

DINITROANILINE HERBICIDE PERSISTENCE UNDER
FALLOW AND IRRIGATED CONDITIONS

by

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ABSTRACT

Nine dinitroaniline herbicides, butralin [4-(1,1-dimethylethyl)-N-(1-methylpropyl)-2,6-dinitrobenzenamine], dinitramine (N⁴,N⁴-diethyl-a,a,a-trifluoro-3,5-dinitrotoluene-2,4-diamine), ethalfluralin [N-ethyl-N-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl)benzenamine], fluchloralin [N-(2-chloroethyl)-2,6-dinitro-N-propyl-4-(trifluoromethyl)aniline], oryzalin (3,5-dinitro-N⁴,N⁴-dipropylsulfanilamide), pendimethalin [N-(1-ethylpropyl)-3,3-dimethyl-2,6-dinitrobenzenamine], prodiamine (N³,N³-di-n-propyl-2,4-dinitro-6-trifluoromethyl-n-phenylenediamine), profluralin [N-(cyclopropylmethyl)-a,a,a-trifluoro-2,6-dinitro-N-propyl-p-toluidine], and trifluralin (a,a,a-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine), were soil applied in early summer to two borders of farmland. One border was irrigated and one was fallow. A biological assay using sorghum [Sorghum bicolor (L.) Moench.] was performed at monthly intervals over an 8 month period. The effects of moisture on herbicide persistence were determined.

Dinitramine was the least persistent of all treatments tested. Butralin, ethalfluralin, and fluchloralin persisted longer than dinitramine but less than oryzalin, pendimethalin, profluralin, and trifluralin. Prodiamine was the most persistent herbicide tested. Moisture reduced the rate of persistence but did not affect the relative order of persistence.

INTRODUCTION

Agricultural weed competition can seriously depress profits through reduced yields, increases costs of production and processing, and decreased product quality. Often herbicides are effective tools to minimize the competition.

Dinitroaniline herbicides are soil-applied to control annual grasses and some broadleaf weeds. They are generally not active against established plants but are effective against germinating seeds and young seedlings. Because they function within the soil, their persistence there becomes a major parameter of effectiveness.

The purpose of this study is to investigate the effects of moisture on the relative soil persistence of the following nine dinitroaniline herbicides: butralin [4-(1,1-dimethylethyl)-N-(1-methylpropyl)-2,6-dinitrobenzenamine], dinitramine (N⁴,N⁴-diethyl-a,a,a-trifluoro-3,5-dinitrotoluene-2,4-diamine), ethalfluralin [N-ethyl-N-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl)benzenamine], fluchloralin [N-(2-chloroethyl)-2,6-dinitro-N-propyl-4-(trifluoromethyl)aniline], oryzalin (3,5-dinitro-N⁴,N⁴-dipropylsulfanilamide), pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine), prodiamine [N³,N³-di-n-propyl-2,4-dinitro-6-trifluoromethyl-n-phenylenediamine], profluralin [N-(cyclopropylmethyl)-a,a,a-trifluoro-2,6-dinitro-N-propyl-p-toluidine], and trifluralin (a,a,a-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine).

LITERATURE REVIEW

Anderson (3) defined persistence as the length of time an herbicide remains active in the soil. For best results, he said that herbicides must remain in the soil in an active and available form until their intended purpose has been accomplished. Two implications are derived from this definition. First, periods of soil persistence less than that required for effective weed control may not provide the weed protection needed to avoid yield damage from weed competition. Second, periods of persistence beyond the time requirement of a crop to reach harvest may allow the chemical to interfere with future rotations. Herbicidal soil persistence, then, becomes an important factor in the overall efficiency of crop production.

Scientific literature pertaining to dinitroanilines has been reviewed through November, 1977.

