

# RESIDUE REVIEWS

Residues of Pesticides and Other  
Contaminants in the Total Environment

VOLUME 84

Editor

FRANCIS A. GUNTHER

JANE DAVIES GUNTHER

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Residues of Pesticides and Other  
Contaminants in the Total Environment

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## Foreword

Worldwide concern in scientific, industrial, and governmental communities over traces of toxic chemicals in foodstuffs and in both abiotic and biotic environments has justified the present triumvirate of specialized publications in this field: comprehensive reviews, rapidly published progress reports, and archival documentations. These three publications are integrated and scheduled to provide in international communication the coherency essential for nonduplicative and current progress in a field as dynamic and complex as environmental contamination and toxicology. Until now there has been no journal or other publication series reserved exclusively for the diversified literature on "toxic" chemicals in our foods, our feeds, our geographical surroundings, our domestic animals, our wildlife, and ourselves. Around the world immense efforts and many talents have been mobilized to technical and other evaluations of natures, locales, magnitudes, fates, and toxicology of the persisting residues of these chemicals loosed upon the world. Among the sequelae of this broad new emphasis has been an inescapable need for an articulated set of authoritative publications where one could expect to find the latest important world literature produced by this emerging area of science together with documentation of pertinent ancillary legislation.

The research director and the legislative or administrative advisor do not have the time even to scan the large number of technical publications that might contain articles important to current responsibility; these individuals need the background provided by detailed reviews plus an assured awareness of newly developing information, all with minimum time for literature searching. Similarly, the scientist assigned or attracted to a new problem has the requirements of gleaning all literature pertinent to his task, publishing quickly new developments or important new experimental details to inform others of findings that might alter their own efforts, and eventually publishing all his supporting data and conclusions for archival purposes.

The end result of this concern over these chores and responsibilities and with uniform, encompassing, and timely publication outlets in the field of environmental contamination and toxicology is the Springer-Verlag (Heidelberg and New York) triumvirate:

*Residue Reviews* (vol. 1 in 1962) for basically detailed review articles concerned with any aspects of residues of pesticides and other chemical contaminants in the total environment, including toxicological considerations and consequences.

*Bulletin of Environmental Contamination and Toxicology* (vol. 1 in 1966) for rapid publication of short reports of significant advances and discoveries in the fields of air, soil, water, and food contamination and pollution as well as methodology and other disciplines concerned with the introduction, presence, and effects of toxicants in the total environment.

*Archives of Environmental Contamination and Toxicology* (vol. 1 in 1973) for important complete articles emphasizing and describing original experimental or theoretical research work pertaining to the scientific aspects of chemical contaminants in the environment.

Manuscripts for *Residue Reviews* and the *Archives* are in identical formats and are subject to review, by workers in the field, for adequacy and value; manuscripts for the *Bulletin* are not reviewed and are published by photo-offset to provide the latest results without delay. The individual editors of these three publications comprise the Joint Coordinating Board of Editors with referral within the Board of manuscripts submitted to one publication but deemed by major emphasis or length more suitable for one of the others.

Coordinating Board of Editors

## Preface

That residues of pesticide and other contaminants in the total environment are of concern to everyone everywhere is attested by the reception accorded previous volumes of "Residue Reviews" and by the gratifying enthusiasm, sincerity, and efforts shown by all the individuals from whom manuscripts have been solicited. Despite much propaganda to the contrary, there can never be any serious question that pest-control chemicals and food-additive chemicals are essential to adequate food production, manufacture, marketing, and storage, yet without continuing surveillance and intelligent control some of those that persist in our foodstuffs could at times conceivably endanger the public health. Ensuring safety-in-use of these many chemicals is a dynamic challenge, for established ones are continually being displaced by newly developed ones more acceptable to food technologists, pharmacologists, toxicologists, and changing pest-control requirements in progressive food-producing economies.

These matters are of genuine concern to increasing numbers of governmental agencies and legislative bodies around the world, for some of these chemicals have resulted in a few mishaps from improper use. Adequate safety-in-use evaluations of any of these chemicals persisting into our foodstuffs are not simple matters, and they incorporate the considered judgments of many individuals highly trained in a variety of complex biological, chemical, food technological, medical, pharmacological, and toxicological disciplines.

