

ASSESSMENT OF THE ENVIRONMENTAL  
DYNAMICS OF SELECTED PESTICIDES  
OF IMPORTANCE IN WESTERN CANADA

by

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## EXECUTIVE SUMMARY

A literature review is given of the persistence and fate of several pesticides which are heavily used in Western Canada: 2,4-D, 2,4-D butyric acid, MCPA, Diclofop-methyl, Dimethoate, Malathion, Trifluralin, Diallate, Triallate, Dicamba and Bromoxynil. Knowledge gaps are identified and research recommendations are made.

## MANAGEMENT PERSPECTIVE

This review was prepared for the Water Quality Branch, Western and Northern Region.

## RÉSUMÉ

Une étude documentaire porte sur la persistance et le devenir de plusieurs pesticides largement utilisés dans l'Ouest du Canada : le 2,4-D, l'acide 2,4-D butyrique, le MCPA, le diclofop-méthyl, le diméthoate, le malathion, la trifluraline, le diallate, le triallate, le dicamba et le bromoxynil. Des lacunes ont été identifiées au niveau des connaissances et des recommandations ont été formulées en matière de recherches.

## PERSPECTIVE-GESTION

La présente étude a été préparée à l'intention de la Direction de la qualité des eaux, région de l'ouest et du nord.

**ABSTRACT**

A literature review was prepared for the Water Quality Branch, Western and Northern Region, on the persistence and fate of several pesticides which are heavily used in Western Canada: 2,4,-D, 2,4-D butyric acid, MCPA, Diclofop-methyl, Dimethoate, Malathion, Trifluralin, Diallylate, Triallylate, Dicamba and Bromoxynil. Knowledge gaps are identified and research recommendations are made.

## RÉSUMÉ

Une étude documentaire a été préparée à l'intention de la Direction de la qualité des eaux, région de l'ouest et du nord, sur la persistance et le devenir de plusieurs pesticides largement utilisés dans l'Ouest du Canada : le 2,4-D, l'acide 2,4-D butyrique, le MCPA, le diclofop-méthyl, le diméthoate, le malathion, la trifluraline, le diallate, le triallate, le dicamba et le bromoxynil. Des lacunes ont été identifiées au niveau des connaissances et des recommandations ont été formulées en matière de recherches.

## INTRODUCTION

Man's use of pesticides has been instrumental in increasing food production on a global scale, and in the control of some diseases. Through these applications, however, some pesticides have become nearly ubiquitous in the environment and some have caused significant damage to the environment. The effects of pesticides on public health and the survival of fish and wildlife species are areas of concern. Sound management of water is intimately linked to a knowledge of the aquatic dissipation and degradation of pesticides and other contaminants. The overall transport process determines in large measure the effects of waterborne substances on quality throughout a water course, and a clear understanding of physical, chemical and biological degradation and dissipation processes is particularly important.

Pesticides are used extensively in agriculture in Western Canada. This report reviews, to January 1986, the aquatic environmental fate and persistence of several pesticides of concern and their degradation products, for the Water Quality Branch, Western and Northern Region. The structures of the parent compounds are shown in Figures 1 and 2.

### 2,4,-D

2,4-Dichlorophenoxyacetic acid is a widely used herbicide for the control of terrestrial and aquatic weeds. Produced by the reaction of

2,4-dichlorophenol (2,4-DCP) and sodium monochloroacetate, the commercial product may contain as much as 5% 2,4-DCP. The herbicide is formulated in many ways such as the sodium salt, amine salts and esters. The acute oral LD<sub>50</sub> of 2,4-D for rats is 375-800 mg/kg (1).

The initial breakdown product of 2,4-D in water is believed to be 2,4-DCP (2). However, it is not a major metabolite in many crops since the residue level of 2,4-DCP is less than 10% of the parent compound (3). Major amino acid conjugates in soybeans are 2,4-D-glutamic acid and 2,4-D-aspartic acid (1). Ring hydroxylation of 2,4-D in beans to yield 2,5-dichloro-4-hydroxy-phenoxyacetic acid and 2,3-dichloro-4-hydroxy-phenoxyacetic acid has been documented, as well as side-chain lengthening to yield 2,4-D-butyric acid (1,4,5).