Basic Chemistry of the Dinitroanilines

The herbicidal properties of unsubstituted dinitroaniline compounds were first reported in 1960 by Alder, Wright, and Soper (2). Two compounds, trifluralin and dipropalin (N,N-dipropyl-2,6-dinitro-p-toluidine), were named and described. Since that beginning, according to Probst, Golab, and Wright (64), trifluralin has been used on many agronomic and horticultural crops. Tolerant crops include cotton (Gossypium hirsutum L.), soybeans (Glycine max. [L.] Merr.), snapbeans (Phaseolus vulgaris L.), lima beans (Phaseolus limensis L.), safflower

(Carthamus tinctorius L.), carrots (Daucus carota L.), and several transplanted crops such as tomatoes (Lycopersicon esculentum Mill.) and peppers (Capsicum frutescens L.). Considerable literature exists on the three older dinitroanilines benefin (N-butyl-N-ethyl-a,a,a-trifluoro-2,6-dinitro-p-toluidine), nitralin [4-(methylsulfonyl)-2,6-dinitro-N,N-dipropylaniline], and trifluralin; but little is known of the newer compounds. Today, according to Parka and Soper (56), at least fourteen compounds have either been registered for crop use or are under development.

Weber and Monaco (84) published reviews of the chemical properties of the dinitroaniline herbicides. They described aniline as a colorless, oil liquid in its pure state. Its relatively high water solubility results from its molecular polarity. Aniline has a basic pH with a pKa value of 4.63. Addition of nitro groups to the aniline molecule produces an orange-yellow crystalline compound demonstrating a strong hydrogen bonding potential. This potential gives the chemical an affinity for proteinaceous material. Compound basicity and lowered water solubility are accounted for by these electron withdrawing properties. The dinitroanilines are typified by nitro groups attached to the 2 and 6 positions on the basic aniline molecule. Radical substitution accounts for most of the inherent differences found between family members.

Alder et al. (2) found the 2,6-dinitro compound more phytotoxic than the 2,4-dinitro compound. Both were more active than the 2,3-dinitroaniline molecule. Dialkyl substitutions onto the amino group of the 2,6-dinitro molecule caused the resultant compound to lose general

herbicidal properties and become highly selective against seedling grasses in preemergence applications. The di-n-propyl substitution was the most active dialkyl substitution. Further activity was achieved by substitution onto the 4 position of the aniline ring. The activity in decreasing order for the 4 position substituents was CF_3 , CH_3 , Cl, and H. The 4- CF_3 formulation was later marketed as trifluralin and the 4- CH_3 as dipropalin.

Working with sixteen substituted toluidine on eight species of plants, Gentner (22) found analogs of CF_3 to be more biologically active in preemergence applications than CH_3 analogs. However, CH_3 analogs demonstrated greater postemergence activity than the CF_3 forms. Pre-emergence toxicity to crops was decreased in both the CF_3 and CH_3 series when the N- substituted compounds contained more than six carbon atoms.

Ford and Massey (18) concluded that dinitroanilines were relatively safe to humans and animals. Acute oral LD_{50} values for adult rats are in the range of 10,000 mg/kg body weight for trifluralin and benefin. The compounds tested had no effect on rat and dog reproduction.

Mode of Action

Parka and Soper (56) reviewed literature dealing with the physiology and mode of action of the dinitroanilines. Seed germination was not directly inhibited but herbicidal effects were visible during and immediately after germination. Inhibition of lateral root development was the most characteristic growth response. Visible injury to plant tops included stunting, intensification of green coloration, a leathery

appearance of the cotyledons, and swelling and brittleness of the stem or hypocotyl. They concluded that the site of uptake into the plant was the monocot shoot and the dicot hypocotyl hook. Plant death does not usually occur when susceptible roots are exposed to the dinitroanilines, although severe root inhibition results. Shoot exposure, in contrast, usually results in plant death. It is not yet known whether these herbicides are absorbed by the plant or adsorbed onto the roots; however, minimal translocation of the material from the root to the shoot occurs. Root tip enlargement is the universally recognized morphological effect. Microscopic cell examination shows these cells to be multinucleate with an increase in the percentage of cells in arrested metaphase due to the disruption of both cortical and spindle microtubules. Trifluralin and oryzalin do not bind to mammalian microtubular protein as does colchicine. The effects of colchicine and trifluralin on chromosomes, however, are similar.