It is hoped that "Residue Reviews" will continue to serve as an integrating factor both in focusing attention upon those many residue matters requiring further attention and in collating for variously trained readers present knowledge in specific important areas of residue and related endeavors involved with other chemical contaminants in the total environment. The contents of this and previous volumes of "Residue Reviews" illustrate these objectives. Since manuscripts are published in the order in which they are received in final form, it may seem that some important aspects of residue analytical chemistry, biochemistry, human and animal medicine, legislation, pharmacology, physiology, regulation, and toxicology are being neglected; to the contrary, these apparent omissions are recognized, and some pertinent manuscripts are in preparation. However, the field is so large and the interests in it are so varied that the editors and the Advisory Board earnestly solicit suggestions of topics and authors to help make this international book-series even more useful and informative.

"Residue Reviews" attempts to provide concise, critical reviews of timely advances, philosophy, and significant areas of accomplished or needed endeavor in the total field of residues of these and other foreign chemicals in any segment of the environment. These reviews are either general or specific, but properly they may lie in the domains of analytical chemistry and its methodology, biochemistry, human and animal medicine, legislation, pharmacology, physiology, regulation, and toxicology; certain affairs in the realm of food technology concerned specifically with pesticide and other food-additive problems are also appropriate subject matter. The justification for the preparation of any review for this book-series is that it deals with some aspect of the many real problems arising from the presence of any "foreign" chemicals in our surroundings. Thus, manuscripts may encompass those matters, in any country, which are involved in allowing pesticide and other plant-protecting chemicals to be used safely in producing, storing, and shipping crops. Added plant or animal pest-control chemicals or their metabolites that may persist into meat and other edible animal products (milk and milk products, eggs, etc.) are also residues and are within this scope. The so-called food additives (substances deliberately added to foods for flavor, odor, appearance, etc., as well as those inadvertently added during manufacture, packaging, distribution, storage, etc.) are also considered suitable review material. In addition, contaminant chemicals added in any manner to air, water, soil or plant or animal life are within this purview and these objectives.

Manuscripts are normally contributed by invitation but suggested topics are welcome. Preliminary communication with the editors is necessary before volunteered reviews are submitted in manuscript form.

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August 27, 1982

F.A.G.  
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## Table of Contents

Bound pesticide residues in soil and plants By SHAHAMAT U. KHAN . . . . .	1
Biological and environmental dynamics of insect growth regulators (IGRs) as used against Diptera of public health importance By LAL S. MIAN and MIR S. MULLA . . . . .	27
Photochemical formation and degradation of polychlorinated dibenzofurans and dibenzo- <i>p</i> -dioxins By GHULAM GHAS CHAUDHRY and OTTO HUTZINGER . . . . .	113
Subject Index . . . . .	163



# Bound pesticide residues in soil and plants

By

SHAHAMAT U. KHAN\*

## Contents

I. Introduction. . . . .	1
II. Definition . . . . .	2
III. Bound residues in soil. . . . .	3
a) Occurrence and distribution . . . . .	3
b) Mechanism of formation. . . . .	9
c) Release and bioavailability . . . . .	11
IV. Bound residues in plants. . . . .	13
a) Nature and distribution . . . . .	13
b) Bioavailability to animals . . . . .	16
V. Bound residues analysis . . . . .	16
Summary. . . . .	18
References. . . . .	22

## I. Introduction

To assess the environmental significance of pesticide<sup>1</sup> residues in soil and plants one must distinguish between two types of residues: those that are extractable with solvents and those that are not extractable with solvents. Bound pesticide residues are basically those residues remaining in soil or plants after exhaustive solvent extraction. These residues would escape detection in the analytical procedures conventionally used in residue analysis.

The significance of bound pesticide residues is chiefly addressed in terms of their bioavailability, both in amounts and forms of uptake. These and other considerations were topics of a research conference sponsored by the Division of Pesticide Chemistry, American Chemical Society (Kaufman *et al.* 1976). The final summary of the conference reflected on the problems and uncertainties

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\*Chemistry and Biology Research Institute, Research Branch, Agriculture Canada, Ottawa, Ontario, Canada K1A 0C6, Contribution No. 1275. This work was part of a coordinated program of research under the sponsorship of the International Atomic Energy Agency.

<sup>1</sup>Pesticides mentioned in text are identified in Table II, pages 20-21.

associated with the bound residues question. Thus in soil and plants, bound pesticide residues may constitute a potential environmental problem for the following reasons:

1. The nature and/or identity of bound residues of a pesticide expected to be present in soil or plants is not known.
2. Little is known about the significance of bound residues in terms of their bioavailability, toxicity and accumulative nature.
3. Conventional analytical methods may not detect these types of residues, thus underestimating the soil or plant burden of total pesticide residues.
4. The environmental fate of bound residues is not known.

