

Review of Disappearance of Substituted Urea Herbicides from Soil

T. J. SHEETS

Crops Research Division,
Agricultural Research Service,
U. S. Department of Agriculture,
Beltsville, Md.

Persistence of substituted urea herbicides in soils is influenced by rainfall, soil properties, soil environment, microbial activity, and characteristics of the herbicides such as solubility, leachability, and adsorption to soil colloids. Soil microorganisms that metabolize certain urea herbicides have been isolated and identified. Photochemical decomposition, volatilization, and absorption and metabolism by plants are also probable pathways of dissipation from soils. Results of extensive research in arid and humid climates indicate that monuron and diuron applied at rates of 1 to 4 pounds per acre for selective weed control in crops may persist under some environmental and edaphic conditions and injure sensitive plants seeded 6 to 12 months after herbicide application. However, accumulation of residues from annual applications to the same soil does not appear to be a problem. Disappearance of phenylurea herbicides from soils appears to conform to a first-order rate equation.

SEVERAL substituted ureas (see Table I for common names used in text) are used at rates of 1 to 4 pounds per acre as selective pre-emergent herbicides for control of weeds in several crops under a wide range of climatic and edaphic conditions. With surfactant, diuron is also an effective postemergent herbicide. At rates of 10 to 60 pounds per acre, several substituted ureas are effective, nonselective soil sterilants. Under identical conditions, persistence of these herbicides in soil varies; some are herbicidally active for 1 to 3 months, and others for 12 or more months.

Problems with persistence of the phenylurea herbicides are sometimes encountered. When monuron and diuron are applied for selective weed control in resistant crops, sufficient residues may remain in the soil to injure susceptible crops planted the following year or crop season (7, 8, 16). Hollingsworth (8) reported that cereals may be injured when seeded in the fall following cotton sprayed pre-emergently with broadcast applications of diuron or monuron at 2 to 4 pounds per acre. The same herbicides at 1 to 1.5 pounds per acre as broadcast, pre-emergent applications did not appear to endanger oats the fall after application if the soil was thoroughly mixed before planting oats. Conversely, the effectiveness of diuron as a pre-emergent herbicide may be reduced if application is followed by dry, sunny weather for 2 or 3 weeks. The reduced effectiveness is probably a consequence of herbicide loss from soil by photodecomposition and volatilization. Safe and efficient use of these compounds for weed control, particularly selective weed control in crops, necessitates a thorough knowledge of principles involved in their persistence.

General Persistence Comparisons

Little or no information is available on the persistence in soils of several substituted urea herbicides listed in Table I. DCU has not been widely used and consequently the need for investigation of soil persistence has not been very urgent. Cycluron, norea, and H 95-1 were introduced recently as herbicides and are presently in the advanced developmental stage; published data on their soil persistence are very incomplete.

H-7175 is being evaluated as a soil sterilant for control of vegetation on industrial sites and noncrop lands, and its persistence in soils appears sufficient for this use. Eight concentrations of H-7175, monuron, and diuron in three alluvial soils of the Mississippi Valley (Bosket sandy loam, Dundee silt loam, and Sharkey clay) were prepared, and persistence of the herbicides was determined by growing successive 4-week crops of seedling oats (15). Initial phytotoxicity of H-7175 was intermediate between that of monuron and that of

diuron. In the Bosket and Dundee soils there was little or no difference between the persistences of these three herbicides. In Sharkey clay, H-7175 appeared to be slightly less persistent than monuron and diuron.

Considerable research has been conducted on the persistence of the phenylurea herbicides in soils, and subsequent discussion in this paper will be restricted to this group. Most of the discussion will be limited to comparisons of substituted phenylureas, and consequently some published papers dealing with a single herbicide may not be cited.

Hill *et al.* (7) studied the persistence of monuron and diuron in field plots in the humid East and Southeast. They observed no great difference in persistence between these two herbicides. In a few cases, phytotoxicity of monuron appeared to persist longer than that of diuron, but chemical analyses indicated little or no difference in levels of the two herbicides 4, 8, and 12 months after application. Workers in California (3) measured greater quantities of diuron than monu-