Little information, according to the same source, was available on the effect of the dinitroanilines on plant carbohydrates, lipids, and nitrogenous compounds. The effect of trifluralin on RNA and DNA varies with the plant species, plant part, time of treatment, and herbicide concentration employed and does not correlate with dinitroaniline susceptible or resistant species. Phytase, dipeptidase, a-amylase, and proteolytic enzyme activity does not appear to be greatly inhibited, but even slight inhibition could cause an indirect effect on plant metabolism. In vivo and in vitro photosynthesis and respiration interference occurs. Parka and Soper concluded that despite all the

work done on this herbicide family, the mode of action was still unclear.

Factors Affecting Persistence in Soil

Seven methods of herbicide loss from the soil, listed by Klingman and Ashton (40) included chemical decomposition, decomposition by microorganisms, adsorption on soil colloids, leaching, molecular volatilization, photodecomposition, and removal of material from the soil by higher plants.

Chemical Decomposition

Probst et al. (64) reviewed the literature concerning dinitroaniline degradation. With few exceptions, dinitroaniline herbicides degrade in similar patterns. Minor differences will be observed, however, as in-depth investigations are extended.

Work with trifluralin by Probst et al. (63) and with benefin by Golab et al. (28) demonstrated that degradation of the dinitroanilines in soil was affected by aerobic and anaerobic conditions. The aerobic pathway proceeded by a series of oxidative dealkylation steps while the anaerobic pathway was initiated through a sequential reduction of nitro groups. Supportive evidence for the dual pathway was provided by Golab and Althaus (24) with isopropalin (2,6-dinitro-N,N-dipropylcumidine); Golab et al. (26) with oryzalin; and Smith et al. (76) with dinitramine.

Long-term degradation studies under field conditions were performed on trifluralin, oryzalin, and isopropalin by Golab and Amundson (25). Golab et al. (26) and Golab and Althaus (24), respectively. The degradation pathways observed with these three herbicides demonstrated,

according to Probst et al. (64), that a variety of mechanisms, i.e., dealkylation, reduction, oxidation, hydrolysis, cyclization, and combinations of these, were involved in the transformation of dinitroanilines in soil. The degradation patterns of various dinitroaniline herbicides currently proposed are not likely to be final. As new investigations proceed with more sophisticated instruments and methodology, the status of degradation products formed under aerobic and anaerobic conditions will be extended to supplement present knowledge.

Degradation by Microorganisms

Probst et al. (63) incorporated trifluralin in both autoclaved and nonautoclaved soil at 8 ppmw to determine if microbes play an important role in dinitroaniline decomposition. Soil was maintained at 75% field moisture capacity, incubated at 27 C, and sampled monthly for 14 months. A large crabgrass [Digitaria sanguinalis (L.) Scop.] bioassay revealed that chemical degradation proceeded slightly more rapidly in nonautoclaved soil than in autoclaved soil. No specific organisms could be found in several trifluralin-treated soils that caused the herbicide degradation. Savage (69) conducted a similar study with similar results.

Golab et al. (28) detected a dealkylated, reduced, and oxidized derivative of benfenin under aerobic conditions. This product, a,a,a-trifluoro-2,6-dinitro-p-cresol is the same as was found by Probst et al. (64) as a derivative of trifluralin. Golab et al. (26) found a corresponding compound, 3,5-dinitro-4-hydroxybenzenesulfanamide, degraded from oryzalin under the same aerobic conditions. This displacement of

the dipropylamino group by a hydroxyl group was not observed with isopropalin. However, Golab and Althaus (24) observed a new degradation product, a,a-dimethyl-3,5-dinitro-4-dipropylaminobenzyl alcohol, resulting from the hydroxylation of the isopropyl group in isopropalin.