In view of the widespread interest and concern for bound pesticide residues in soil and plants, it appears appropriate to present a brief account of the information available at this time on such pesticide residues. The author has also discussed his own results in order to describe the present state of the art of work on bound pesticide residues.

## II. Definition

A discussion of bound pesticide residues is exceedingly difficult and awkward without a meaningful interpretation of the proper terminology. In 1975 an American Institute of Biological Sciences-Environmental Task Group provided the following definition for *soil bound pesticide residue*: "that unextractable and chemically unidentifiable pesticide residue remaining in fulvic acid, humic acid, and humin fractions after exhaustive sequential extraction with nonpolar organic and polar solvents" (Anonymous 1975). There are inherent difficulties in the interpretation of results based only on the knowledge of the distribution of bound residues in humic fractions. Furthermore, techniques are now available by which some of the bound or nonextractable residues can be chemically identified. Therefore, the definition as stated is unacceptable not only to the pesticide scientist, but to our administrators and regulatory agencies as well.

*Bound pesticide residues* in soil and plants may be defined as chemical species, originating from pesticides usage, that cannot be extracted by methods commonly used in residue analyses. The chemical species here refer either to the intact pesticide or compounds derived from it. Extraction refers to the exhaustive removal of the chemical species by solvents from a soil or plant matrix. It is important that in each study concerned with bound residues the extraction procedure should be described. Bound residues exclude fragments of the chemical species possessing no pesticidal activity and recycled into the natural polymeric products through metabolic pathways of a biological system. Furthermore, some ionic chemical species that are not extractable by the ordinary organic solvents should not be regarded as bound residues as suitable pH and salt regimes can release them unchanged from the substrate.

The unextractability of bound pesticide residues from soil and plants has little meaning unless it is related to their bioavailability. It is important to know the availability of bound residues to living organisms, particularly to animals and to those plants consumed in the animal diet. Therefore, in the broadest sense, the bound pesticide residues should be categorized as follows:

1. Biounavailable Bound Residues: (a) Those bound residues in soil, which are not taken up by plants and/or soil-inhabiting animals, and (b) those bound residues in plants that when administered orally to animals are not absorbed from the gastrointestinal tract and are excreted in the feces.
2. Bioavailable Bound Residues: (a) Those bound residues in soils, which are taken up by plants and/or soil-inhabiting animals, and (b) those bound residues in plants which when administered orally to animals, are absorbed from the gastrointestinal tract.

### III. Bound residues in soil

#### *a) Occurrence and distribution*

Bound pesticide residues in soil are the focal point of several recent studies in various laboratories. Table I summarizes some of the work reported during the past few years on bound residues in different soils for a number of pesticides. In most of these studies, radiolabeled pesticides were used and the bound radioactivity was determined by combusting the extracted soil to produce  $^{14}\text{CO}_2$ , which was then quantitated by scintillation counting. The bound residues expressed as % of applied pesticide ranged from 7 to 90%. A significant quantity of bound residues is being 'any amount of unextractable residue, greater than 10% expressed as the parent compound, remaining one year after a single treatment' (Anonymous 1975). Therefore, in situations where significant concentrations of bound pesticide residues occur in soil, some relevant properties of these residues, such as bioavailability, persistence, and mobility in soil should also be investigated.

In laboratory experiments formation of bound residues have been shown to increase with incubation time. Utilizing  $^{14}\text{C}$ -ring labeled prometryn, the amount of bound  $^{14}\text{C}$  residues in an organic soil increased steadily over a 150-day incubation period (Khan and Hamilton 1980). Thus, at the end of the incubation period, extractable  $^{14}\text{C}$  residues decreased to 36.5% while the bound  $^{14}\text{C}$  residues (determined by combustion to  $^{14}\text{CO}_2$  after the soil had been exhaustively extracted) increased to 43.0% of the initially added  $^{14}\text{C}$  (Fig. 1). The disappearance of radiocarbon added to the soil could not be accounted for only by the extractable and bound  $^{14}\text{C}$  residues (Fig. 1). It is apparent that  $^{14}\text{CO}_2$  and/or volatile degradation products were evolved from  $^{14}\text{C}$ -prometryn treated soil and that these constituted up to about 20% of the applied radioactivity during the incubation period. Persistent pesticides (dieldrin, DDT) differ from

Table I. Bound residue levels of some pesticides in soils.