In soils, the rate of degradation of 2,4-D depends upon soil characteristics such as pH, organic matter content, moisture content, chemical composition and climatic conditions, as well as the amount applied. In Finnish soil, 2,4-D applied at the 10 ppm level was completely degraded after 24 w, and at the 1000 ppm level it took >72 w (6). In Saskatchewan soil (pH 6.2-7.8), complete degradation took 14 d (unknown application rate) (7). In a Northern Ontario forest (application rate 2.24 kg/ha), the dissipation half-lives were 7 d in clay soil and 23 d in the top 10 cm of sandy soil (7). In a pond treated with 2,4-D-dimethylamino salt, the half-life of 2,4-D was determined to be 35 d. An identical half-life was found for 2,4-D in a pond treated with 2,4-D-butoxyethyl ester (8).

2,4-D-Butyric Acid (2,4-DB)

Relatively little information is available on the persistence and degradation of 2,4-DB in aquatic environments. 2,4-DB was first used to control weeds in legumes. The herbicidal properties of 2,4-DB arise from  $\beta$ -oxidation of the aliphatic side chain to give 2,4-D (9-11).

MCPA (4-chloro-2-methylphenoxyacetic acid)

MCPA is used to control annual and perennial weeds in cereal crops, grassland and rice fields, and is used against scrub in forestry. Since 1979, MCPA has been applied as the dimethylamino salt (12). In this formulation, about 1% by weight of 2-methylphenoxyacetic acid is present. In the past, 4-chloro-o-cresol comprised as much as 4% of the sodium salt formulation.

The two major metabolites of MCPA in soils and vegetation are 4-chloro-o-cresol and 5-chloro-3-methylcatechol (13-17).

Various degradation rates have been reported for MCPA in soils. Key factors affecting the rate are soil organic content, pH, moisture content and climatic conditions as well as amount applied. MCPA persisted in some Saskatchewan soils (pH 6.2-7.8) for as long as 70 d. Half-lives for a Finnish sandy clay soil and a Bangladesh sandy loam soil (both at 23-25°C) were 50 and 23 d, respectively (6, 14-16).

In a dilute (1.0 ppm) aqueous solution at pH 8.3, MCPA was photochemically degraded with a half-life of 18 d. Sunlight



irradiation of a MCPA-dimethylamino spray formulation (14.7 g/L) and the semisolid residue remaining after its evaporation on a glass surface resulted in >80% loss of MCPA within 6 d and formation of 4-chloro-o-cresol and many other products. An MCPA spray solution (14.7 g/L) irradiated in a photoreactor with no evaporation showed a half-life of 8 d (18).

Diclofop-methyl

(Methyl 2-[4-(2',4'-dichlorophenoxy)phenoxy] propionate)

Diclofop-methyl or Hoe 23408 OH is used mainly as a post-emergence herbicide although it also has some pre-emergence activity. It selectively controls the growth of a few annual grass weeds in cereal crops (19).

Diclofop-methyl initially degrades to diclofop in soils as well as in plants, apparently as the result of esterase activity. The esterase may be excreted by plant roots or be of microbial origin in soil degradation. In soils, diclofop has been reported as the major metabolite and only trace amounts of phenolic derivatives have been detected. The initial hydrolysis of diclofop-methyl in soil was very rapid; 40-85% of the ester had undergone hydrolysis in three different soils after a 24-h incubation period at 20°C. After 24 h, the hydrolysis rate slowed, and traces of diclofop-methyl could be detected after 10 w. The product diclofop was strongly bound to soils and was only extractable by hot alkali treatment (20).