Funderburk et al. (19) found trifluralin to be the only radioactive compound present in extracts of ¹⁴C-labeled trifluralin-enriched soil. Four species of fungi, Sclerotium rolfsii, Aspergillus niger, Fusarium sp., and Trichoderma sp., were grown in liquid medium containing trifluralin. Extracts of the solutions showed little change in trifluralin concentration. The extract of Aspergillus niger, however, contained not only trifluralin but also a small quantity of a,a,a-trifluoro-2,6-N-propyl-p-toluidine.

Addison (1) mass inoculated soil with six actinomycetes, three fungi, and one bacterium, all native to soil, and found them to be of little or no value in the degradation of trifluralin. Similar results were obtained using five facultative anaerobes.

Hamdi and Tewfik (30) isolated a bacterium from cotton field soil previously treated with trifluralin which was capable of decomposing trifluralin in the presence of acetate, lactate, glutamate, or yeast extract. The microorganism, Pseudomonas sp., degraded 95% of a 0.01% concentration of trifluralin incorporated in the medium in 21 days at a pH of 7.4.

Messersmith, Burnside, and Lavy (49) used ¹⁴C-propyl-labeled trifluralin at 1 ppm and 100 ppm in a silt clay loam soil and a sandy loam soil. They found the rate of dissipation was greater at a field

capacity of 1.6 as compared to 0.8. The amount of $^{14}\text{CO}_2$ liberated from the soils was 5 and 3%, respectively.

Laanio, Kearney, and Kaufman (42) studied the metabolism of four dinitroanilines with various species of fungi. Dinitramine was found to be degraded by Aspergillus fumigatus, Fusarium oxysporum, and a Paecilomyces sp. into mono and idealkylated derivatives and 2,4-dinitro-6-trifluoromethyl-m-phenylenediamine.

Kearney, Plimmer, and Williams (38) enriched solution cultures with butralin and inoculated them with Paecilomyces sp. Trace amounts of dealkylated product and a polar compound were isolated. The polar compound was shown to be $\text{C}_{14}\text{H}_{21}\text{N}_3\text{O}_5$ and a comparison of fragmentation pathways suggested an oxidation of the N-sec-butyl moiety. Such an oxidation products supports a proposed intermediate identified in the photodecomposition of trifluralin.

Microbial degradation of trifluralin in soil may be of more significance in fields receiving repeated applications, according to Carter and Camper (15). Using a chromatographic analysis, a probable microbial degradation product was found. They concluded that it was probable that a physiological adaptation was induced in the cells by prolonged contact with trifluralin. This may involve degradation.

Parka and Tepe (57) and Probst et al. (63) observed that trifluralin at moisture conditions significantly above field capacity was degraded much more rapidly as compared to moisture levels of field capacity or lower. At 200% field capacity, 50% of the added trifluralin disappeared in 10 days and 84% in 24 days. Anaerobic microorganism degradation could not account for the rapid demise of the herbicide.

The moisture content of the soil at 200% field capacity was not specified.

Parr and Smith (61) studied trifluralin under aerobic and anaerobic conditions. Their study listed four points of evidence for microorganism involvement in the initial anaerobic degradation of trifluralin. First, there was an enhanced degradation in the presence of an organic substrate. Second, no trifluralin degradation occurred in a moist, anaerobic environment after autoclaving. Third, a resumption of respiratory activity occurred in autoclaved systems after reinoculation. This corresponded with increased degradative activity. Fourth, a temporary lag period, or a period of respiratory activity suppression, resulted in a decrease in trifluralin degradation from the presence of KN_3 . With the dissipation of this biological inhibitor, a resumption of degradation and respiration occurred.