Table I. Common Names and Designations of Substituted Urea Herbicides

Structural Name	Common Name or Designation
Dichloral urea	DCU
3-Cyclooctyl-1,1-dimethylurea	Cycluron
3-[5-(3a,4,5,6,7,7a-Hexahydro-4,7-methano-indanyl)]-1,1-dimethylurea	Norea
3-(4-Chlorophenyl)-1-methyl-1-isobutylurea	H 95-1
3-(Chloro-2-norbornyl)-1,1-dimethylurea	H-7175
3-Phenyl-1,1-dimethylurea	Fenuron
3-(4-Chlorophenyl)-1,1-dimethylurea	Monuron
3-(3,4-Dichlorophenyl)-1,1-dimethylurea	Diuron
3-(3,4-Dichlorophenyl)-1-methylurea	DMU
3-(3,4-Dichlorophenyl)-1-methyl-1-n-butylurea	Neburon
3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea	Linuron

ron 6 months after application, but the diuron was less phytotoxic on a unit concentration basis in Yolo clay. Shadbolt and Whiting (13) compared the persistences of monuron and neburon in Ramona sandy loam under field conditions at Riverside, Calif. Fifty per cent of the applied monuron (2, 4, and 8 pounds per acre) disappeared in 4 to 5 months, whereas an 8- to 9-month period was required for neburon to reach the 50% level. Oats were used as a test plant by Hill *et al.* (7). Since, in the absence of clay or soil, diuron was more toxic to barley and oats than monuron (1, 17), availability of diuron for uptake by plant roots was probably less than that of monuron.

In a greenhouse experiment in which leaching was eliminated, the persistences of monuron, diuron, fenuron, and DMU were compared in 17 California soils (16). Persistence was evaluated by growing successive crops of seedling oats. Fenuron was inactivated most rapidly and diuron least rapidly. The rates of detoxification of monuron and DMU were intermediate between those of fenuron and diuron in most soils. Fenuron is also less persistent than monuron and diuron under natural conditions in the field. That diuron was more persistent than monuron in soils is supported by results of Ashton and Sheets (3) but appears contradictory to results from other field applications (1, 7) where little or no difference between persistences of monuron and diuron was observed. An explanation for this variance in terms of environment or physical and chemical properties of herbicides and soils is not readily apparent.

Ogle and Warren (11) found that monuron inactivation was most rapid in muck, intermediate in a silt loam, and least in a sand. Differences in rates of inactivation were attributed to organic-matter content and microbial activity. In the investigation with 17 soils (16), inactivation of DMU and diuron was most rapid in soils containing the greatest amounts of organic matter. However, there were exceptions to this generalization. The relation appeared to be much poorer for monuron than for DMU and diuron. Inactivation of fenuron apparently was unrelated to soil organic matter.

In greenhouse experiments by Crafts and Drever (5), the persistences of fenuron and monuron were compared in three soils of the Sacramento River Valley of California. Effects of leaching were eliminated by the experimental procedure. Persistence was evaluated by growing successive crops of seedling oats. Herbicidal activity of fenuron disappeared more rapidly from the three soils than that of monuron. Rates of inactivation of monuron were approximately equal among the three soils,

whereas fenuron was most persistent in Egbert loam, intermediately persistent in Yolo fine sandy loam, and least persistent in Yolo clay loam. The Egbert loam, a mixed organic soil, had a greater cation exchange capacity and higher clay and organic matter contents than the other two soils. That fenuron was most persistent in the Egbert soil appeared unusual. Initially fenuron and monuron were least phytotoxic in the Egbert soil. Therefore, fenuron was most persistent in the soil in which greatest adsorption of the herbicides appeared to occur.

Phytotoxicity from linuron, a methoxy derivative, applied at rates used for selective weed control, disappeared from a wide variety of soils in the field within 3 to 4 months (9). In a greenhouse experiment, the herbicidal activity of linuron disappeared from four Maryland soils more rapidly than that of monuron (15). These results indicate that linuron should present fewer soil residue hazards than monuron and diuron. There should be little or no danger of linuron phytotoxicity to crop plants which follow a treated crop in a rotation system.

Processes Involved in Inactivation of Phenylureas in Soil

After a herbicide is applied to soil, it is subjected to the action of several processes which promote inactivation, such as adsorption and metabolism by soil microorganisms; adsorption to mineral and organic colloids; leaching by rainfall and irrigation water; chemical reactions (nonbiological); photochemical alterations; volatilization; and adsorption by higher plants.

These processes are directly and indirectly influenced by several soil properties (types of clay minerals, amounts of clay minerals, structure, texture, organic matter, temperature, moisture, and pH); properties of herbicides (water solubility, structure, reactivity, charge, and polarity); and environmental variables (rainfall and irrigation water, temperature, light, and wind).

