with 1.251 L of water are given in Tables 3 and 4, respectively. Under the present experimental conditions, the DFB present in technical, SC-48 and WP-25 did not move beyond 10 cm length of the column even at the highest fortification level (630 g A.I./ha). None of the leachates contained any detectable levels (0.05 µg/L) of the chemical. The recoveries of DFB from sandy loam and clay loam soil segments ranged respectively from 84.7 to 90.1% (mean 87.8%) and from 81.2 to 88.5% (mean 85.6%) and were below the average extraction efficiencies observed for the fortified sandy (96%) and clay (93%) loam soils. The apparent low recoveries were perhaps due to irreversible adsorption (Nimmo 1986) and microbial degradation (Nimmo et al. 1984; Chapman et al. 1985) of DFB during its interaction (elution and storage) with soil matrices. Somewhat low residue levels were recovered in clay loam soil (mean 85.6% than in sandy loam soil (mean 87.8%) probably due to stronger binding of pesticides to organic matter (Table 1) in the clay loam compared to sandy loam soil (Hamaker and Thompson 1972).

The data in Tables 3 and 4 clearly indicate that even under the worst case situation of fortification at 630 g A.I./ha, i.e., nine fold in excess of the optimum dosage of 70 g A.I./ha recommended for forestry use (Pfizer 1982), the chemical did not move downward in the columns beyond the 10 cm level. At 70 g A.I./ha, the technical and SC-48 moved down to the 5 cm level; with increasing dosage, the amount and the extent of mobility gradually increased although the bulk of the DFB was still present within 2.5 cm segment. In contrast, the downward mobility of DFB in WP-25 was lower compared to the technical and SC-48 (Table 4), even at the highest dosage level. The gradual decrease in mobility of DFB in SC-48 and WP-25 compared to the technical material, as seen from the data in Table 3, is attributable to the presence of adjuvants in them which probably enhanced the binding of DFB to soil matrices. Comparison of the mobility data with clay loam soil (Table 4) showed that the downward movement of DFB is not only retarded by the presence of adjuvants but also influenced by soil type. The chemical, like other pesticides, is adsorbed strongly by lipophilic sites in the clay loam, compared to the sandy loam (Swanson et al. 1954; Geissbuhler 1969; Helling 1971; Farmer and Aochi 1974; Weed and Weber 1974) through several bonding mechanisms involving van der Waal's hydrogen and hydrophobic bondings, ligand exchange, etc. (Khan 1980; Stevenson 1982). In addition, clay loams have a much larger internal surface area (Bailey and White 1970; Edwards 1972) than sandy soils and this could also contribute to a greater retention of the chemical onto them. Sorbed pesticide molecules tend to resist displacement by water from organic soil matter. Several investigators (Hill et al. 1955; Hamaker et al. 1966; Eshel and Warren 1967; Gray and Weierich 1968) have shown inverse relationships between adsorption and leaching of organic chemicals by water through soil.

Other factors which contributed to the negligible leaching of DFB in both types of forest soils are: its poor water solubility (0.14 mg/L at 20°C) (Hartley and Kidd 1983) [leachability is inversely related to solubility (Bailey and White 1964)] leading to stronger linkage via hydrophobic bonding to soil colloids (Hance 1965; Weber 1970; Khan 1980) and low soil pH (5.1 to 5.6) leading to protonation and bonding (ion-dipole type) to soil particulates (Stevenson 1982). The structural factors of DFB such as the presence of pi electrons, carbonyl (= CO) and imino (= NH) groups and its high K_{ow} (7.8×10^3) (Anon. 1985) are conducive to dipole-dipole attraction between adsorbent and adsorbate and for the formation of H-bonds and hydrophobic interactions between them (Khan 1980), restricting the downward mobility of the chemical. Also, the coordination between soil cations Fe^{3+} , Ca^{++} , Mg^{++} , etc. and DFB, especially through the N atoms with their lone pair of electrons cannot be ruled out as a possibility for adsorption.