Pesticide	Soil	Organic matter (%)	Rate (ppm)	Time <sup>a</sup>	Bound <sup>14</sup> C residues (% of applied)	Reference
<i>Herbicides</i>						
Butralin	silt loam	1.5	10	7 m	17	Helling & Krivonak (1978 a)
Chloridrine	silt loam	1.5	10	7 m	17	Helling & Krivonak (1978 a)
2,4-D	sandy loam	4.0	2	35 d	28	Smith & Muir (1980)
3,4-Dichloroaniline	sandy loam	1.0	0.7	18 m	90	Viswanathan <i>et al.</i> (1978)
Dinitramine	silt loam	1.5	10	5 m	8	Helling & Krivonak (1978 a)
	silt loam	—	0.6	244 d	55	Smith <i>et al.</i> (1973)
Flamprop-isopropyl	peat	—	50	28 w	19	Hitchings & Roberts (1979)
	sandy loam	—	17	28 w	10	Hitchings & Roberts (1979)
Fluchloralin	silt loam	1.5	10	7 m	21	Helling & Krivonak (1978 a)
Isopropalin	silt loam	—	11	12 m	27	Golab and Althaus (1975)
Methabenzthiazuron	sandy	2.2	10	111 d	41	Fuhr & Mittelstaedt (1980)
Pirimicarb	—	—	0.5	24 m	70	Hill (1976)
Oryzalin	silt loam	—	—	36 m	35	Golab <i>et al.</i> (1975)
	silt loam	—	—	12 m	56	Golab & Amundson (1975)
Oxadiazon	loam	1.5	10	25 w	13	Ambrosi <i>et al.</i> (1977 b)
Pentachlorophenol	silty clay loam	2.3	10	24 d	45	Murthy <i>et al.</i> (1979)
Profluralin	silt loam	1.5	10	7 m	11	Helling & Krivonak (1978 a)
Prometryn	organic	85	12.4	150 d	43	Khan & Hamilton (1980)
Propanil	sandy loam	6.0	5	20 d	73	Bartha (1971)
	clay loam	4.1	6	25 d	73	Chisaka & Kearney (1970)
Trifluralin	silt loam	—	0.8	12 m	50	Golab & Amundson (1975)
	silt loam	1.5	10	7 m	7	Helling & Krivonak (1978 a)
	loam	—	—	36 m	38	Golab <i>et al.</i> (1979)
	silty clay loam	3.9	10	63 d	72	Wheeler <i>et al.</i> (1979)

*Insecticides*

Bassa R	loam clay	4.7	20	30 d	35	Ogawa <i>et al.</i> (1976)
Carbaryl	loamy sand	3.3	2	32 d	32	Kazano <i>et al.</i> (1972)
	loamy sand	12.8	2	32 d	49	Kazano <i>et al.</i> (1972)
Cypermethrin	sandy clay	2.4	10	24 w	23	Roberts & Standen (1981)
	loam					
p,p-DDT	silt loam	4.2	1	28 d	25	Lichtenstein <i>et al.</i> (1977)
Dieldrin	silt loam	4.2	1	28 d	7	Lichtenstein <i>et al.</i> (1977)
Fenitrothion	organic	44.4	74	50 d	48	Spiller <i>et al.</i> (1979)
	sandy loam	5.4	74	50 d	50	Spiller <i>et al.</i> (1979)
Fonofos	silt loam	4.2	1	28 d	35	Lichtenstein <i>et al.</i> (1977)
Methyl-parathion	silt loam	4.2	6	46 d	32	Fuhremann & Lichtenstein (1978)
						Katan <i>et al.</i> (1976)
Parathion	sandy loam	1.3	1	28 d	18	Katan <i>et al.</i> (1976)
	loam	4.7	1	28 d	45	Lichtenstein <i>et al.</i> (1978)
Phorate	silt loam	4.7	4.0	1 w	26	Ambrosi <i>et al.</i> (1977 a)
Phosalone	silt loam	1.5	10	84 d	80	

<sup>a</sup> d = day, w = week, m = month.

