PERSISTENCE AND MOBILITY OF PESTICIDES IN SOIL AND WATER

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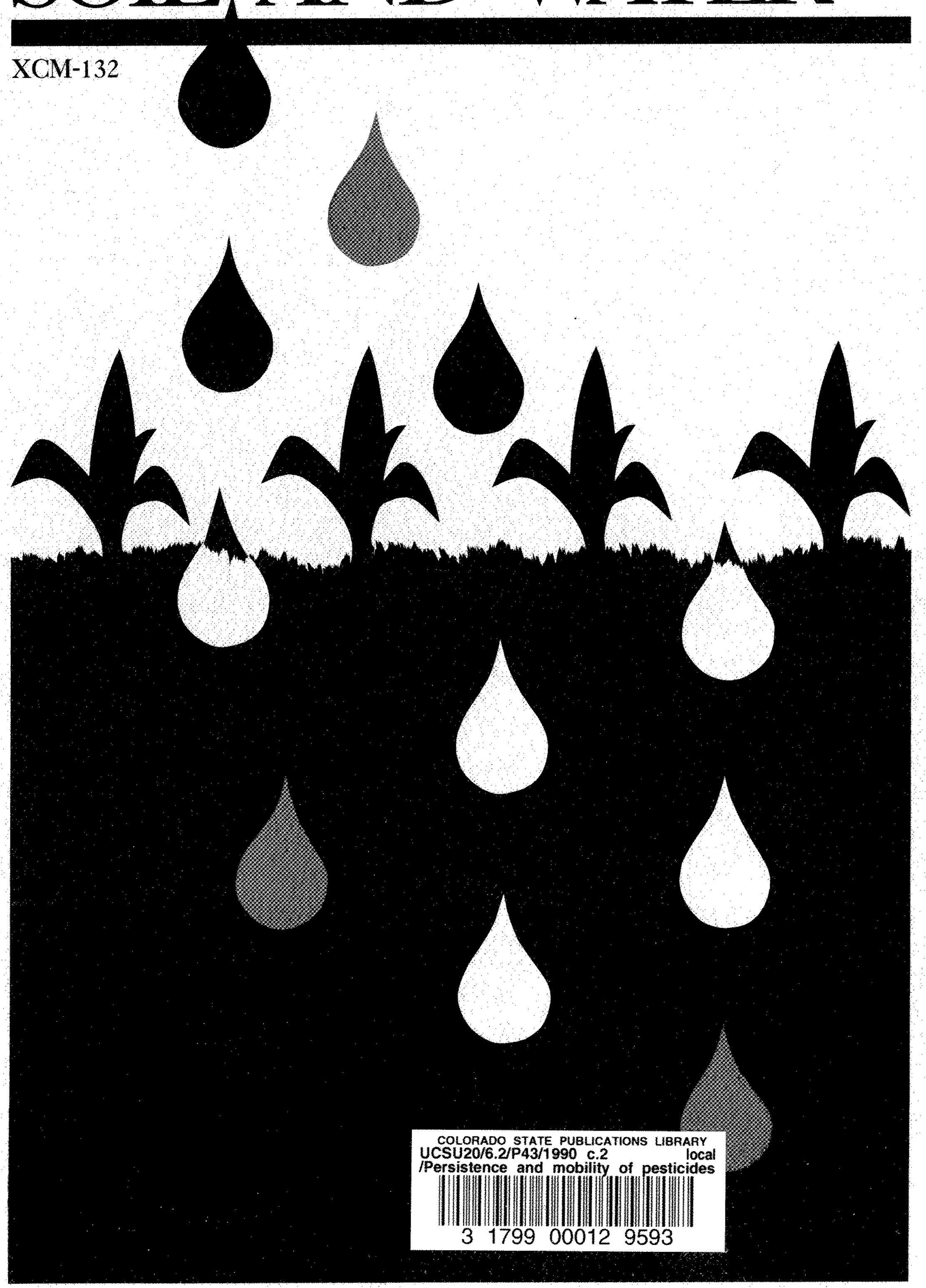

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INTRODUCTION

This publication provides information on factors involved in pesticide movement to ground water. The tables give the relative persistence and mobility of pesticides used in Colorado. Bare in mind that the classification assigned to each pesticide is approximate because local environmental factors influence persistence and mobility. Whenever several pesticide options exist for the pest/site to be treated, these data help pesticide users and advisers select the pesticide that presents the least potential for movement to ground water. This is particularly important when pesticide applications are anticipated in areas with a high risk for ground water contamination.