Variations in soil properties, soil microorganisms, climate, and physical and chemical properties of the herbicides must account for differences in persistence from soil to soil and region to region.

Inactivation of the phenylurea herbicides occurs under soil conditions favorable for growth of microorganisms, but loss of activity does not occur or occurs very slowly in dry soil or autoclaved soil (7, 10, 11, 17). A species of *Pseudomonas* utilized monuron as a sole carbon source (6, 7). Utilization of monuron by another *Pseudomonas* isolate was greatly accelerated by addition of yeast extract to the culture medium. Other bacteria (species of *Xanthomonas*, *Sarcina*, and *Bacillus*) and fungi (species of *Penicillium*

and *Aspergillus*) utilized monuron as a sole carbon source in agar medium (6). In soil autoclaved before addition of the herbicides, the relative phytotoxicities of monuron, fenuron, diuron, and DMU were approximately the same 1 and 5 months after treatment (17). In non-autoclaved soil, fenuron, one of the most toxic initially, was least toxic by the fifth month. This observation suggests that fenuron was inactivated more rapidly by microorganisms than monuron, diuron, and DMU. Although all available evidence suggests that soil microorganisms play a major role in the disappearance of the phenylurea herbicides from soils, effective soil microorganisms apparently do not proliferate readily. Two possible explanations for this pattern of breakdown are that certain microorganisms may utilize the phenylureas but not preferentially or selectively to other energy sources, and that the adsorption-desorption equilibria of these herbicides in soil systems may lie toward the adsorbed state so that the concentration in the soil solution remains low, and slow uptake and consequently slow metabolism result.

The relation of soil adsorption and adsorption-desorption equilibria to decomposition and inactivation of the phenylureas, and other herbicides as well, has not been clearly defined or demonstrated experimentally. The phenylureas are adsorbed to clay and organic colloids in soils (6, 18, 20), and their phytotoxicity is reduced apparently in proportion to the degree of soil adsorption (4, 16). Sherburne and Freed (18) suggested that monuron might persist longer in soils of high adsorptive capacities such as clays or soils containing high levels of organic matter than in sands or other soils with low adsorptive capacities. The adsorbed fraction, probably unavailable for uptake by plant roots and soil microorganisms, would be slowly released to the solution phase as monuron is removed from the solution by leaching, uptake by plants, and metabolism by soil microorganisms. The rate of inactivation would be a function of the soil-solution concentration, which in turn is related to soil adsorption. This concept appears to conflict with the conclusion that inactivation of diuron and monuron is directly related to the amount of soil organic matter. However, differentiation must be made between the active fraction and the total herbicide residue in the soil.

The results of Crafts and Drever (5) for fenuron support the concept that the rate of decomposition is related to the herbicide concentration in the soil solution. They maintained soil cultures of fenuron and monuron for approximately 3.5 years, and the extended persistence of fenuron in the high adsorptive soil (Egbert loam) did not become

measurable until several months after application because of the experimental technique employed. Also, the difference was measurable by their biological method only at relatively high fenuron concentrations. In short-term experiments and in those with only low concentrations of herbicides, adsorption to organic and inorganic colloids may mask differences in actual decomposition of herbicides between soils when semi-quantitative bioassays are used to assess residue levels. Diuron appeared to be more persistent but less active than monuron in Yolo clay (3), and diuron was adsorbed more than monuron (4, 20). Neburon persisted longer in Ramona sandy loam than monuron (13), and neburon appeared to be adsorbed more to clay than monuron (4). Therefore, the results of Ashton and Sheets (3) and Shadbolt and Whiting (13) also appear to support the concept that the concentration of substituted urea herbicide in the soil solution may influence or partially determine the rate of decomposition but not the rate of inactivation.

Numbers of soil microorganisms usually increase as soil organic matter increases, and microorganisms present in agricultural soils are known to metabolize monuron (7). Therefore, inactivation of the phenylurea herbicides could presumably occur more rapidly in soils high in organic matter than in other soils as a result of microbial activity. Metabolism by the large and active populations of microorganisms present in soils high in organic matter might, therefore, offset the effects of adsorption on availability in the soil solution and the consequentially reduced inactivation. Discrepancies in the literature on the relation of soil organic matter and persistence of the phenylurea herbicides in soils can probably be explained by differences in microbial populations, experimental techniques, and herbicide residue actually being measured (total residue or active residue).