The major metabolite of diclofop-methyl in wheat is an acidic aryl-0-glucoside of ring-hydroxylated diclofop while the major metabolite in wild oat is the neutral glucose ester of diclofop which easily reverts to diclofop (cf. Fig. 3) (19, 21, 22).

#### Dimethoate

(O,O-dimethyl S-(N-methylcarbamoylmethyl) phosphorothioate)

Dimethoate is registered in Canada for systemic insect control in cereals, oil seeds, commercial and home gardens, forage crops, trees and shrubs. In Saskatchewan, one of the main uses of dimethoate is for grasshopper control in wheat. The production of dimethoxon (replace P=S with P=O in Fig. 1) is responsible for the toxicity of dimethoate to susceptible insects. There is no evidence for the carcinogenicity of dimethoate (23).

It must be borne in mind that many studies of the persistence of dimethoate were only concerned with the ability to detect the parent compound, as opposed to detecting products of reaction. It is possible that physical loss through a variety of mechanisms is responsible for the imputed "degradation".

The aqueous solubility of dimethoate at 20°C is greater than 5 g/L (24), and its log  $K_{ow}$  is 0.77 (25).

Dimethoate is stable in distilled water at pH 7 for at least 40 d, with no volatilization (26). Experiments on stability up to 160 d which showed greater than 50% loss of dimethoate may have been

complicated by bacterial contamination (26). No products were identified. There is no information on sunlight photolysis of dimethoate in water.

Eichelberger and Lichtenberg (27) found that the disappearance half-life of dimethoate in river water at room temperature was 8 w (cf. 1 w for malathion), but identified no products.

In soil, 77% of applied dimethoate was unaccounted for after 2 w, but products or unextractable residues were not determined (28).

In plants, the half-life of extractable dimethoate is generally less than 3 w (29-34). Dimethoxon, which is perhaps the only metabolite with appreciable toxicity, was frequently detected, albeit at low concentrations. Lucier and Menzer (29) isolated 18 metabolites from bean leaves, but only identified seven. No metabolite accounted for more than 4% of the initially applied radiolabel.

Dimethylthiophosphate, a hydrolysis product of both dimethoxon and malaoxon, is only 3% as effective at inhibiting human plasma acetylcholinesterase as are the parent compounds, hence it is not a toxicologically significant degradation product (35).

#### Malathion

(0,0-dimethyl S-(1,2-di(ethoxycarbonyl)ethyl) phosphorodithioate)

Malathion was introduced by the American Cyanamid Company in 1950. This insecticide is considered much safer than parathion to mammals and birds. Its safety to higher vertebrates is attributed to

the action of carboxyesterase enzymes which degrade it to relatively nontoxic compounds faster than it is oxidized to the more potent acetylcholinesterase inhibitor malaoxon (replace P=S with P=O in Fig. 1). The production of malaoxon is responsible for its selective toxicity to susceptible insects, which have little, if any, carboxyesterase enzymes. The high margin of safety of malathion to mammals and birds, and its selectivity against target insects, coupled with its amenability to ultra-low volume applications, make it a good general purpose contact insecticide for household, garden, greenhouse, agriculture, forestry and public health applications.

Isomalathion in malathion spray formulations was deemed to be responsible for the poisoning of spray crews in the 1976 Pakistan Malaria Control Program (36). The structure of isomalathion is shown in Fig. 4. This isomer was present at 0.3-3.1% by weight. The mammalian toxicity of isomalathion is about three times that of malathion (23).

A number of early studies on the persistence of malathion in various environmental "compartments" were only concerned with ability to detect the parent malathion. It is possible that malathion had become conjugated with the host matrix, or that it was lost physically.

Malathion appears not to persist in the environment. Estimates of its persistence in natural water range from 1 d to 2 w (36). Its persistence in soil has been estimated to be 1 w (36). Algal and bacterial cultures apparently degrade it with half-lives of 1 w (36).

In none of these studies, however, were degradation products identified.

