BEHAVIOR, PERSISTENCE & DEGRADATION OF CARBAMATE AND THIOCARBAMATE HERBICIDES IN THE ENVIRONMENT

Reed A. Gray

Stauffer Chemical Company, Agricultural Research Center,
Mountain View, California

I. CHEMICAL, PHYSICAL AND BIOLOGICAL PROPERTIES WHICH AFFECT BEHAVIOR IN THE ENVIRONMENT

Carbamates are esters of carbamic acids, and thiocarbamates are esters of thiocarbamic acids. Carbamic acids are unstable compounds and decompose spontaneously into carbon dioxide and amines, but the esters used as herbicides are very stable compounds and can be stored on the shelf for years without change. The thiocarbamate herbicides show similar stability with no decomposition when stored as technical materials or as formulated products in the absence of water for many years. However, when these herbicides are placed in moist soils in contact with microorganisms, or when they are taken up by plants or ingested by animals, they are degraded quite rapidly.

The fundamental groups which identify herbicides as carbamates are shown in Figure 1. The only difference noted going from a carbamate to a thiocarbamate is that a sulfur atom replaces the oxygen atom in the ester linkage. In dithiocarbamates, both oxygen atoms of carbamates are replaced by sulfur atoms. The dithiocarbamates play rather a minor role as herbicides, since only two commercial herbicides, Vegadex and Capam, are used to any great extent.. There are many fungicides which are dithiocarbamates, and Vapam, a soil fumigant is both a herbicide and a fungicide and has different properties than carbamate and thiocarbamate herbicides. Because of this difference in properties and the small number of dithiocarbamate herbicides in use, they will not be discussed further in this report.

Another interesting difference in the basic structure (Figure 1) is that all the carbamate herbicides have a hydrogen atom as the R_2 substituent attached to nitrogen and an aklyn or aryl group as the R_3 group, while in all of the thiocarbamate herbicides both R_2 and R_3 are alkyl groups. This difference undoubtedly accounts for some of the differences in biological activity noted between the two groups. The carbamates contain a $(\overset{O}{\overset{\|}{-C}}-\overset{H}{\overset{|}{N}}-)$ linkage common to all proteins and can thus form stronger hydrogen bonds with proteins than the corresponding group $(\overset{O}{\overset{\|}{-C}}-\overset{R}{\overset{|}{N}}-R)$ in thiocarbamate herbicides where no hydrogen is present to share in hydrogen bonding. Although the carbamate herbicides and thiocarbamate herbicides are similar in structure and in mechanism of degradation, they are much different in herbicidal activity and behavior in the soil as I will point out later. If the herbicides were to be classified according to herbicide symptoms and mode of action, then the carbamates would not be classified with the thiocarbamates.

The trade name, common name, structure and main crop usages are shown in Figure 2. for the best known carbamate herbicides used in the U.S. Note the presence of the imino hydrogen group in all compounds. The first five compounds are all phenyl carbamates, the next two are methyl carbamates and the last is a tertiary butyl carbamate. Tandex also has a stustituted urea group in addition to a carbamate group and therefore would not be expected to behave like other carbamates. The alcohol group on the left of each structure is different for all compounds except IPC and CIPC which are the same. Betanal is somewhat different from the other compounds since it contains two carbamate groups instead of one.

The carbamates are mostly preemergence herbicides which control both grass and broadleaf weeds by root uptake. Exceptions are Carbyne and Betanal which are applied postemergence to the weeds. CIPC and Tandex are also applied postemergence in some cases. In general the carbamates and thiocarbamates are the most effective herbicides known for selectively controlling wild oats in various crops.

Generally speaking, all the carbamate and thiocarbamate herbicides are available as both emulsifiable liquid formulations and/or granular formulations.

CIPC is a mitotic poison; it disrupts mitosis in the roots of many plants. CIPC is also a photosynthesis inhibitor. Other carbamates may have similar modes of action. Tandex is a very strong inhibitor of photosynthesis, and Sirmate is an inhibitor of chlorophyll synthesis.