If microorganisms play a role in anaerobic degradation, that role is not well understood. Gingerich and Zimdahl (23) studied the soil persistence of oryzalin and isopropalin. They found anaerobic degradation by Arrhenius activation energies suggested that the degradation processes were non-biological.

Probst et al. (63), Funderburk et al. (19), and Messersmith et al. (49) concluded that microbial action on dinitroaniline herbicides could not be accepted as a major pathway of degradation.

Adsorption to Soil Colloids

Bailey and White (8) reviewed organic pesticide adsorption and desorption literature. They concluded that there existed two levels of

adsorption phenomena. The first level describes the kinds of adsorption that can exist within the soil structure and is regulated by the electrical charge on the colloid surface. Positive adsorption occurs when there is attraction between the adsorbate and adsorbent resulting in the concentration of the adsorbate being higher at the interface than in the adjoining phases. Negative adsorption occurs when the adsorbate is repelled from the interface and thus the adsorbate concentration is greater in the bulk solution than at the interface. The second level concerns two general types of adsorption. One is the physical, or Van der Waals, adsorption, due to orientation or dipole-dipole interactions, and ion-dipole interactions in conjunction with Born repulsion interactions. The other type is chemical adsorption due to coulombic forces arising from bond formation between adsorbent and adsorbate. The strength with which a chemical is held in the soil may be regarded as the summation of the effects of these different forces acting between the adsorbent and adsorbate. The authors stressed that only the surface layer of adsorbate was chemically bonded to the soil colloid. Outer layers were held by dipole attraction, that is, by physical adsorption.

Bailey and White also evaluated the various factors involved in the adsorption of a chemical onto soil colloids. For convenience, the factors were divided under two headings: the macrofactors which affect the periodicity and amount of moisture that accumulates at the soil surface and percolates on through the soil profile; and the microfactors which exert a more direct influence on the adsorption and desorption of pesticides by soil colloids.

Two factors were listed under macrofactors. The first was the physical properties of the soil as a substrate. These properties include the pore size and its effect on the amount of moisture that could pass a given point in an increment of time, the continuity of the air space reflecting the restriction of clay soils to molecular diffusion, and the soil color with its effect on soil temperature. The second macrofactor listed was the soil climatic factors. Low moisture content may cause the pesticide to be highly adsorbed, while frequent rainfall may maintain the moisture level significantly high enough to decrease adsorption and enhance bioactivity through pesticide desorption.

Several factors were listed as macrofactors. These included the nature of the soil colloid, including cation exchange capacity, organic matter content, total clay, and soil pH; the nature of the adsorbate; the effect of the saturating cation on the soil system; soil moisture level; temperature; and the nature of the formulation.

Organic colloids, because of their high ion exchange capacity and surface area greater than that of mineral colloids, have a high adsorption potential. Organic matter content of soils is thus an important parameter of soil adsorption.

Hartley (33) found that adsorption, as influenced by soil properties could either retard, or more frequently, accelerate chemical reactions by actions similar to enzymes in biosystems. Lignin residues have accessible internal surfaces which, apparently, are more favorable to the binding of organic molecules than are exchange sites of the alumina-silica lattice. Clay has little relevance to the adsorption of large organic molecules.

Bardsley, Savage, and Childers (9) reported increasing amounts of organic matter to effect increased retention of trifluralin in toxic form. The increased trifluralin toxicity with increased organic matter was due to greater retention or adsorption of the vapor phase of the herbicide. This observation led to the conclusion that the increased adsorptive capacity of organic matter was instrumental in the retention of the vapor phases. Vapor loss may also be affected by soil conditions and properties other than organic matter. It was the conclusion of Ford and Massey (18) that more adsorptive soils showed the greatest retention of herbicides.

Rappardini and Bencivelli (66) compared trifluralin with linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea] in heavy and light soils at 2.5 kg/ha. In general, higher rates of both compounds were required on heavier soils.