In a study of the chemical degradation of malathion in water, Wolfe et al. (37) showed that the hydrolysis rate was at a minimum at pH 4 and increased with both increasing and decreasing pH. At 20°C, the half-life of malathion in water ranged from 40 d at pH 6 to 1 d at pH 8. The mechanism of hydrolytic degradation is shown in Fig. 5. The rate of production of the diacid was about 18 times slower than the rate of production of the monoacids. No malaoxon formation was observed in oxygen-saturated water at pH 6 over a period of 2 w.

Wolfe et al. (37) also examined the photolysis of malathion using wavelengths >290 nm, and determined the half-life in distilled water at pH 6 to be 40 d. In natural water in sunlight, malathion was 50% dissipated in 16 h, but no degradation products were determined.

Bender (38) has shown that one of the hydrolysis products, diethyl fumarate, is about twice as toxic as malathion to the fathead minnow (Pimephales promelas, Rafinesque), but no information is available on the toxicity of the monoacids.

Trifluralin (2,6-dinitro-N,N-di-n-propyl-4-trifluoromethylaniline)

Trifluralin is a herbicide used for selective pre-emergence control of a wide variety of grasses and broadleaf weeds. It was introduced by Eli Lilly and Company in 1960. It has low mammalian toxicity, but moderate to high fish toxicity (for rainbow trout, 24 hr

LC-50 values are 100-400 µg/L at 2-13°C (39)). An early report by the U.S. National Cancer Institute (40) that trifluralin was a liver carcinogen in female mice was disputed by the U.S. EPA (41), which claimed that the trifluralin used by NCI contained about 85 ppm nitrosamines, which were responsible for the observed carcinogenicity. Eli Lilly and Company has since reduced the nitrosamine content of its trifluralin preparation to less than 4 ppm (41).

Trifluralin can persist from year to year in soil (42-44), both controlling weeds and damaging sensitive crops (45). Volatilization can be a significant pathway of disappearance (46-49), and for this reason trifluralin is usually incorporated into the soil.

In soil, trifluralin is subject to microbial degradation, and slowly becomes converted to unextractable (and unidentified) residues (43,44,47,50-53). Aerobic degradation in soil proceeds by N-dealkylation followed by progressive reduction, whereas anaerobic degradation occurs with a preliminary reduction prior to dealkylation. Twenty-eight degradation products have been identified (44). None exceeded 3% of the initially applied trifluralin. After 3 years, less than 1.5% of the applied trifluralin could be detected in soil, 4% was distributed among numerous transformation products, and 38% remained as (unidentified) soil-bound residues.

Trifluralin on soil, in water or in air decomposes fairly readily in sunlight (54-56), through mechanisms of dealkylation and reduction, to a largely unresolvable mixture of numerous trace products. Leitis

and Crosby (54) speculated that 2-ethyl-7-nitro-5-trifluoromethyl-benzimidazole (cf. Fig. 6), which is the most stable of the photoproducts, might persist in the environment long enough to be detectable.

It is reasonable to assume that most of the trifluralin which may reach aquatic ecosystems will do so absorbed to soil particles. Such adsorption to soil, of course, greatly reduces the toxicity of trifluralin to fish (57). In an atypical situation, that of trifluralin entering a river in the effluent of a trifluralin-manufacturing plant, Spacie and Hamelink (58) observed bioconcentration in various species of fish by factors up to 6000. Depuration half-lives were less than 2 months.

Diallate (S-2,3-dichloro-2-propenyl)-bis(1-methylethyl)carbamothioate)  
and Triallate

(S-2,3,3-trichloro-2-propenyl)-bis(1-methylethyl) carbamothioate)

Diallate is marketed by the Monsanto Company under the trade name "Avadex" as a pre- or post-emergent herbicide for controlling such weeds as wild oat, windgrass and slender foxtail in crops of beet, potato, beans, pea, and winter Canola. The acute oral LD50 of diallate is 395 mg/kg in rats and 510 mg/kg in dogs. It is an oily liquid, with a b.p. of 150°C at 9 mm. It is soluble in most organic solvents such as acetone, benzene, toluene and alcohols, and its water solubility is 14 mg/L at 25°C. Diallate is a carcinogen in mice (59).