FACTORS

Of principal importance in transport is movement of dissolved pesticides (leaching) in water as it percolates downward through the soil. The potential for pesticide leaching to ground water exists wherever pesticides are used, but the extent varies with the chemical nature of the pesticides, the soil, volatilization (with subsequent loss to the atmosphere), decomposition and adsorption. Volatilization and decomposition reduce the total amounts of pesticides available for downward movement, and soil adsorption decreases the rate of downward movement.

To compare the tendency of different pesticides for movement to ground water and evaluate differences among soils, the best results are obtained from uniform tests under laboratory or field conditions (Helling and Dragun, 1981; Weber and Whitacre, 1982).

Many possible combinations of conditions exist ranging from those pesticides likely or unlikely to cause ground water contamination. The former (likely) are persistent and mobile pesticides applied to soils with little adsorption capacity that have shallow water tables and high annual precipitation. At the other extreme (unlikely) are pesticides that are rapidly decomposed or strongly adsorbed applied to soils that have considerable adsorption capacity with deep water tables and low annual precipitation conditions.

The amount of pesticide applied affects the potential for ground water contamination. The potential movement to ground water of relatively mobile water-soluble pesticides may be much increased where large amounts have entered the soil, such as areas used for fill stations, tank rinsing and equipment washing. In most areas, these practices should be carried out on concrete pads, and the liquid should be collected for disposal.

VOLATILIZATION

Pesticides that are volatile (easily evaporated) and have a low water solubility tend to be lost from the soil to the atmosphere. Because of evaporation loss they are unlikely to be transported extensively into soil and to ground water.

The volatility of a pesticide may be described quantitatively by its saturation vapor pressure and/or Henry's Law constant. Larger saturation vapor pressures and larger Henry's constants imply greater volatility. Since saturation vapor pressure is an increasing function of temperature, comparisons for different pesticides must be made at the same temperature. An example of a volatile and relatively insoluble pesticide is butylate, a thiocarbamate herbicide with a vapor pressure of 0.00002 atmosphere at 77°F and solubility of 45 parts per milllion (ppm) in water. Although this vapor pressure is far lower than that of water (0.031 atmosphere at 77°F), it is high for pesticides. Butylate is unlikely to cause ground water contamination problems.

The same is not true, however, for all volatile pesticides. For example, ethylene dibromide (EDB) and 1,2-dibromo-3-chloropropane (DBCP) are volatile liquids that have been used for nematode control and are relatively soluble in water (4,300 and 700 ppm, respectively). The solubility in water, together with the typically large quantities applied and the low adsorption by soil, help explain why these substances have been found in ground water despite their volatility. All soil uses of these substances have been canceled by the Environmental Protection Agency.

DECOMPOSITION

SUNLIGHT. Sunlight breaks down organic molecules (a process known as photodecomposition), so organic pesticides applied to plants or soil may lose effectiveness from photodecomposition much more rapidly than those incorporated into the soil.

According to a review by Helling *et al.* (1971), studies show that a number of herbicides, insecticides and fungicides are decomposed at measurable rates by sunlight. Organic pesticides that are not broken down by sunlight appear to be in the minority. Pyrethrins for example are insecticides that photodegrade within a few hours. Crosby and Li (1969) expressed that conditions exist under which nearly all present-day herbicides and plant-growth regulators will be decomposed by sunlight. Some herbicides that are shown to be effectively degraded by sunlight include 2,4-D, MCPA, and bromoxynil (Crosby and Tutass, 1965); simazine (Jordan *et al.*, 1964a); and diuron (Jordan *et al.*, 1964b). Wolfe *et al.* (1977) found that the insecticide methoxychlor is rapidly decomposed by sunlight in aquatic systems. Research suggests that similar breakdown products are produced by sunlight, microorganisms and plant metabolism.

WATER. Some pesticides react with water in soil to form new compounds. The rate of the reaction may vary with the soil pH. From the standpont of potential ground water contamination, pesticides may be placed in two classes depending on the pesticidal properties of the hydrolysis products.