Soils high in organic matter were found by Hollist and Foy (36) to adsorb the greatest amounts of trifluralin. At the same time, organic matter was the most effective method to reduce the phytotoxicity of the herbicide. Trifluralin did not adsorb onto the internal surfaces of montmorillonite and only the external surfaces were available for the adsorbent. Increasing water content appeared to block the exterior active sites

Koren (41) concluded that water molecules occupy adsorptive sites, allowing more downward movement of trifluralin and oryzalin. Greater movement was found in wet soil than in dry.

Trifluralin was adsorbed mainly by nonionic exchange resins as reported by McCall et al. (45). Physical bonds at sites on the resins

where no coulombic forces existed were found to be the main adsorption pathway. Generally, polar solids adsorbed polar compounds more strongly than nonpolar compounds.

Molecular volume or the molecule parachor was listed by Weber and Monaco (84) as being related to the amount of dinitroaniline adsorption in soil. Larger molecules were adsorbed in greater amounts than smaller molecules.

According to Grover (29), activated charcoal adsorbed trifluralin in greater amounts than wheat (Triticum aestivum L.) straw which, in turn, was greater than kaolinite and montmorillonite. Trifluralin was found to readily desorb in water.

Harvey (34) found trifluralin more strongly adsorbed than dinitramine, nitralin, and oryzalin. Finding that soil moisture affected the adsorption of dinitroaniline herbicides, he concluded that soil adsorption could possibly affect field performance.

Zimdahl and Gwynn (88) and Gingerich and Zimdahl (23) studied the soil persistence of isopropalin, oryzalin, trifluralin, and benefin. The rate of degradation was directly correlated with temperature and moisture content. First order kinetics adequately described the rate of degradation at 15 C but the simple first order assumption was not sufficient to describe degradation at 30 C. They felt that at 30 C, two rates or processes may operate in the soil degradation. Their data showed an initial rapid first order rate of degradation with a subsequent change to slower first order processes. First half lives of trifluralin, benefin, and 2,6-dinitro-N-(3-pentyl)-a,a,a-trifluoro-p-toluidine ranged from 0.4 to 1.8 months at 30 C and were consistently

lower in a loam soil than in a sandy loam soil. The aerobic rate of disappearance of isopropalin was slower than that of oryzalin in soil. Aerobic half lives were 3.5 months at 30 C and 13.3 months at 15 C for isopropalin and 1.4 months at 30 C and 4.35 months at 15 C for oryzalin. Both isopropalin and oryzalin dissipated more rapidly under anaerobic conditions than under aerobic conditions. Arrhenius activation energies suggested that the degradation processes were non-biological.

In numerous instances, Helling (35) writes, bioactivity of a pesticide is closely related to soil texture. He felt that this was valid also for the dinitroanilines, since recommendations call for greater rates on silty clay loam and clay loam soils than on sandy loam and silt loam soils. Harvey (34) concluded that adsorption as conventionally reported may be inadequate for predicting comparative behavior among dinitroanilines.

Leaching, Diffusion, and Runoff

Dinitroanilines do not leach from the soil in significant quantities. Ashton (5) reported that these herbicides do not leach under heavy rainfall conditions. Probst et al. (63) stated that trifluralin does not leach. Belles (11) repeatedly leached soil columns containing dinitramine and metabolites with 1.27 cm of water. From tests conducted between 25 and 45 days after treatment, he concluded that leaching does not readily take place.

Determination of leaching patterns by Anderson, Richards, and Whitworth (4) indicated that trifluralin, nitralin, and benefin leached

in varying patterns. Nitralin was leached very little while benefin was affected the most.

After a 3-year study, Willis, Rogers, and Southwick (86) found that the highest concentration of herbicide lost from soil due to drainage usually occurred during rainfall soon after application. The maximum loss of trifluralin during the season was 0.05%.