Triallate is also marketed by Monsanto under the trademarks "Avadex BW" and "Fargo". It is used as a pre- and post-emergent herbicide primarily for control of wild oats in cereals, beets and peas. The acute oral LD50 of triallate to rats is 1500-2000 mg/kg. It is also an oily liquid with a boiling point of 148-9°C at 9 mm. It is also soluble in most organic solvents and has a water solubility of 4 mg/L at 25°C.

Both herbicides are relatively nonpersistent in soils with the major loss routes being degradation, bound residue formation and volatilization in decreasing order of importance (60,61). The half-life of diallate in a variety of soils was 20 w or less (62). Half-lives of triallate were three to four times longer than diallate for the same soils. Measurable amounts of undegraded triallate could be detected after 52 w (61).

Both diallate and triallate are promutagens, exhibiting mutagenic activity in bacterial systems after microsomal oxidation. The initial step appears to involve the formation of unstable sulfoxides that undergo rearrangement followed by a 1,2-elimination reaction to give 2-chloroacrolein from diallate and 2-chloroacrylyl chloride from triallate. In addition, both diallate and triallate sulfoxides react to produce carbamoylsulfonyl chloride. The cis-diallate sulfoxide reacts ten-fold faster than the trans-diallate or triallate sulfoxides. The 2-haloacrylic acids have been proposed as indicators of 2-haloacrolein intermediate production in vivo in rats (63-65).



Diallate and triallate photodecompose in oxygenated water to products that are mutagenic in the Ames assay. The route of this reaction appears to be photochemical sulfoxide production followed by 2-chloroacrolein production via decomposition of the sulfoxide (66).

Dicamba (3,6-dichloro-2-methoxybenzoic acid)

Dicamba is a postemergence herbicide used to control broadleaf and grassy weeds in cereals, pasture and turf. It is formulated as the alkali or amine salt, or as the free acid.

It is metabolized in soil to 3,6-dichlorosalicylic acid (I), and by plants and animals to 5-hydroxydicamba (II) (cf. Fig. 7) (53, 66-76).

Breakdown is rapid in warm soil with a half life of 1-4 w. 3,6-Dichlorosalicylic breaks down more slowly, and accumulates in the soil for a few weeks or more. Dicamba is mobile in soil whereas 3,6-dichlorosalicylic acid is strongly adsorbed. In spite of its high water solubility and soil mobility, dicamba appears to be metabolized in soil before it can enter the aquatic environment. Metabolite monitoring in the aquatic environment could be done for 3,6-dichlorosalicylic acid on suspended sediment rather than for dicamba in water. Note that analytical methods employing methylation do not distinguish between the salicylic acid and dicamba (77-80).

Dicamba is not likely to persist in the aquatic environment nor to bioaccumulate. It disappears quickly in pond water in the presence of sediment. It does not bioaccumulate in model ecosystems (81-88).

Normal uses of dicamba are unlikely to lead to concentrations in the aquatic environment that approach the level of concern. Acute toxicities to aquatic species are 10-100 mg L<sup>-1</sup> (89-94). The genotoxicity of dicamba is low, being negative in most tests and positive only for DNA damage in prokaryotes and mutagenic in a plant bioassay (95-98).

In summary, dicamba has low toxicity, breaks down readily in soil and aquatic environments, and does not bioaccumulate. The literature on dicamba is quite complete with no major gaps. No high priority research needs could be identified, although more information would be useful on volatilization and the potential for groundwater contamination in porous soils.

#### Bromoxynil (3,5-dibromo-4-hydroxybenzotrile)

Bromoxynil is a postemergence herbicide used for control of broad-leaved weeds. It is formulated as the alkali or amine salt, or the octanoate. The octanoate is metabolized by cereals (winter wheat) and soil microorganisms to bromoxynil which is further metabolized to the amide, acid and other products (99-103).