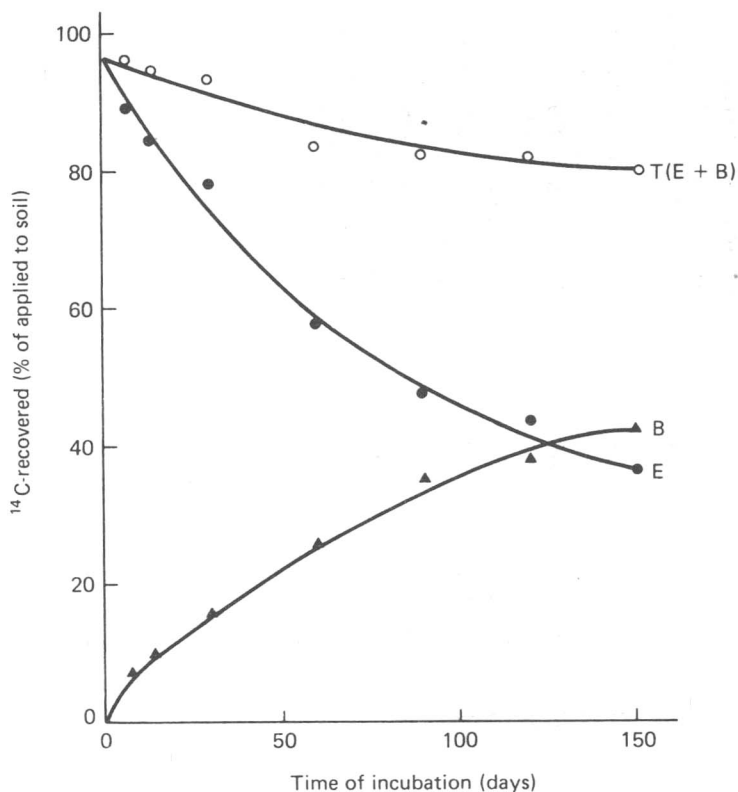


Fig. 1. Extractable and bound radioactivity in an organic soil treated with  $^{14}\text{C}$ -prometryn (12.4 mg/kg, 0.94  $\mu\text{Ci}$ ) and incubated aerobically under moist conditions for 150 days: curve *E*, extracted  $^{14}\text{C}$ , curve *B*, bound  $^{14}\text{C}$  determined by combusting soil to  $^{14}\text{CO}_2$ , and curve *T*, total of extractable and bound (Khan and Hamilton 1980).

nonpersistent pesticides (methyl parathion, fonofos) in their relatively low binding properties and their high extractability from soils (Lichtenstein *et al.* 1977, Fuhremann *et al.* 1978, Lichtenstein 1980).

It is possible that in addition to the parent pesticide, the degradation products formed may also become bound in the production of soil-bound residues. Katan *et al.* (1976) and Katan and Lichtenstein (1977) demonstrated rapid binding of the parathion amino analogue. In a study of trifluralin binding to a soil, Wheeler *et al.* (1979) also observed a significant relationship between the amount of binding and the substitution on the amino nitrogen. Thus, it was postulated that some of the metabolites containing secondary or primary amino functional groups may have become part of the bound residues in soil. It has been suggested that the free- $\text{NH}_2$  groups are responsible for the soil binding

behavior of certain trifluoromethanesulfonanilide pesticides and related compounds (Bandal *et al.* 1976). Spillner *et al.* (1979) implicated 2-methylhydroquinone, an oxidative product of 3-methyl-4-nitrophenol, as the precursor to the formation of fenitrothion bound residues in aerobic soil. However, under anaerobic conditions binding was thought to proceed through the intermediates. Golab *et al.* (1979) suggested that  $\alpha,\alpha,\alpha$ -trifluorotoluene-3,4,5-triamine, a degradation product of trifluralin, may be a key compound in the formation of soil-bound residues. In our experiments it was observed that, following a soil incubation period of one year with  $^{14}\text{C}$ -prometryn and exhaustive methanol-water extraction, more than half of the total bound residues in the organic soil was in the form of parent compound (Khan 1982). The remainder constituted small amounts of hydroxypropazine and unidentifiable methanol-soluble material.