The trade name, common name, structure and main crop usage are shown for each of the thiocarbamate herbicides used in the United States in Figure 3. Note that only alkyl and cycloalkyl groups are attached to the nitrogen atom on the right. Only small differences in structure are noted going from one compound to the next, usually with only one methyl group difference. Ordram has a cyclic amine group, and is very similar to Eptam in structure, but has different herbicidal activity. Other than Ordram, all the remaining thiocarbamates have alkyl groups on the nitrogen which are either ethyl, propyl, isopropyl, butyl, isobutyl or cyclohexyl. The alkyl groups attached to sulfur on the other end of the molecule are either ethyl, propyl, dichloroallyl or trichloroallyl. All of the first six herbicides in Table 2 have an ethyl group attached to sulfur except Tillam and Vernam which have propyl groups.

The thiocarbamates are particularly effective when incorporated preplant in the soil for selectively controlling wild oats, grass weeds and nutgrass in many crops. Many broadleaf weeds are also controlled. Tolerant crops are mostly broadleaf types but high selectivity for controlling grass weeds in grass crops are shown by Ordram, Sutan and Avadex BW.

The comparative toxicity of the carbamates to small laboratory animals is shown in Fugure 4 along with the water solubility and melting point for each compound. In general, the carbamates are relatively non-toxic to animals with Swep being the most toxic and Azak the least. The water solubility is rather low and may explain the relative immobility of the carbamate herbicides in the soil due to leaching and diffusion. The melting points indicate that the carbamates are all solids at room temperature. This points out a very clear-cut distinction between the carbamate herbicides and the thiocarbamate herbicides, since the latter are all liquids at room temperature. All the carbamates are rather low melting except for Betanal, Azak and Tandex. The vapor pressure of CIPC is approximately 1×10^{-5} mm of Hg at 25% C. The vapor pressure of the other carbamates were reported as very low or nil. IPC sublimes slowly at room temperature and this could explain its loss from soil surfaces.

The toxicity to rats, the water solubilities and boiling points of the thiocarbamate herbicides are shown in Figure 5. Widespread use of thiocarbamates has presented no toxicology problems. The animal toxicity as indicated by the acute oral LD_{50} of Ordram, which contains a cyclic azepine ring, is somewhat greater than related thiocarbamates. Longer chain alkyl groups leads to less toxicity to animals as shown by the very low toxicity (high LD_{50}) of Ro-Neet and Sutan. Avadex is the most toxic thiocarbamate, but it is still within a reasonable range of toxicity. It is interesting that Avadex BW is much less toxic to rats than Avadex.

The water solubilities vary from a low of 4 ppm for Avadex BW to a high of 912 ppm for Ordram. Tests conducted in our laboratories show a direct relationship between the water solubilities of the compounds and the degree of leaching in soils. Lateral movement in the soil may also be related to the solubility in water.

The boiling points at reduced pressure indicate that Eptam is the most volatile of the group and Avadex and Avadex BW the least volatile. Vaporization studies to be described later indicate that loss from soil surfaces by vaporization is in the same order as the boiling points indicate. The vapor pressure of Eptam was found to be 34 microns (0.034 mm) of mercury at 25°C and the other thiocarbamates have lower vapor pressures. Accurate vapor pressures for these compounds are difficult to determine because of the presence of small amounts of volatile impurities in the liquid products. Since they are all rather volatile, all the thiocarbamates should be incorporated in the soil to avoid loss by vaporization.

II. BEHAVIOR, PERSISTENCE AND DEGRADATION IN THE ENVIRONMENT

Carbamates:

I have had no first hand experience with the behavior and persistence of the carbamate herbicides in the environment, so I will summarize briefly the information that has been published. A review of the literature has been reported recently by Herritt (1), so this will not be repeated in this report.

The degradation of the carbamate herbicides in the environment is summarized in Figure 6 using CIPC as a representative example of the group. When applied to the surface of soils, CIPC and IPC can be lost by some vaporization or sublimation, but they are tightly absorbed by some soils and this reduces volatilization. Water can displace the carbamates from adsorption sites and cause them to be lost by volatility. CIPC and Sirmate are highly resistant to leaching.