Breakdown occurs quite rapidly in warm soil (half-life of 2-3 w or less) but more slowly at lower temperature (104-110). The

most likely time for it to appear in surface water would be in the fall if it were applied to winter wheat grown under reduced tillage farming, or perhaps in a pulse during spring runoff. Due to its relatively high water solubility, it should appear in the dissolved phase rather than suspended solids or sediment. No information was found on soil mobility or bioaccumulation.

There is very little information on toxicity to aquatic species. Existing data indicate that ppm levels are required for acutely toxic effects (111-114).

Analytical methods based on both gas chromatography and high performance liquid chromatography have been developed for bromoxynil (78, 79, 115, 116). If residue analysis is to be done then a method should be used which includes the amide and acid metabolites as well.

In summary, there is insufficient information in the literature to adequately assess the fate and effects of bromoxynil in the aquatic environment. The most important gaps in available information are:

1. the seasonal pattern of persistence due to lower rate of degradation at lower temperatures;
2. the mobility of bromoxynil and metabolites in the soil;
3. persistence of metabolites and their toxicity to aquatic and terrestrial organisms.

There is a need for gas chromatography-mass spectrometry studies to identify metabolites produced in soil and water, and by photodegradation on plant surfaces.

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**FIGURE CAPTIONS**

Figure 1. Structures of 2,4-D, 2,4-DB, MCPA, Diclofop-methyl, Dimethoate and Malathion.

Figure 2. Structures of Trifluralin, Diallate, Triallate, Dicamba and Bromoxynil.

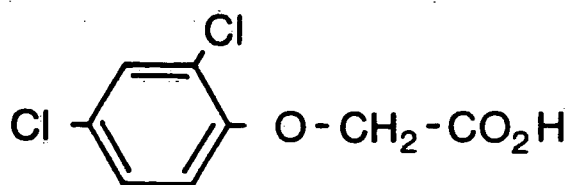
Figure 3. Transformations of diclofop-methyl.

Figure 4. Structure of isomalathion.

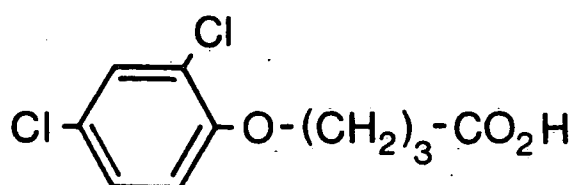
Figure 5. Hydrolysis of malathion.

Figure 6. Structure of a trifluralin photolysis product, 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole.

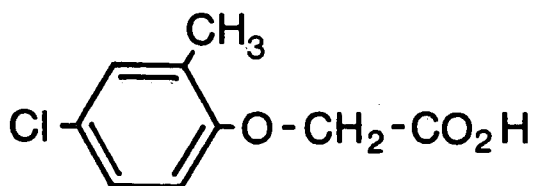
Figure 7. Dicamba degradation products.