In the formation of bound residues with the herbicide propanil, the bulk of the immobilized aromatic propanil moiety was chemically bound to humic acid (HA) to form a humus-3,4-dichloroaniline complex (Bartha 1971). More than half of the 3,4-dichloroaniline is converted to nonhydrolyzable residues, which may be integrated into the soil organic matter nuclei (Hsu and Bartha 1973). The insecticide phosalone was degraded rapidly in both moist and flooded soil with an accumulation of  $^{14}\text{C}$  from the benzoxazolone moiety into the soil-bound fraction (Ambrosi *et al.* 1977 a). The radioactivity in the bound fraction was most extensively associated with the fulvic acid (FA) fraction, where it appeared to be fairly stable. For the herbicide oxadiazon the distribution of radioactivity in the bound residue fractions of the moist soil was  $\text{FA} > \text{HA}$  or humin, whereas radioactivity was fairly evenly distributed in the flooded bound-residue fractions (Ambrosi *et al.* 1977 b). Spillner *et al.* (1979) observed that bound radiocarbon [(ring- $^{14}\text{C}$ ) fenitrothion] was associated mainly with HA and FA fractions. The binding was explained through an intermediate, 2-methylhydroquinone, which copolymerizes with humic substances during the formation to yield radioactive products incorporated into the soil organic matter. Golab *et al.* (1979) suggested that a triamine derivative of trifluralin was either itself bound to the humic substances or that it is an intermediate to other compounds that are chemically bound or complexed with humic substances. These and other studies (Golab and Amundson 1975, Helling 1976, Harvey and Han 1978; Murthy *et al.* 1979, Helling and Krivonak 1978 a, Smith and Muir 1980) indicate that bound pesticide residues may be associated mainly with humic substances in soil. It should be noted that soil bound radioactivity extracted by alkali into humic substances could not be further partitioned into organic solvents in amounts sufficient to pursue identification. Kazano *et al.* (1972) were unable to extract by ethyl ether any bound radioactivity associated with HA.

Recently, we determined the distribution of bound  $^{14}\text{C}$  residues among various humic fractions of an organic soil treated with  $^{14}\text{C}$ -prometryn (Khan 1980). The method of extraction, separation, and purification of humic materials outlined in Figure 2 is analogous to that described by Schnitzer and Khan