Table 3. Downward mobility and distribution of diflubenzuron in sandy loam soil columns found by analysis after completion of leaching

Formulation	DFB content ^a (% of applied) of oven-dried soil ^b											
	Dosage: 70 g A.I./ha				Dosage: 210 g A.I./ha				Dosage: 630 g A.I./ha			
	0-2.5 cm	2.5-5 cm	5-10 cm	Total	0-2.5 cm	2.5-5 cm	5-10 cm	Total	0-2.5 cm	2.5-5 cm	5-10 cm	Total
Tech.	86.4	3.7	N.D. ^c	90.1	84.8	4.1	N.D.	88.9	79.4	7.7	1.1	88.1
SC-48	88.7	0.9	N.D.	89.6	85.2	2.0	N.D.	87.2	79.8	6.3	0.5	86.6
WP-25	89.3	N.D.	N.D.	89.3	85.6	N.D.	N.D.	85.6	80.9	3.8	N.D.	84.7

^a Each value is the mean of three replications, with two determinations per replication. Standard deviation (not shown) was less than 10%. None of the soil segments after 10 cm and the column leachates contained any detectable levels of DFB.

^b Moisture content of the soils ranged from 39 to 44%; mean value of 41%.

^c N.D. Not detected; limit of quantification of 0.05 µg/g of wet soil.

Table 4. Downward mobility and distribution of diflubenzuron in clay loam soil columns found by analysis after completion of leaching

Formulation	DFB content ^a (% of applied) of oven-dried soil ^b											
	Dosage: 70 g A.I./ha				Dosage: 210 g A.I./ha				Dosage: 630 g A.I./ha			
	0-2.5 cm	2.5-5 cm	5-10 cm	Total	0-2.5 cm	2.5-5 cm	5-10 cm	Total	0-2.5 cm	2.5-5 cm	5-10 cm	Total
Tech.	88.4	N.D. ^c	N.D.	88.4	87.4	1.1	N.D.	88.5	85.1	2.2	N.D.	87.3
SC-48	86.9	N.D.	N.D.	86.9	86.2	N.D.	N.D.	86.2	81.8	1.7	N.D.	83.5
WP-25	84.9	N.D.	N.D.	84.9	83.5	N.D.	N.D.	83.5	80.7	0.5	N.D.	81.2

^a Each value is the mean of three replications, with two determinations per replication. Standard deviation (not shown) was less than 10%. None of the soil segments after 10 cm and the column leachates contained any detectable levels of DFB.

^b Moisture content of the soils ranged from 44 to 49%; mean value of 46%.

^c N.D. Not detected; limit of quantification of 0.05 µg/g of wet soil.

In a recent aerial spray trial in southern Ontario using Dimilin WP-25 in water at the constant dosage rate of 70 A.I./ha and at variable emission rates of 10, 5 and 2.5 L/ha, the maximum deposit levels found on the forest floor were respectively 54, 22 and 13 g A.I./ha (Sundaram et al. 1988a,b). At these rates of deposition, the maximum levels of DFB deposited on 24.62 cm² surface area of the soil column would be respectively 13.3, 5.4 and 3.2 µg. The present study has demonstrated unequivocally that at these fortification levels in the soil columns, the chemical would not have moved beyond the depth of 2.5 cm. Even assuming an extreme situation, in which all the sprayed material had reached the forest floor, the value would only increase to 17.2 µg which is again too low for downward movement beyond the 2.5 cm level. From our results, it may be concluded that Dimilin WP-25, used properly in forest management at a dosage rate of 70 g A.I./ha, is unlikely to be leached into water from a site of application.