When incorporated in the soil the carbamates disappeared under conditions favorable for microbial growth . Carbyne and CIPC persisted much longer in sterile soil than in non-sterile soil. Kaufman and Kearny isolated several soil microorganisms which hydrolyzed CIPC to 3-chloroaniline. They later isolated an enzyme from *Pseudomonas striata* which hydrolyzed CIPC to 3-chloroaniline, CO_2 and isopropyl alcohol.

The half-life of IPC in soil at 85° F was approximately 1 week, while the half-life of CIPC was 4 weeks at 85° F. In moist soils under Summer growing conditions, the carbamates were readily degraded by soil microorganisms. In fact the residual in the soil of carbamates is so short that many workers have tried to extend their soil life by various methods. Certain methyl carbamates were found to act as inhibitors of the hydrolysis of CIPC by the enzyme from *Pseudomonas striata,* and such a product has been developed to make CIPC last longer in the soil.

Tandex may be an exception to the other carbamates, since it may also be classified as a substituted urea, and it's soil residual may be a year or more depending on the rate used for soil sterilization. The other carbamates would be expected to have a relative short soil residual similar to CIPC.

Tolerant plants degraded CIPC to 3-chloroaniline, but sensitive plants metabolized CIPC by a different pathway to a water-soluble conjugate which contained the intact carbamate (Figure 6). Carbyne was also metabolized in wheat and wild oats to a water soluble conjugate which contained the intact carbamate. Hydrolysis of the metabolite with 10% caustic gave 3-chloroaniline showing that the ring was not hydroxylated. Sirmate was also metabolized to a water soluble compound containing the intact carbamate in sensitive plants, but tolerant plants caused rapid degradation. The results show that carbamates are readily degraded in the environment, especially by soils, microorganisms and plants.

Thiocarbamates:

I would like to discuss in more detail the behavior of the thiocarbamate herbicides in soils and plants, since I have quite a bit of first hand experience with these compounds. I will not review the literature on this subject because this was done recently by Fang (2). Instead, I will summarize some of the results obtained in our laboratories.

Persistence when Applied to the Soil Surface: Vapor trapping studies showed that Eptam and other thiocarbamates were rapidly lost by vaporization after application as sprays to the surface of moist soils, but there was very little loss from dry soils. The thiocarbamates were collected in chilled traps unchanged with no evidence of photodecomposition. The main factor affecting the loss by vaporization from soil surfaces was the moisture content of the soil. Letting the surface of freshly cultivated moist soil dry out for two hours before spraying with Eptam, greatly reduced the loss by vaporization in small field plots. On dry soil there was some loss of Eptam during the first 15 minutes after application while the spray was drying, but it was tightly adsorbed to the dry soil as soon as the water from the spray had evaporated. When Eptam granules were applied to a dry soil surface, no loss could be detected in two hours, while 60% loss occurred in two hours after applying the granules to a moist soil surface. Soils low in moisture content behaved the same as dry soil. There appeared to be a critical moisture level (10% for a loamy sand) for each type of soil, above which, large losses of Eptam occurred after surface application. Immediate incorporation into the soil prevented any loss of Eptam sprays on dry soil and reduced the loss to insignificant amounts in moist soil.

Increasing the temperature caused only a slight increase in loss of five thiocarbamate herbicides from the soil surface. Eptam was lost at the greatest rate from the soil surface followed by Vernam, Tillam, Ordram and Ro-Neet in order of decreasing rate of loss by vaporization.

Persistence when Incorporated in the soil: The thiocarbamates persisted much longer when incorporated in the soil according to the label recommendation than when applied to the soil surface. Incorporation to a depth of 2 to 3 inches in moist soil was necessary in small field plots in order to prevent substantial losses of Eptam in several days when light rain or light sprinkler irrigation kept the soil moist after treatment. Good retention at shallow depths (½ to 1 inch) of incorporation occurred when Eptam was incorporated into moist soil and the soil was allowed to dry out after treatment.

Several thiocarbamates were incorporated 3 inches deep in different soils contained in glass jars for persistence tests. Some treated soils were kept in the greenhouse at 70-90° F and others were placed in an environmental growth chamber at 40° F. The moist soils were watered lightly every few days, and duplicate samples were removed at weekly intervals and analyzed quantitatively by the steam distillation-colorimetric method. These tests showed that 70-90% of the Eptam, Vernam, Tillam, Sutan, Ordram and Ro-Neet applied at 6 lb/A disappeared from the moist soils in 8 weeks at 70-90° F. At 40°F the loss was about one-half the loss observed at 70-90°F. After incorporation into dry soil very little loss (5-20%) could be detected in 8 weeks at 70-90° F.