The first class includes pesticides that react with water to produce new compounds that lack the pesticidal properties of the original compounds and are usually less toxic. Captan reacts rapidly with water (Wolfe *et al.*, 1976) to form an innocuous product, so downward movement of the parent fungicides to ground water is not a matter for great concern.

Pesticides of the less common second class behave in an opposite manner. That is, the chemical is designed to react with water to form a solution with the desired pesticidal properties. This reaction is described as activation. An example is sesone, a phenoxy-type herbicide that is not active until it reacts with water and forms 2,4-D in the soil. When such pesticides are used, the rate of reaction is rapid. The initial formulation may be a matter of chemical convenience, or it may have some other useful property, such as reducing the volatility to avoid undesired loss of pesticides sprayed on plants.

MICROORGANISMS. The predominant means of pesticide breakdown in soils are biochemical processes carried out for the most part by microorganisms and to a smaller extent by plants (pesticides taken up by plants may be broken down by plant enzymes). Fertile soils contain millions of microorganisms per ounce of surface soil. Organic pesticides may serve as sources of nutrients and energy for microorganisms. The rate of microbiological breakdown of pesticides varies with their chemical structures and is influenced by factors such as pesticide concentration, the presence or absence of free oxygen, soil temperature, soil moisture, pH, prior pesticide use, soil fertility, and plant cover.

HALF-LIFE. The persistence of a pesticide in soils under a given set of conditions is often expressed in terms of the half-life or length of time required for 50 percent of the pesticide to decompose to products other than the original pesticide. The concentration of a pesticide remaining in the soil after t days may be estimated from

$$C(t) = C(0)\ 1/2^{(t/t')}$$

where $C(t)$ is the concentration on day t
$C(0)$ is the concentration on day 0 (initial concentration)
t' is the half-life in days.

For example, suppose a given pesticide has a half-life of seven days. After seven days the remaining concentration will be one-half the initial concentration. After 14 days, one-fourth the initial concentration will remain, etc. If the half-life is short, e.g., one to two weeks, no appreciable movement of the pesticide to ground water should occur in most instances despite an otherwise high potential for downward movement. Rapid degradation of pesticides in soils is probably the major reason that certain pesticides of moderate to high mobility have not been detected in ground water.

In a summary of 12 studies, Tinsley (1979) noted that the 50 percent decomposition times for certain pesticides increased in the following order: malathion, 2,4-D, diazinon, atrazine, diuron, DDT. Wide differences in the speed of degradation were found, depending upon the experimental conditions. For example, the half-life for DDT was 240 days in a tropical environment, 3,840 days in a temperate environment, and 33 days in a laboratory test done in the absence of free oxygen. The half-lives were greater when measured in subsoil samples than in surface soil samples, presumably because of lesser microbiological activity in the subsoil samples. Reported half-lives for pesticides in soil may include chemical and biological degradation processes as well as volatilization. The actual half-life of a given pesticide in the field may vary greatly from reported values, and the above equation is only a crude approximation. Therefore, calculations of pesticide dissipation are subject to large errors.

SOIL RETENTION

Retention of organic pesticides by soil generally is referred to as adsorption. Adsorption retards the downward flow of pesticides, thus adsorption increases the length of time pesticides are subject to decomposition by microorganisms in the more active surface soil. The tendency of a given pesticide to adsorb on soil particles is quantified by an adsorption coefficient K_d. The value of K_d depends on the pesticide and soil properties. The larger the adsorption coefficient of a given pesticide, the greater the degree of adsorption and the greater the retardation of downward flow velocity. In other words, greater adsorption coefficients imply slower leaching of the pesticide and more opportunity for degradation before the pesticide reaches ground water. Pesticides that are strongly adsorbed are relatively immobile in soils. Pesticides that are not adsorbed move at the same rate as the water in which they are dissolved percolates through the soil.

Pesticides are retained by soils to different degrees depending on the properties of the pesticides, the soils and their interaction. The soil property of greatest importance for most pesticides is the organic matter content. The greater the organic matter content, the greater is the adsorption. The capacity of the soil to hold positively charged ions in an exchangeable form is important with paraquat and other pesticides that are positively charged. Soil pH is of some importance. Adsorption increases with decreasing soil pH for ionizable pesticides, including 2,4-D, 2,4,5-T, picloram (Tordon), and atrazine.