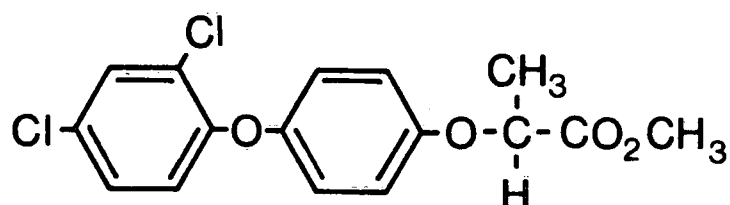
2,4-D



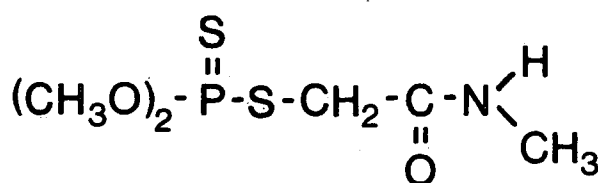
2,4-DB



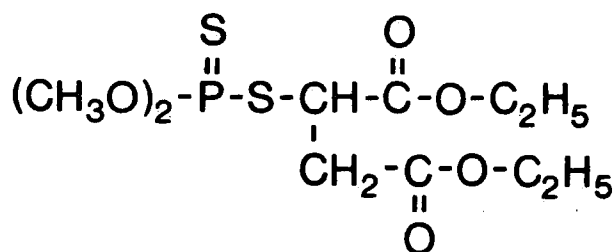
MCPA



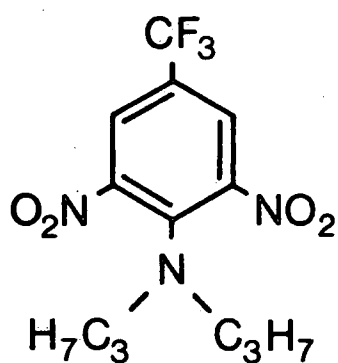
DICLOFOP-METHYL



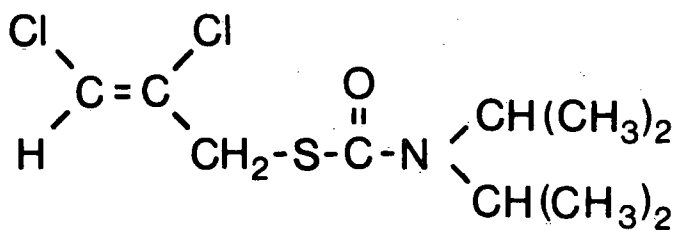
DIMETHOATE



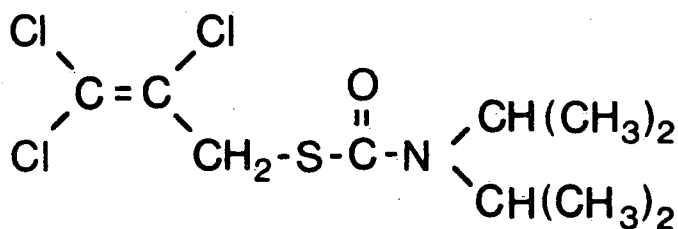
MALATHION



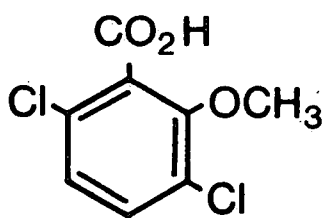
TRIFLURALIN



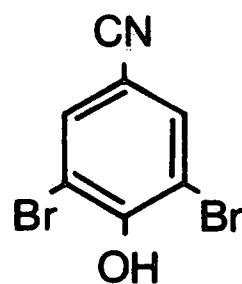
DIALLATE



TRIALLATE

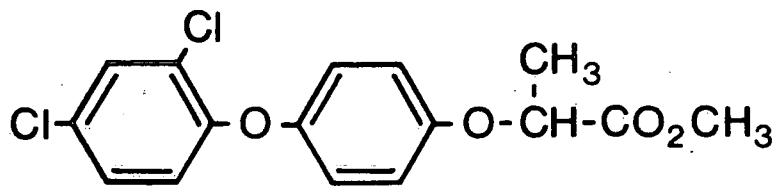


DICAMBA

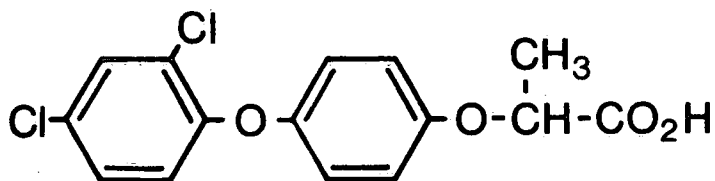
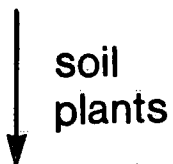