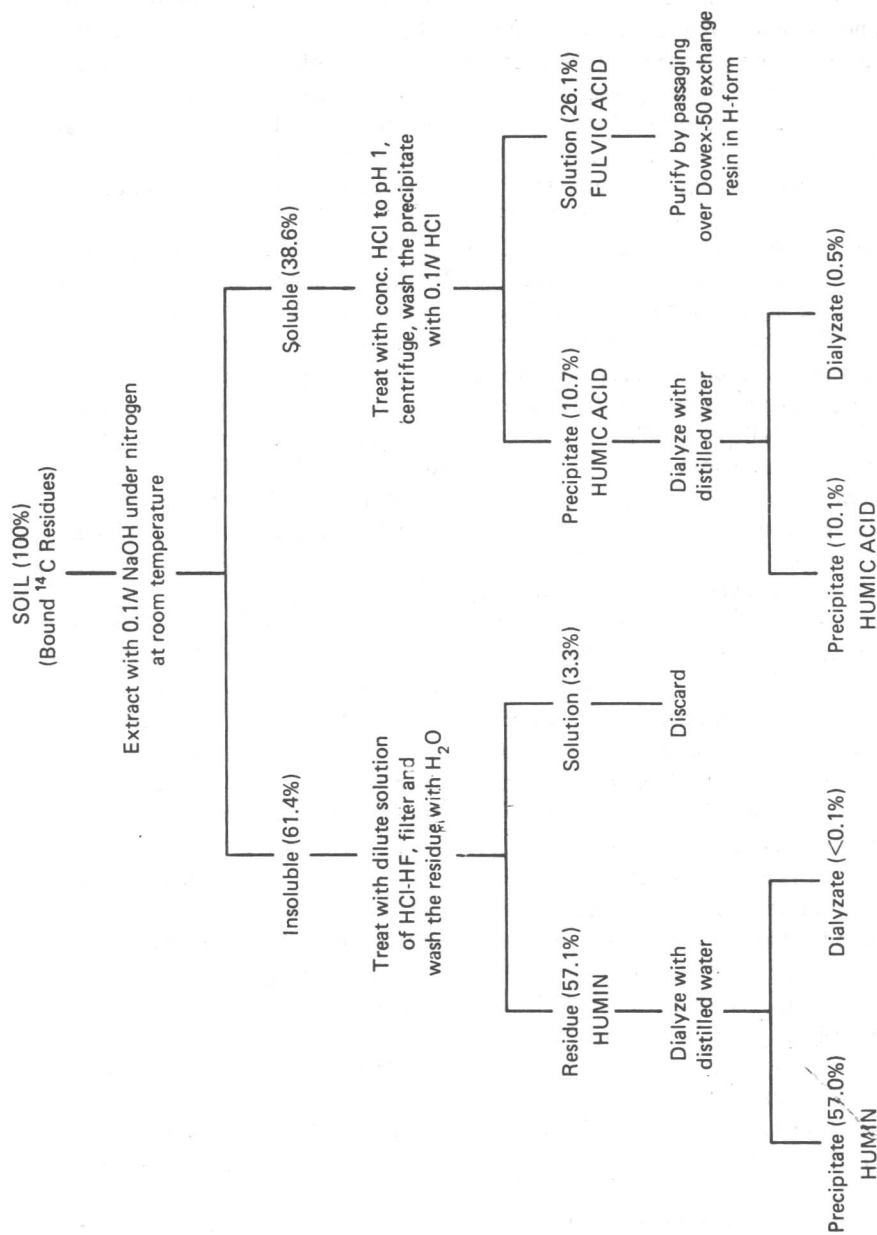


Fig. 2. Flow diagram of the fractionation of soil containing bound  $^{14}\text{C}$  residues. Numbers in parentheses show the percentage of  $^{14}\text{C}$  relative to the total  $^{14}\text{C}$ -bound residues in soil (Khan 1982).



(1972). Proportions of total bound  $^{14}\text{C}$  in humin, HA, and FA fractions were 57, 11, and 26%, respectively (Fig. 2). The incorporation of  $^{14}\text{C}$ -bound residues into humic materials observed in our study is consistent with those reported for other pesticides described earlier. The  $^{14}\text{C}$ -residues were concentrated in the humin fraction (Fig. 2). Furthermore, only a small amount of  $^{14}\text{C}$  (3.3%) was released in solution by solubilizing the mineral fraction from humin by the HCl-HF treatment. The average molecular weight of bound  $^{14}\text{C}$  residues associated with humin and HA appeared to be greater than  $\approx 12,000$  since very little  $^{14}\text{C}$  was dialyzable. The presence of  $^{14}\text{C}$  bound residues in FA fraction (26%) is of special interest. The latter is a naturally occurring water-soluble, low molecular weight polyelectrolyte and is considered to be the dominant soluble organic fraction present in the soil solution under field conditions. It is also well known that FA is present in many surface waters and imparts a yellow to brown color in natural water (Christman and Minear 1971, Schnitzer and Khan 1972). It is likely that bound residues associated with the soluble FA fraction may become bioavailable to both plants and exposed aqueous or soil fauna.

In our experiments it was observed that a considerable proportion of  $^{14}\text{C}$  residues in humic materials was comprised of the parent herbicide, *i.e.*, prometryn, and its monodealkylated product, namely, 2-(methylthio)-4-amino-6-(isopropylamino)-*s*-triazine (Khan 1982). However, the FA fraction contained an appreciable amount of the 2-hydroxy analogue of prometryn [2-hydroxy-4,6-bis(isopropylamino)-*s*-triazine]. Trace amounts of the mono-dealkylated analog of prometryn [2-(methylthio)-4,6-diamino-*s*-triazine] were also identified in humin and HA (Khan 1982). Alkaline extraction with 0.1*N* NaOH under nitrogen, widely used for the extraction of humic materials from soil, was thought to hydrolyze or chemically degrade the herbicide residues in soil. However, our experiments revealed nearly quantitative recoveries of unchanged prometryn from aqueous solutions when the herbicide was extracted with 0.1*N* NaOH (pH 13). Hitching and Roberts (1979) used 1.25 *N* aqueous NaOH solution at 80°C for 2 hr for extraction of humic materials containing bound residues and were able to identify small amounts of the total radioactivity in HA.

### *b) Mechanism of formation*

The general consensus appears to be that in the formation of bound residues, the pesticide or its metabolites are chemically bound into the soil organic matter. However, our recent data provide evidence that support the contention that physical binding may also play an important role in the formation of soil-bound residues.

Isothermal heating has been used for investigating the mechanism of thermal decomposition of organic matter (Schnitzer and Hoffman 1965). It was thought that thermoanalytical methods applied to soil and humic materials containing bound residues may provide useful information on the nature of pesticide binding (Khan 1982). The thermal profiles of  $^{14}\text{C}$  bound residues of soil and