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REFERENCES

- Ali, A. and Mulla, M.S. Environ. Entomol. 7, 21-27 (1978a).
- Ali, A. and Mulla, M.S. Arch. Environ. Contam. Toxicol. 7, 483-491 (1978b).
- Anon. Env. Protec. Agency, U.S.A. "Guidelines for Registering Pesticides in U.S.; Subpart N, Chem. Requirements: Env. Fate." Unpublished Draft (1981).
- Anon. "Dimilin", Tech. Inf. Rep. (9th edn.), Duphur, B.V., Weesp, Holland, 36 p. (1985).
- Anon. "Guidelines for Determining Environmental Chemistry and Fate of Pesticides," Agric. Canada Food Production and Inspection Br., Unpublished Rep., 56 p. (1987).
- AOAC, "Official Methods of Analysis" (8th edn.), Assoc. Official Anal. Chem., Washington, D.C. 1008 p. (1955).
- Apperson, C.S., Schaefer, C.H., Colewell, A.E., Werner, G.H., Anderson, N.L., Dupras, E.F. Jr., and Longanecker, D.R. Jour. Econ. Entomol. 71, 521-527 (1978).
- Bailey, G.W. and White, J.L. Jour. Agric. Food Chem. 12, 324-332 (1964).
- Bailey, G.W. and White, J.L. Residue Rev. 32, 29-92 (1970).
- Chapman, R.A., Tu, C.M., Harris, C.R. and Harris, C. Jour. Environ. Sci. Health B20, 489-497 (1985).
- Colwell, A.E. and Schaefer, C.H. Jour. Fish. Aquat. Sci. 37, 632-639 (1980).
- Costlow, J.D. Effect of Dimilin® on development of larvae of the stone crab *Menippe mercenaria* and the blue crab *Callinectes sapidus*. In "Marine Pollution: Functional Responses", (eds.) W.B. Vernberg, A. Calabrese, F.P. Thurberg and F.J. Vernberg, Academic Press, New York, N.Y., pp. 355-364 (1979).
- Cunningham, P.A. Environ. Entomol. 5, 701-706 (1976).
- Edwards, C.A. Insecticides. In "Organic Chemicals in the Soil Environment", (eds.) C.A.I. Goring and J.W. Hamaker, Marcel Dekker Inc., New York, N.Y., pp. 515-568 (1972).
- Eshel, Y. and Warren, G.F. Weeds, 15(2), 115-118 (1967).
- Farmer, W.J. and Aochi, Y. Soil Sci. Soc. Amer. Proc. 38, 418-423 (1974).

- Geissbuhler, H. The substituted ureas. In "Degradation of Herbicides", (eds.) P.C. Kearney and D.D. Kaufman, Marcel Dekker Inc., New York, N.Y., pp. 79-111 (1969).
- Graham, J. Rev. Pure Appl. Chem. 14, 81-90 (1964).
- Gray, R.A. and Weierich, A.J. Weed Sci. 16(1), 77-79 (1968).
- Guenzi, W.D. and Beard, W.E. Soil Sci. Soc. Amer. Proc. 31, 644-647 (1967).
- Gulka, G., Doscher, C.M. and Watabe, N. Bull. Environ. Contam. Toxicol. 25, 477-481 (1980).
- Hamaker, J.W. and Thompson, J.M. Adsorption. In "Organic Chemicals in the Soil Environment", (eds.) C.A.I. Goring and J.W. Hamaker, Marcel Dekker Inc., New York, N.Y., pp. 49-144 (1972).
- Hamaker, J.W., Goring, C.A.I. and Youngson, C.R. Sorption and leaching of 4-amino-3,5,6-trichloropicolinic acid in soils. In "Organic Pesticides in the Environment", (ed.) R.F. Gould, Amer. Chem. Soc. Adv. Chem. Series 60, 23-37 (1966).
- Hance, R.J. Weed Res. 5, 108-114 (1965).
- Hansen, S.R. and Garton, R.R. Arch. Environ. Contam. Toxicol. 11, 1-10 (1982).
- Haque, R. Role of adsorption in studying the dynamics of pesticides in a soil environment. In "Environmental Dynamics of Pesticides", (eds.) R. Haque and V.H. Freed, Plenum Press, New York, N.Y., pp. 97-114 (1975).
- Hartley, D. and Kidd, H. "The Agrochemicals Handbook", Roy. Soc. Chem. The University, Nottingham, NG7 2RD, England. (1983).
- Helling, C.S. Soil Sci. Soc. Amer. Proc. 35, 743-748 (1971).
- Hill, G.D., McGahen, J.W., Baker, H.M., Finnerty, D.W. and Bingman, C.W. Agron. Jour. 47, 93-104 (1955).
- Julin, A.M. and Sanders, H.O. Mosq. News, 38, 256-259 (1978).
- Khan, S.V. "Pesticides in the Soil Environment", Elsevier, New York, N.Y., p. 240 (1980).
- Lacey, L.A. and Mulla, M.S. Mosq. News, 38, 264-268 (1978).
- Miura, J. and Takahashi, R.M. Jour. Environ. Entomol. 3, 631-636 (1974).
- Nimmo, W.B. "Adsorption of Diflubenzuron to Soils", Duphar, B.V., Crop Protec. Div. Rep. 56635/07/86, Doc. No. 03140, p. 10 (1986).