The approximate half-life in moist soil at 70-90 F for each of the thiocarbamates, CIPC and IPC is shown in Figure 7. The half-life reported in Figure 7 for each of the first six compounds was determined in moist Sorrento loam in the greenhouse, using a rate of 6 lb/A, except for Eptam which was done in small field plots in the same soil. The value for Tillam was estimated. The half-life values reported in Figure 7 for Avadex, IPC and CIPC were reported from other laboratories using different soils. The results indicate that the thiocarbamate and carbamate herbicides persist in the soil for relatively short periods, since the half-lives range from 1 to 4 weeks.

Microbial Degradation: All of the thiocarbamate herbicides disappeared much faster in non-autoclaved moist soil than in autoclaved moist soil, indicating that microbial breakdown was responsible for a large part of the disappearance which occurred after incorporation into the soil. These tests were carried out in sealed glass jars where no loss by vaporization could occur. A slight amount of loss occurred in autoclaved soils, indicating that some chemical breakdown probably by hydrolysis also occurred. The slow disappearance in dry soils and in cold moist soils also indicates that little breakdown takes place under conditions which are unfavorable for microbial activity.

In other tests, it was found that several soil fungi degraded radioactive Ro-Neet and Sutan in just 3 to 7 days in shake flask cultures. Several amines were identified as microbial breakdown products in the soil and in pure cultures. Radioactive carbon dioxide was evolved from soils treated with ring-labelled and chain-labelled Ordram, and from other carbon-14 labelled thiocarbamate herbicides. These results showed that the thiocarbamate herbicides were degraded by microorganisms in the soil to small molecules.

The evidence suggests that microbial degradation was the main mechanism by which the thiocarbamate herbicides disappeared from soils when they were incorporated into the soil.

Persistence tests in distilled water and tap water in clean glass containers showed very very slow degradation of the thiocarbamates by hydrolysis over a period of months. However in pans of water containing soil, microbes and growing plants, Ordram and several other thiocarbamates disappeared rather rapidly in a period of several weeks.

Leaching: Quantitative leaching tests conducted in soils contained in glass columns showed that the thiocarbamate herbicides leached downward in direct relation to their water solubilities. Ordram leached to the greatest depth followed by Eptam, Vernam Tillam, Ro-Neet and Sutan in order of decreased amount of leaching. Ordram and Eptam leached downward to a depth of 9-15 inches in sandy soil when incorporated in the upper 3 inches of soil at 10 lb/A and leached with 8 inches of water, but the other compounds stayed near the top 3-6 inches. In loam and heavier clay soils, all compounds remained in the upper 6 inches of soil when leached with 8 inches of water. In peat soil, no leaching out of the treated zone could be detected with any of the thiocarbamate herbicides. The leaching data indicated that in most soils the thiocarbamates stayed in the upper 3 to 6 inches of soil after incorporation into the upper 2 inches of soil and leaching with 8 inches of water. Under most conditons the compounds would disappear by microbial action before they could reach the deeper layers of soil by leaching.

Lateral Movement: The lateral movement of the thiocarbamates was studied by placing the compounds on filter paper discs which were placed in the soil along with weed seeds. Eptam, Vernam and Tillam moved laterally to form a circle of weed control about 4-5 inches in diameter using ryegrass or oats as test species. Ordram, Ro-Neet and Sutan gave smaller zones of weed control. The carbamates, IPC, CIPC, Azak and Sirmate, formed very small zones of weed control indicating that their lateral movement was much less than that of the thiocarbamates. The thiocarbamates also moved laterally more than most other commercial herbicides as shown by their effect on grass weeds. However the size of the zone depended on the activity of the herbicide on the test species as well as on the amount of movement. When a disc containing Eptam was placed 3 inches deep in the soil, no zone of weed control was detected. The data indicated that the thiocarbamates moved outward in a spherical pattern when applied to a concentrated spot in the soil. This property of lateral diffusion enables the thiocarbamates to be effective herbicides when applied by injection.