Movement downward in soils dilutes herbicides, exposes them to new adsorption sites, and reduces the concentration in the soil solution. Differences in movement of fenuron, monuron, and diuron in soils are related to water solubility and adsorption (2, 6, 76). Fenuron, being more soluble and less strongly adsorbed than monuron and diuron, moves more readily with water. Mobility in soils explains why fenuron effectively controls several chaparral and desert species of brush in the southwestern U. S. Similarly monuron is more soluble and less strongly adsorbed than diuron and consequently is moved more readily with water. Thus, inactivation due to soil dilution should be greatest with fenuron, intermediate with monuron, and least with diuron. The relative persistence of these three her-

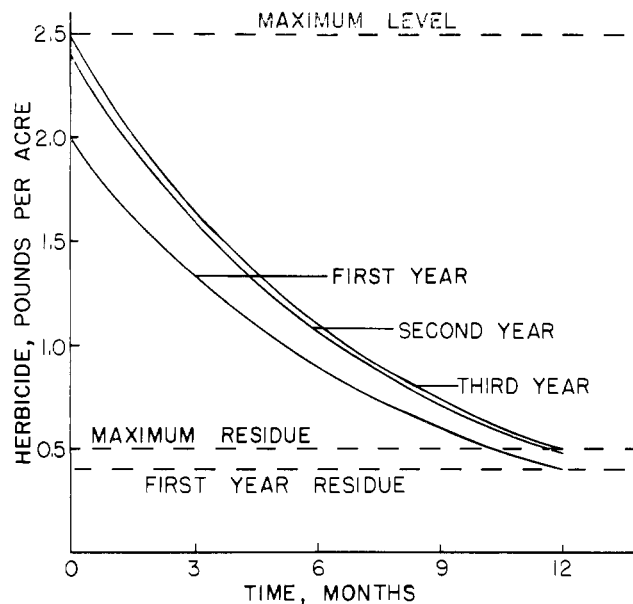


Figure 1. Theoretical curves showing the amount of herbicide as a function of time in soil sprayed annually with 2 pounds per acre

(assume 80% loss per year)

bicides sometimes follows this order, but in field applications residual activities of monuron and diuron are often about equal.

In the absence of (or when not associated with) microorganisms, hydrolysis of the phenylureas to the respective nonphytoxic aniline derivatives might account for some disappearance of these herbicides from soils. However, because monuron and diuron are stable in aqueous solutions, Hill *et al.* (7) considered disappearance by this process and by nonbiological oxidation of little or no importance.

Loss of monuron from an aqueous solution exposed to sunlight was demonstrated by Hill *et al.* (7). Weldon and Timmons (79) showed that exposure of crystalline monuron and diuron to radiation from a mercury vapor lamp caused changes in the ultraviolet absorption spectra. Exposure of both herbicides for 28 hours caused a 75% decrease in biological activity. Sheets (74) reported that the activity of monuron and diuron disappeared more rapidly from soil exposed to sun than from shaded soil. However, possible losses by vaporization and chemical reactions were not controlled or measured. Hill *et al.* (7) concluded that photodecomposition might explain the loss of monuron from the soil surface in arid areas of the western and southwestern U. S.; but in humid regions where frequent rains move the herbicides into the soil, they suggested that only a small part of the applied herbicide would be decomposed by this process. However, the reduced effectiveness of diuron as a pre-emergent herbicide, when application is followed

by a drought of 2 or more weeks in normally humid areas, may be partially attributable to radiation-induced inactivation. Also, this reduced effectiveness may be partially a consequence of volatility losses.

The vapor pressure of monuron at 25° C. is 5×10^{-7} mm. Hg; therefore, losses of phenylureas by volatilization are probably important only when the herbicides remain on the soil surface exposed for several days or weeks to hot, dry conditions (7). Rates of volatilization from soils have not been determined.

Herbicide molecules are absorbed by plants growing in treated soil. Therefore, a small amount of herbicides may be lost from soil either by metabolism in the plant or by removal of the plant from the treated soil. The importance of absorption by higher plants as a method of dissipating herbicide residues from soils has not been critically determined.