OCCURRENCE IN GROUND WATER

In 1988, EPA reported (Williams *et al.*, 1988) that normal agricultural use has led to the detection of 46 pesticides in ground water in 26 states. In 1989 very few data are available in Colorado on pesticide concentrations in ground water in agricultural areas. However, some of the pesticides commonly used in the state are prone to leaching, and careful management is needed to prevent future contamination problems.

INSECTICIDES

Organochlorines such as DDT and endrin were among the early synthetic organic insecticides. These materials have low water solubility and strong tendency to adsorb to soil. Thus despite their long history of use, they have rarely appeared as ground water contaminants that result from agricultural applications.

Organophosphorus insecticides present a wide spectrum of physiochemical properties and agricultural uses. They generally are less persistent than organochlorines and have been used to replace some organochlorine insecticides no longer registered in the United States. Breakdown in soil typically begins from reaction with water by natural and microbial hydrolysis. Examples of organophosphorus compounds include mevinphos, malathion and methyl parathion, listed in order of increasing persistence. These insecticides rarely have been detected in ground water.

Five important members of the carbamate group are carbaryl, methomyl, oxamyl, carbofuran, and aldicarb. Aldicarb (used also as a nematicide) is readily oxidized in soil. Aldicarb, aldicarb metabolites and carbofuran all have been detected in ground water.

Pyrethroids and pyrethrins usually are degraded quickly in soil and are unlike to leach. Pyrethrins are natural products and pyrethroids are synthetic derivatives. This group of insecticides includes permethrin (Ambush, Pounce) and cypermethrin (Ammo, Cymbush, Dagger, Torpedo).

HERBICIDES

Total pesticide usage and rate per acre, as well as persistence and mobility in the soil, influence buildup in the environment and ground water contamination. Herbicides account for the largest percentage of pesticide usage in agriculture. Alachlor (Lasso) herbicide has been detected in ground water of several cornbelt states despite the fact that it is relatively nonpersistent and nonmobile. Alachlor movement into ground water probably can be attributed to its extensive use in those areas.

The ten most widely used herbicides in Colorado include 2,4-D, trifluralin (Treflan), atrazine, alachlor (Lasso), dicamba (Banvel), bromoxynil, glyphosate (Roundup), metolachlor (Dual), EPTC (Eptam), and metsulfuron (Ally). Fortunately, most of these pesticides are not likely to reach ground water sources because they are either nonpersistent or nonmobile. However, atrazine, 2,4-D, trifluralin, and dicamba all have been detected in ground water in other states (Williams *et al.*, 1988).

Herbicides that are widely used, somewhat persistent, and somewhat mobile in the soil would be most likely to reach ground water. The herbicides most likely to contaminate Colorado ground water are picloram (Tordon), the sulfonylurea herbicides (Ally), and the triazine herbicides (atrazine and alachlor [Lasso]).

Picloram (Tordon) commonly is used in pasture and rangeland to control perennial weeds. Picloram is quite persistent and moderately mobile. Therefore, picloram could move through the soil profile and reach the ground water sources prior to degradation. Picloram has been detected in some ground water sources in at least three states and should not be used in water drainage areas or on soils with a shallow water table.

The sulfonylurea herbicides chlorsulfuron (Glean) and metsulfuron (Ally) are only slightly mobile but could reach ground water sources since they may persist in high pH soils for several years. The triazine herbicides such as atrazine and simazine also have long persistence in high pH soils and pose a threat to contaminate ground water sources. Because of heavy usage in corn, atrazine probably is the herbicide most often detected in ground water throughout the corn belt states.

FUNGICIDES

Fungicides rarely have been implicated in ground water pollution problems, perhaps because water solubility of fungicides usually is low. However, at least one fungicide, chlorothalonol, has been found in ground water (Williams *et al.*, 1988). The dithiocarbamates, such as maneb, are degraded rapidly in soil and water. The benzimidazole, benomyl, readily hydrolyzes to a fungitoxic product but benomyl is adsorbed readily to clay or organic matter in the soil. Binapacryl, a dinitrophenol ester, probably hydrolyzes to form the free phenol, identical in structure to the herbicide dinoseb. Only after such a transformation might there be some potential for leaching. A few other chemical groups include phthalimides, organotins, quinones, pyrimidines, and various other aromatic and nonaromatic fungicides.