Site of Uptake: A charcoal barrier method was developed for exposing only the shoots, roots or seeds of plants to Eptam. Several published reports indicated that Eptam caused injury only when the shoots were exposed to Eptam treated soil, and that exposing only the roots or seeds did not lead to injury. Results obtained with the charcoal barrier method showed that root exposure to Eptam-treated soil caused more injury to barley, ryegrass, nutgrass, barnyardgrass and other seedlings than shoot exposure. Oats showed more injury from root exposure than shoot exposure when planted 1 inch deep, but shoot exposure caused more injury when planted 1.5 or 2 inches deep. Many tests showed that exposing all parts (shoots, seeds and roots) of the seedlings gave the most injury to all weed seedlings, indicating that the thiocarbamates should be placed in the soil to give the maximum amount of exposure to all parts of the weed seedlings for the greatest effectiveness.

Site of Herbicidal Action and Injury Symptoms: In tests where only the roots of oat plants were exposed to 1 to 4 ppm Eptam in nutrient solution, the shoots were severly injured. The elogation of the roots was enhanced by treating the roots. Although the roots appeared to be the most important site of uptake, the site of action was in the shoots where leaf growth was inhibited. The site of herbicidal action was also shown in young cereal grass seedlings, by digging them out of the soil several days after planting in thiocarbamate treated soil. No effect on root growth was detected, while the young leaves failed to grow enough to emerge from the coleoptiles. At lower rates, the grass leaves emerged from the coleoptile and showed injury symptoms of twisting, looping, leaf-sticking, malformation and stunting.

Carbamates such as IPC and CIPC, on the other hand, produced injury symptoms of swollen root tips and inhibited root growth as well as malformation and stunting of the shoots. Carbamates inhibited photosynthesis while thiocarbamates did not. Since the injury symptoms caused by thiocarbamates are so different than those caused by carbamates, these two groups of herbicides should not be classified together as showing similar sites of action and modes of action. The thiocarbamates produced injury symptoms on grasses very similar to those caused by dalapon and TCA, while the carbamates, IPC and CIPC, caused injury symptoms similar to those produced by Treflan.

Plant Uptake and Metabolism: Studies with radioactive Eptam, Tillam, Vernam, Ordram, Ro-Neet and Sutan showed that the herbicides were rapidly taken up by the roots of plants, and the radioactivity was rapidly translocated upward throughout the leaves and stems. Substantial amounts of radioactive carbon dioxide was evolved when the alkyl group attached to sulfur was labelled with carbon-14 as well as when the alkyl group attached to nitrogen was labelled with carbon-14. In trying to identify other radioactive metabolites by paper and thin-layer chromatography, many of the radioactive spots were identified as amino acids, fatty acids, organic plant acids and sugars. Radioactivity was also found in the proteins, starch, cellulose, pigments and other lipids. Apparently both the dialkyl amine portion and the alkyl mercaptan portion of the molecules were degraded in plants to radioactive carbon dioxide which entered the CO_2 pool and became incorporated into many naturally occurring plant constituents.

A summary showing the pathways by which the thiocarbamates are degraded in the environment is shown in Figure 8 using Eptam as a model. Other pathways also occur in which conjugates of the thiocarbamates and amine breakdown products are produced.

It may be concluded that the thiocarbamate herbicides are rapidly degraded in the environment and do not present any persistence and pollution problems. The same is true for the carbamate herbicides.

LITERATURE CITED

1. Herrett, Richard A., 1969. Methyl-and phenylcarbamates, Chapter 4 pp. 113-145 in Degradation of Herbicides, edited by P. C. Kearney and D. D. Kaufman, Marcel Dekker, Inc. N. Y.

2. Fang, S. C., 1969. Thiolcarbamates, Chapter 5, pp. 147-164 in Degradation of Herbicides, edited by P. C. Kearney and D. D. Kaufman, Marcel Dekker, Inc. N. Y.

Figure 1.