BROMOXYNIL

Fig. 3

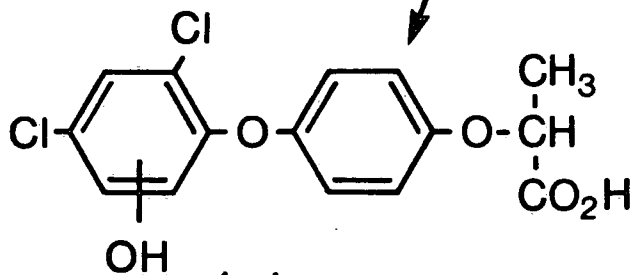


DICLOFOP-METHYL

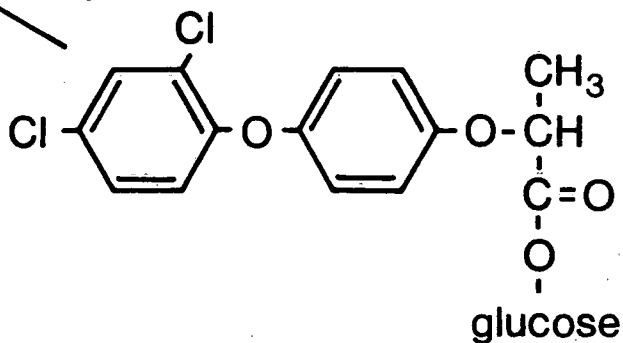


DICLOFOP

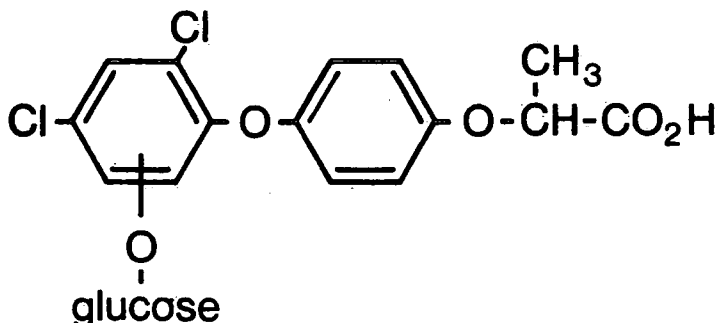
wheat



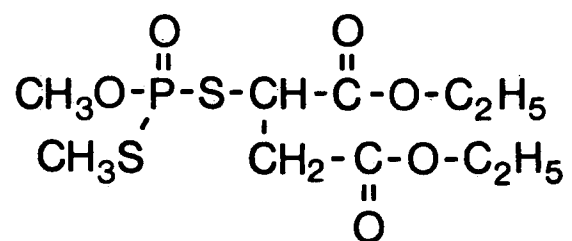
wild oat



NEUTRAL GLUCOSE ESTER



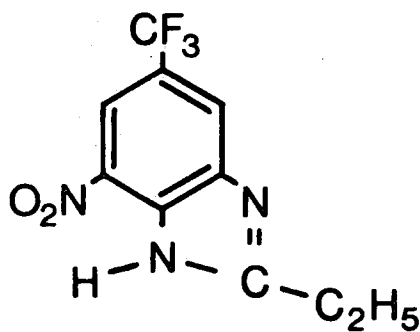
ACIDIC ARYL GLUCOSIDE



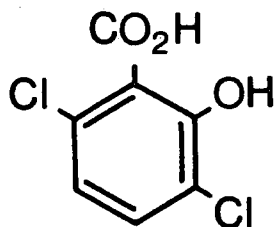
ISOMALATHION





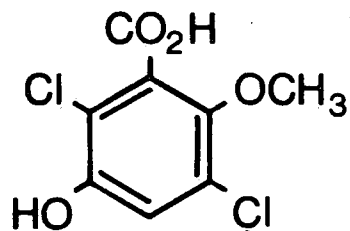


2-ETHYL-7-NITRO-5-TRIFLUROMETHYLBENZIMIDAZOLE



3,6-DICHLOROSALICYLIC ACID

( I )



5-HYDROXYDICAMBA

( II )