LOCAL CONSIDERATIONS

The likelihood that a given pesticide will contaminate ground water depends on pesticide properties, soil properties and amount of water that percolates through the soil. Soils with higher organic matter content provide more adsorption sites and are less prone to pesticide contamination problems. Coarse or cracking soils provide rapid movement of both water and dissolved pesticides and are more likely to be associated with ground water contamination. Obviously, shallower water table depths are more likely to result in contamination than deeper ones. Thus pesticide selection should consider local soil and hydrologic factors as well as pesticide characteristics.

Soil and water management practices also are important in minimizing ground water contamination. Over irrigation that results in excessive deep percolation is never a good idea. Choice of tillage practices is less clear cut, however. No-till farming generally reduces storm runoff, soil erosion and associated transport of chemicals to streams. However, no-till may require increased use of herbicides and may increase opportunity for leaching along with increased infiltration. The best management approaches from a water quality standpoint may often be those that integrate both limited tillage and chemical use, with proper scouting to minimize unnecessary operations.

GLOSSARY OF TERMS AND DEFINITIONS

1. Adsorption - Retention of organic pesticides by soil particles.
2. Adsorption coefficient - The ratio of the adsorbed concentration of a given chemical (on soil particles) to the concentration of the chemical in solution of equilibrium.
3. Decomposition - The process by which organic matter is converted (broken down) into constituent elements, i.e., decaying process.
4. Degradation - Changing of a chemical compound to a less complex compound.
5. Fungicide - A chemical that kills fungi.
6. Henry's Law Constant - The ratio of the concentration (vapor density) of a chemical in air to the concentration in solution when the vapor and liquid phases are in equilibrium.
7. Herbicide - A chemical used to destroy or inhibit undesirable plant growth. Usually a selective weed killer that will not injure crop plants when properly used.
8. Hydrolysis - Chemical process of (in this case) pesticide breakdown or decomposition that involves a splitting of the molecule and addition of a water molecule.
9. Insecticide - A chemical that kills insects.
10. Leaching - The movement of a pesticide chemical or other substance downward through soil as a result of water movement.
11. Microorganism - An organism of microscopic size, such as bacteria or protozoa.
12. Pesticide - An "economic poison" defined in most state and federal laws as any substance used to control, prevent, destroy, repel, or mitigate any pest. Includes fungicides, herbicides, insecticides, nematicides, rodenticides, dessicants, defoliants, plant growth regulators, etc.
13. Photodecomposition - Break down or decomposition of organic molecules by sunlight (radiant energy).
14. ppb (parts per billion) - The number of parts of toxicant per billion parts of the substance in question.
15. ppm (parts per million) - The number of parts of toxicant per million parts of the substance in question. This may include residues in soil, water, plants or animals.
16. Saturation Vapor Pressure - The partial pressure of a vapor phase when in equilibrium with its liquid phase. Saturation vapor pressure is an increasing function of temperature.
17. Solubility - The amount of a substance that will dissolve in a given amount of another substance.
18. Volatilization - The process by which chemicals give off vapors. "Volatile" chemicals are those that readily vaporize.

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TABLE 1: RELATIVE PERSISTENCE AND MOBILITY OF INSECTICIDES IN SOILS.

INSECTICIDE	PERSISTENCE[a]	MOBILITY[b]
acephate (Orthene)	M	VM
aldicarb (Temik)	M	MM
azinphos-methyl (Guthion)	N	NI
biphenthrin (Brigade, Capture, Talstar)	M	I
carbaryl (Sevin)	N	NI
carbofuran (Furadan)	M	MM
chlorpyrifos (Lorsban, Dursban)	M	NI
cypermethrin (Ammo, Cymbush, Dagger, Torpedo)	M	I
diazinon	M	SM
dimethoate (Cygon, De-Fend)	N	MM
disulfoton (Di-Syston)	N	NI
endosulfan (Thiodan)	N	NI
esfenvalerate (Asana)	M	I
fonofos (Dyfonate)	M	NM
malathion (Cythion)	N	NI
methamidophos (Monitor)	N	VM
methomyl (Lannate, Nudrin)	N	SM
methyl parathion (Penncap-M)	N	I
methidathion (Supracide)	N	SM
parathion	N	I
permethrin (Ambush, Pounce)	N	I
phorate (Thimet)	N	NI
phosphamidon (Dimecron)	N	MM
terbufos (Counter)	N	NI
tralomethrin (Scout)	M	I
trichlorfon (Dylox)	N	VM
trimethacarb (Broot)	M	NI