CARBAMATES

THIOCARBAMATES

DITHIOCARBAMATES

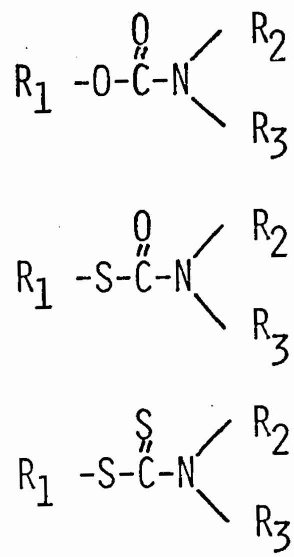


Figure 2 CARBAMATE HERBICIDES

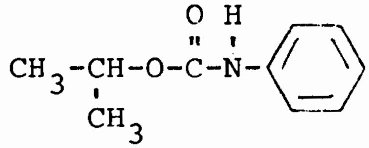
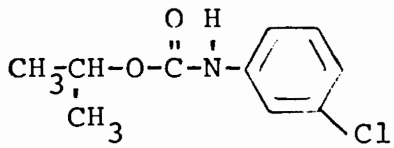
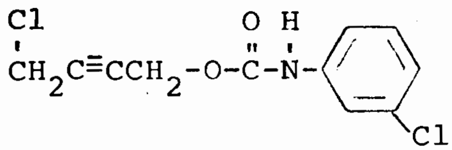
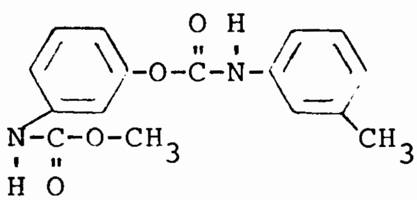
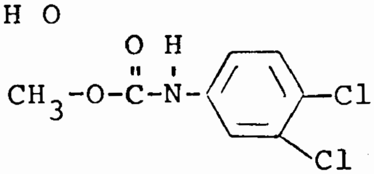
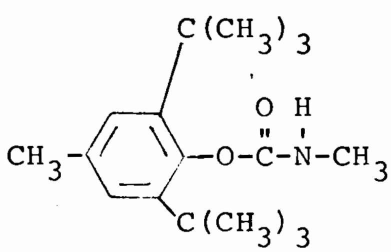
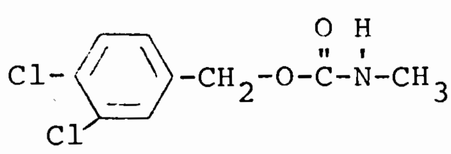
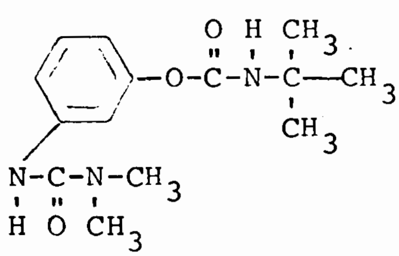
Trade Name	Common Name	Structure	Main Crop Usage
CHEM-HOE	IPC		Alfalfa, Clover, Peas, Lettuce, Spinach, Lentils, Sugarbeets.
CHLORO-IPC	CIPC		Alfalfa, Clover, Beans, Carrots, Soybeans, Safflower, Sugarbeets, Lima Beans, Garlic Onions, Peppers, Tomatoes.
CARBYNE	Barban		Wheat, Barley, Flax Sugarbeets, Lentils, Peas, Soybeans, Mustard.
BETANAL	Phenmedipham		Sugarbeets, Table Beets.
SWEP	NIA-2995		Cotton, Rice, Beans.
AZAK	Terbutol		Turf.
SIRMATE	UC 22463		Corn, Beans, Etc.
TANDEX	NIA 11092		Soil Sterilization, Brush Control