Parka and Worth (58) reviewed a report by the Fish and Wildlife Service that described trifluralin as one of the most toxic herbicides tested on fish. LC_{50} values ranging from 12 to 40 ppb were derived from static water fish tests and were believed to be unrealistic under field conditions. The properties of trifluralin, its unusually low solubility and high affinity to organic matter, make it difficult to move enough soil into water to arrive at a lethal concentration to fish.

In a comparative soil column study of 28 herbicides, Harris (32) assigned relative mobility factors. Monuron [3-(p-chlorophenyl)-1,1-dimethylurea] was defined as 1 with dipropalin assigned 0.5; trifluralin, 0.6; nitralin, 0.5 to 0.6; and benefin, 0.4 to 0.7. Benefin movement was not detected in Hagerstown silty clay loam soil.

Although nitralin did not leach in a clay soil, according to Palmer, Reeves, and Merkle (55), Smith, Berner, and Walter (74) found enough nitralin had moved into a loamy sand soil to maintain weed control when rainfall occurred within a day after application. Under sprinkler irrigation, small quantities of nitralin were found as deep as 15 to 20 cm. However, rainfall cannot be substituted for mechanical incorporation of trifluralin.

Gagnon and Hamilton (21) detected no leaching of butralin, dinitramine, nitralin, profluralin, and trifluralin during a 1-year period in which 145 cm of rainfall and irrigation water entered the sandy loam soil.

Diffusion may be a more important mode of transport than mass flow. Rahman and Ashford (65) found a slight redistribution of trifluralin occurring after 1 year in a clay loam soil. Oliver and Frans (54) suggested an upward movement due partly to volatilization. Although apparent diffusion coefficients for benefin and trifluralin were lower than for the other herbicides tested by Scott and Phillips (71), trifluralin diffusion increased as soil water content decreased. This contrasted to the behavior of the other compounds. The effect was attributed to substantial vapor phase movement.

Bode et al. (13, 14) studied trifluralin diffusion through Mexico silt loam soil. Bulk densities between 1.2 and 1.4 g/cm³ had similar magnitudes of vapor and solution diffusion. Below 1.2, vapor diffusion was a more important factor. Vapor diffusion was decreased about 50% for each 10% decrease in air-filled porosity. Diffusion was found to greatly increase with temperature.

Runoff is a mechanism of movement that could lead to contamination of surface waters. Helling (35) indicated that shallow incorporation of the herbicide after application reduces the likelihood of loss. Axe et al. (6) found 0.04 ppm the highest concentration of trifluralin in runoff water from a silty clay loam soil. From 41 ha, 1 ha-cm of runoff water would theoretically remove 0.36 kg of trifluralin. Bailey et al. (7) found the total loss of trifluralin from an upland Piedmont

watershed to be greater in the water phase than in sediment, but neither runoff nor leaching was a major process in decreasing the herbicide concentration during the growing season.

Volatilization

Bardsley, Savage, and Walker (10) and Savage and Barrentine (70) reported that most dinitroanilines should be incorporated into soil within a few hours of application to prevent major loss of herbicidal activity. Palmer et al. (55) recovered almost all of nitralin applied to soil immediately after application but only 24 to 70% of trifluralin could be recovered. They suggested that trifluralin had volatilized. Harper et al. (31) studied microclimate effects on trifluralin volatilization and found that high soil temperature and moisture generally enhanced volatilization losses. Even butralin, which is essentially nonvolatile at 50 C, will significantly volatilize in 22 hr in the presence of water, according to Bishop, Damiano, and McLane (12).