Possible Persistence Hazards

Hill *et al.* (7) presented data indicating that disappearance rates of monuron and diuron from soil followed first-order equations. This result has been substantiated by others. Hill *et al.* concluded that although the rates of inactivation of monuron and diuron were often altered by soil moisture and temperature, the first-order equation was probably applicable under usual field conditions. When monuron and diuron were applied at rates of 1 and 2 pounds per acre in humid regions of the United States, major portions of the herbicides were inactivated each year. Accumulation from applications on the same soil 2

years in succession was negligible. Rahn and Baynard (12) found that monuron applied at 3.6 pounds per acre in two applications for 3 years in succession did not persist from one year to the next. When monuron was applied at 6.4 pounds per acre, phytotoxicity persisted from one year to the next, but accumulation did not occur.

In Arizona, the same plots were sprayed each year for 8 years with fenuron, monuron, or diuron at 0.8 and 1.6 pounds per acre for selective weed control in cotton (1). Although carry-over from one year to the next sometimes occurred, the herbicides did not appear to accumulate. Similar results were obtained from a 6-year field experiment in California (1).

In another experiment in California (3), plots of Yolo clay were sprayed with 0.25, 0.5, 1, and 2 pounds per acre of monuron and diuron in November for control of weeds in spinach. Applications were repeated each fall for 4 years, and persistence of the herbicides was determined in the greenhouse by quantitative bioassay of soil samples. Residues were detected approximately 6 months after each application of 2 pounds per acre of monuron and diuron and 1 pound per acre of monuron. Twelve months after application, measurable residues were detected only after the fourth annual application of 2 pounds per acre. This residue the fourth year was probably due to weather conditions as observed by Arle *et al.* (1); however, the possibility that a slow accumulation over the 4-year period occurred cannot be ruled out. If some accumulation occurred, the magnitude was not great.

Calculations based on the concept that

the disappearance of the phenylurea herbicides conforms to a first-order rate equation show possible accumulation levels in soils. The theoretical curves in Figure 1 are based on the same principle as the curves of Hill *et al.* (7), and show the concentration of herbicide as a function of time in soil sprayed each year with 2 pounds per acre. An 80% loss per year was assumed as a reasonable minimum rate of loss of phenylurea herbicides for most soil type-environment situations in the U. S. Inactivation is greater than 80% in many cases (7). Figure 1 shows that if the same soil was sprayed annually with 2 pounds per acre of a herbicide, and if 80% of the herbicide dissipated each year, the amount in the soil immediately before reapplication would eventually approach 0.5 pound per acre. The amount in the soil immediately after application would approach 2.5 pounds per acre. Different rates of application or different loss assumptions would, of course, change the curves in Figure 1.

Rates of inactivation of herbicides vary tremendously in response to differences in soils and climate. Carry-over of monuron and diuron can be expected under some conditions; but results indicate that possibilities of massive accumulation in soils are nil.

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METABOLISM OF HERBICIDES

Metabolism of α -Chloro-N,N-diallyl-acetamide(CDAA) and 2-Chloroallyl-N,N-diethyldithiocarbamate(CDEC) by Plants

THE METABOLISM of pesticides in general has received wide and intensive study, particularly within the past decade. These investigations have been initiated in many instances because of a desire and need to know the persistence, metabolism, and fate of subsequent degradation products of a given pesticide in crop plants. In many cases, such studies have resulted in collateral findings regarding detoxification mechanism, possible modes of action, bases of selectivity, bases of resistance, and other facts pertinent to the fields of pharmacology, physiology, and bio-

chemistry. Thus, the development of modern pesticides has also had a direct and indirect influence upon the development of modern biology.

This symposium is directed toward reviewing our knowledge of the metabolic fates of various herbicides in plants, animals, and soil. This paper reviews work on two pre-emergent herbicides which possess remarkable qualities of specificity, particularly within the monocotyledonous species of plants (1-3).

The first material is α -chloro-N,N-diallylacetamide (CDAA) (Randex, reg-

ERNEST G. JAWORSKI
Agricultural Division,
Monsanto Chemical Co.,
St. Louis, Mo.

istered Monsanto trademark). This grass-specific, pre-emergent herbicide is used quite widely, particularly in corn and soybeans, for the control of foxtail, brome grass, cheat grass, crabgrass, and certain broadleaf weeds (2, 3). It is an amber liquid, highly soluble in organic solvents, with a fair degree of water solubility (ca. 1%).

Two types of studies were undertaken with this material—one in which the carbonyl carbon was labeled with C¹⁴ and an other where the allyl moiety was labeled with C¹⁴. Treating soil seeded to various crop plants with the