Figure 3. THIOCARBAMATE HERBICIDES

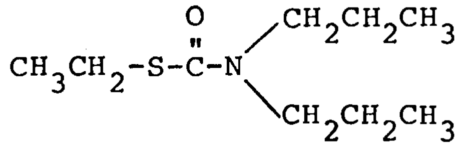
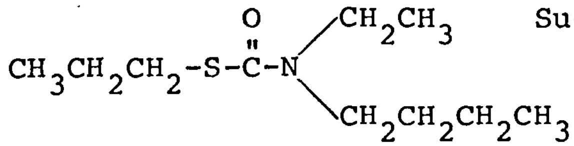
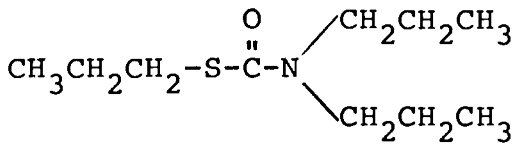
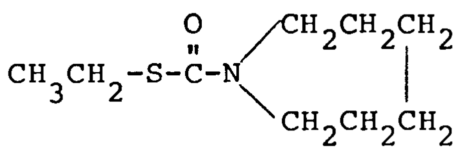
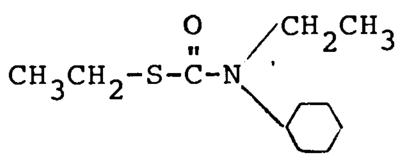
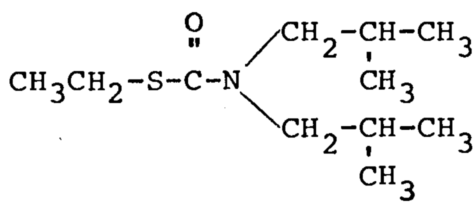
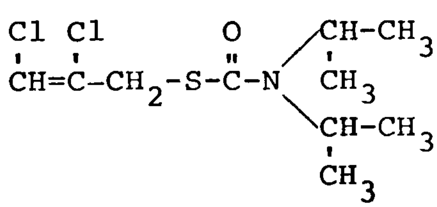
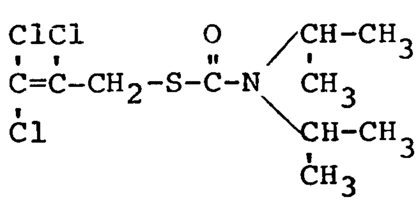
Trade Name	Common Name	Structure	Main Crop Usage
EPTAM	EPTC		Beans, Potatoes, Alfalfa, Trefoil, Clover, Lespedeza Safflower, Almonds, Citrus.
TILLAM	Pebulate		Sugarbeets, Tomatoes Tobacco.
VERNAM	Vernolate		Peanuts, Soybeans Sweet Potatoes, Tobacco.
ORDRAM	Molinate		Rice.
RO-NEET	Cycloate		Sugarbeets, Spinach, Table Beets.
SUTAN	Butylate		Field Corn, Sweet Corn.
AVADFX	Diallate		Sugarbeets, Barley, Peas, Lentils, Potatoes, Corn Safflower.
AVADEX BW	Triallate		Barley, Wheat, Peas.

Figure 4. Carbamate Herbicide Properties

Herbicide	Acute Oral LD_{50} for Rats Mg/Kg	Water Solubility At Room Temp. PPM	Melting Point ° C
CHEM-HOE	5000	250	88
CHLORO-IPC	6250	88	40
CARBYNE	1350	11	75
BETANAL	8000	10	144
SWEP	552	-	114
AZAK	34600	7	201
SIRMATE	2000	170	52
TANDEX	3000	325	176

Figure 5. Thiocarbamate Herbicide Properties

Herbicide	Acute Oral LD_{50} For Rats Mg/Kg	Water Solubility At 20-22° C PPM	Boiling Point °C
EPTAM	1630	375	127 at 20 mm
TILLAM	1120	92	143 at 20 mm
VERNAM	1780	107	140 at 20 mm
ORDRAM	720	912	137 at 10 mm
RO-NEET	4100	85	146 at 10 mm
SUTAN	4650	45	138 at 21 mm
AVADEX	395	14	150 at 9 mm
AVADEX BW	2165	4	149 at 9 mm