- Nimmo, W.B., de Wilde, P.C. and Verloop, A. *Pestic. Sci.* 15, 574-585 (1984).
- Nimmo, D.R., Hamaker, T.L., Moore, J.C. and Wood, R.A. Acute and chronic effects of Dimilin® on survival and reproduction of *Mysidopsis bahia*. In "Aquatic Toxicology" (eds.) J.B. Eaton, P.R. Parrish and A.C. Hendricks, Amer. Soc. Testing Materials, Publicn. No. STP 707, Philadelphia, Pennsylvania, pp. 366-376 (1980).
- Pfizer, Dimilin® WP-25, Registrn. No. 13,816, Pest Control Products Act, Agric. Can., Ottawa, Ont. Canada (1982).
- Post, L.C., DeJong, B.J. and Vincent, W.R. *Pestic. Biochem. Physiol.* 4, 473-483 (1974).
- Rabenort, B., de Wilde, P.C. de Boer, F.G., Korver, P.K., DiPrima, S.J. and Cannizzaro, R.D. Diflubenzuron. In "Analytical Methods for Pesticides and Plant Growth Regulators - Vol. 10", (eds.) G. Zweig and J. Sherma, Academic Press, New York, N.Y. pp. 57-72 (1978).
- Retnakaran, A. and Wright, J.E. Control of insect pests with benzoyl-phenyl ureas. In "Chitin and Benzoylphenyl ureas" (eds.) J.E. Wright and A. Retnakaran, Dr. W. Junk Publishers, Dordrecht, The Netherlands (1987).
- Stevenson, F.J. "Humus Chemistry", John Wiley & Sons, New York, N.Y., p. 443 (1982).
- Sundaram, K.M.S., Kingsbury, P.D. and Sundaram, A. *Jour. Agric. Food Chem.*, in press (1988a).
- Sundaram, K.M.S., Kingsbury, P.D. and Sundaram, A. *Jour. Environ. Sci. Health*, in press (1988b).
- Swanson, C.L.W., Thorp, F.C. and Friend, R.B. *Soil Sci.* 78, 379-388 (1954).
- Tester, P.A. and Costlow, J.D. Jr. *Mar. Ecol. Prog. Ser.*, 5, 297-302 (1981).
- Weber, J.B. *Residue Rev.* 32, 93-130 (1970).
- Weber, J.B. Model soil systems, herbicide leaching and sorption. In "Research Methods in Weed Science", (ed.) R.E. Wilkinson, XXV Ann. Commemorative Issue, Southern Weed Sci. Soc., pp. 146-160 (1972).
- Weed, S.B. and Weber, J.B. Pesticide-organic matter interactions. In "Pesticides in Soil and Water", (ed.) W.D. Guenzi, Soil Sci. Soc. of Amer. Inc., Madison, Wisc., pp. 39-66 (1974).

Weis, J.S. and Ma, A. Bull. Environ. Contam. Toxicol. 39, 224-228 (1987).

Worthing, C.R. and Walker, S.B. "The Pesticide Manual", 7th ed. British Crop Protection Council, 144-150 London Road, Croydon CRO 2TD, England., p. 695 (1983).