[a] P=persistent, M=moderately persistent; N=non-persistent
[b] VM=very mobile; MM=moderately mobile; SM=slightly mobile; NI=nearly immobile; I=immobile

TABLE 2: RELATIVE PERSISTENCE AND MOBILITY OF HERBICIDES IN SOILS

HERBICIDE	PERSISTENCE[a]	MOBILITY[b]
acifluorfen (Blazer, Tackle)	M	NI
alachlor (Lasso)	N	SM
amitrole (Amitrol T, Cytrol)	N	MM
atrazine (Several Trade Names)	P (at high pH)	SM
AC 222,293 (Assert)	M	SM
barban (Carbyne)	N	I
bentazon (Basagran)	N	NI
bromoxynil (Buctril)	N	SM
butylate (Sutan, Genate)	N	NI
chloramben (Amiben)	N	VM
chlorsulfuron (Glean, Telar)	P	MM
clomazone (Command)	M	SM
clopyralid (Stinger, Reclaim)	M	MM
cyanazine (Bladex)	N	SM
cycloate (Ro-Neet)	N	NI
dalapon (Dalapon 85)	N	VM
desmedipham (Betanex)	N	I
diallate (Avadex)	M	NI
dicamba (Banvel, Trooper)	N	VM
diclofop (Hoelon)	N	NI
diethatyl (Antor)	N	SM
difenzoquat (Avenge)	M	I
DPX-M6316 (Harmony)	N	MM
endothale (Several Trade Names)	N	SM
EPTC (Eptam, Eradicane, Genep)	N	NI
ethalfuralin (Sonalan)	M	I
ethofumesate (Nortron)	M	NI
fenoxaprop (Whip, Acclaim)	N	NI
fluazifop-P (Fusilade 2000)	N	NI
glyphosate (Roundup, Acord, Honcho, Ranger, Rodeo)	M	I
lactofen (Cobra)	M	NI
linuron (Lorox)	M	NI
MCPA (Several Trade Names)	M	MM
metolachlor (Dual)	M	NI
metribuzin (Sencor, Lexone)	M	MM
metsulfuron (Ally, Escort)	P (at high pH)	MM
naptalam (Alanap-L)	N	VM
paraquat (Glamoxone Super, Cyclone)	P	I
pendimethalin (Prowl)	M	NI
phenmedipham (Betenal)	N	I
picloram (Tordon, Grazon)	P	MM
propachlor (Ramrod)	N	SM
propanil (Stampede)	N	SM
pyrazon (Pyramin)	N	SM
sethoxydim (Poast)	N	NI
simazine (Princep, Aquazine)	P	SM
triallate (Far-Go, Avadex BW)	M	NI
tridiphane (Tandem)	N	NI
trifluralin (Treflan)	M	I
2-4,D (Several Trade Names)	N	MM
2-4,DB (Butyrac, Butoxone)	N	MM

[a] P=persistent; M=moderately persistent; N=non-persistent

[b] VM=very mobile; MM=moderately mobile; SM=slightly mobile; NI=nearly immobile; I=immobile

TABLE 3: RELATIVE PERSISTENCE AND MOBILITY OF FUNGICIDES IN SOILS.

FUNGICIDE	PERSISTENCE[a]	MOBILITY[b]
benomyl (Benlate, Tersan 1991)	P	I
chlorothalonil (Bravo, Daconil)	M	I-MM[c]
copper hydroxide (Champ, Kocide)	P	I
maneb (Several Trade Names)	M	I
mancozeb (Dithane M-45, Manzate 200, Penncozeb)	N	NI
metalaxyl (Ridomil, Subdue)	M	SM
propiconazole (Banner, Tilt)	P	I
sulfur (Several Trade Names)	P	I
thiabendazole (Mertect)	M	I
thiophanate methyl (Topsin M)	M	I
triadimefon (Bayleton)	P	NI
triphenyltin hydroxide (Du-ter, Super Tin, TN IV, Triple Tin)	P	I

[a] P=persistent; M=moderately persistent; N=non-persistent

[b] VM=very mobile; MM=moderately mobile; SM=slightly mobile; NI=nearly immobile, I=immobile

[c] =Immobile in most soil types; moderately mobile in sand.