Figure 6. DEGRADATION OF CARBAMATE HERBICIDES IN THE ENVIRONMENT

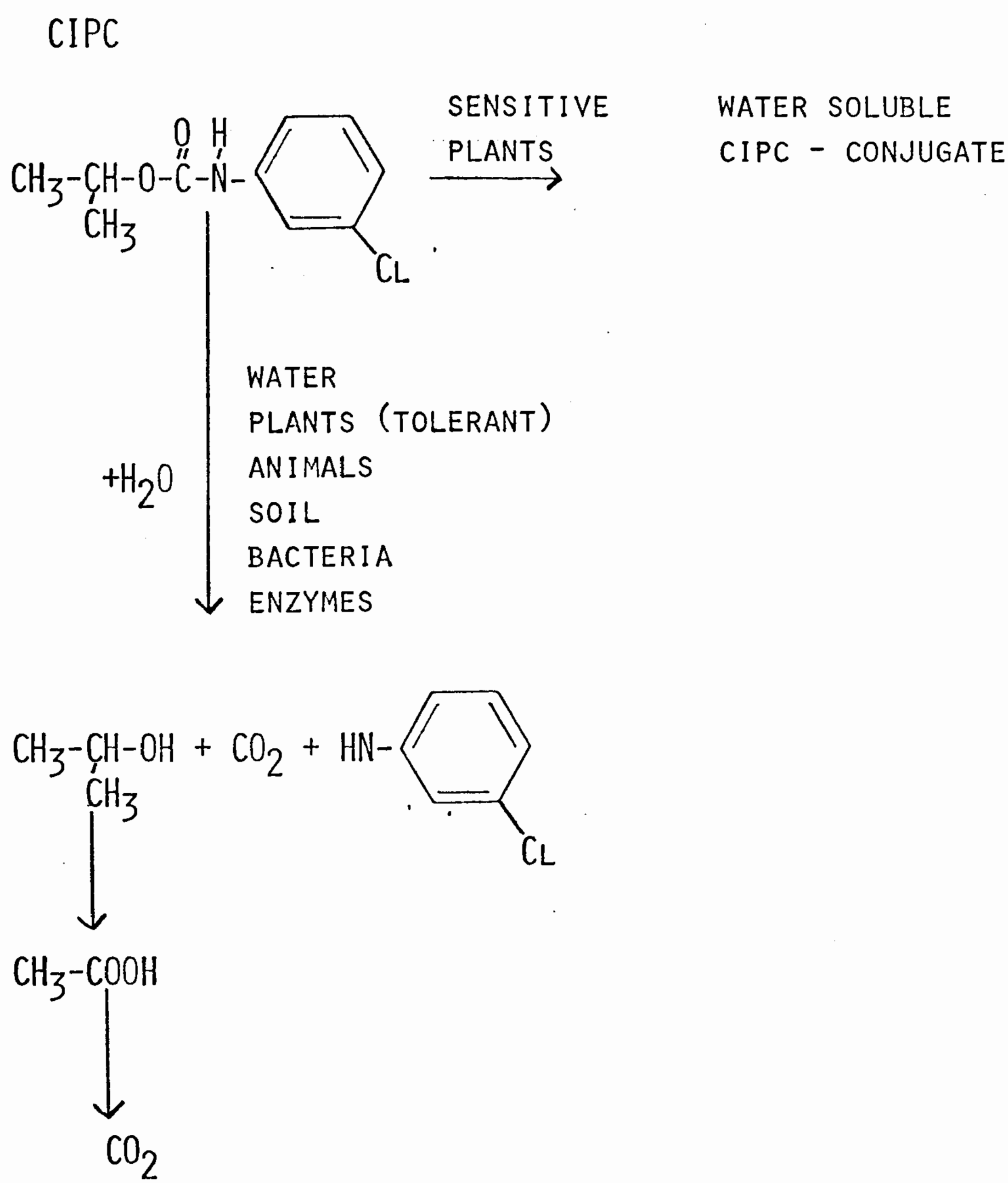


Figure 7. PERSISTENCE OF THIOCARBAMATE AND CARBAMATE HERBICIDES IN MOIST SOIL UNDER SIMULATED SUMMER GROWING CONDITIONS AT 70-90° F

HERBICIDE	HALF-LIFE IN MOIST LOAM SOIL AT 70-90° F WEEKS
EPTAM	1
VERNAM	1.5
TILLAM	2
SUTAN	3
ORDRAM	3
RO-NEET	3.5
AVADEX	4
IPC	1
CIPC	4

Figure 8. DEGRADATION OF THIOCARBAMATE HERBICIDES IN THE ENVIRONMENT