Analysis of trifluralin vapors above treated soils has confirmed that the greatest loss occurs from wet soils. Ketchersid, Bovey, and Merkle (39) found 50% volatilization of trifluralin in 24 hr in the laboratory. However, Swann and Behrens (81) found less than 5% in 12 hr, with very little loss thereafter. Volatilization loss was reduced four to ten times when trifluralin was applied in floodwater as compared to a sequence of spraying, incorporating, and flooding to bring the soil to the same moisture level as produced by direct flooding. Flooding apparently allowed the herbicide to penetrate soil aggregates. Such carriers as paraffin, reported by Weaver, Meyer, and Merkle (83), and

diesel oil, by Weaver, Meyer, and Merkle (82) have decreased trifluralin volatilization from moist soil. In laboratory experiments by Parr and Smith (61) trifluralin volatilization was nearly eliminated by maintaining water over the soil.

Bardsley et al. (10) and Swann and Behrens (81) reported trifluralin loss from soil was proportional to the concentration. Bardsley et al. also found the losses were greater when soil was saturated rather than at field capacity, presumably because more free water was available to be vaporized itself and to dissolve more trifluralin. Parochetti, Dec, and Burt (59) discovered that volatility of dinitroanilines decreased as soil moisture increased beyond field capacity. In sunlight, an increased loss followed an increase in soil temperature, as reported by Ketchersid et al. (39).

Spencer and Cliath (78) found that the vapor density of trifluralin in Gila silt loam soil increased as trifluralin concentration increased, reaching a saturated vapor density equivalent to trifluralin without soil at a soil water content of 19%. Vapor density was much reduced in drier soils and was inversely related to soil organic matter content. Trifluralin volatilized more rapidly when surface applied than when soil incorporated but the total volatilization was slight from dry soil. Trifluralin vapor density increased about five times for each 10° increase in temperature between 20 and 40 C. Field measurements by Leonard et al. (44) have shown maximum trifluralin concentration above the soil to occur between midnight and 8:00 a.m. This corresponds to the period of maximum soil water content in the top 1 cm of soil.

Maximum vapor loss in the field occurred on the first day after application.

Parochetti et al. (59) found no detectable volatilization of nitralin and oryzalin. Under the same conditions, 25% of trifluralin and 13% of benefin was lost as vapors (60).

Studies by Harvey (34) and Swann and Behrens (80) showed trifluralin vapors to be phytotoxic to plants and thereby affect herbicide effectiveness. Studies of volatilization are thus doubly important (35).

Photodecomposition

Wright and Warren (87) sprayed trifluralin as a thin film on glass and soil and exposed each to sunlight and an artificial light from a mercury vapor source. Changes in the absorption spectrum occurred within 2 hr of exposure. Marked alteration in absorbance and a decrease in the inhibitory effect on german millet [Setaria italica (L.) Beauv.] were observed after 4 to 6 hr of exposure. Photodecomposition also occurred on the soil surface but to a lesser degree.

Rieck et al. (67) found that losses of trifluralin from glass surfaces in growth chambers at 10, 21, 32, and 43 C were dependent on temperature. Nitralin loss was attributed to light absorption leading to the expectation that nitralin should be more affected by light than trifluralin.

Leitus and Crosby (43) reported on oxidative N-dealkylation, nitro-reduction, and cyclization involved with photodecomposition of trifluralin. The dealkylation may be a free radical oxidation by

atmospheric oxygen. Trifluralin was unstable in sunlight, especially in the presence of an organic solvent.

Crosby and Moilanen (16) stated that trifluralin underwent rapid vapor-phase photodecomposition in a lab photoreader to provide the dealkylated products, benzimidazoles, and nonvolatile polar products. These same products were found in air above trifluralin-treated soils.

Soderquist et al. (77) confirmed vapor phase photodecomposition of trifluralin in the laboratory and the field. Soil surface photolysis followed by volatilization was suggested to be the main route by which photoproducts reached the atmosphere.

Fluchloralin was examined in aqueous solution on soil and silica thin layer chromatographic plates by Nilles and Zabik (52). Degradation was rapid in sunlight. After 13 days only 16% remaining was the parent material and after 48 days 3% remained. On soil, fluchloralin was 20% degraded in simulated sunlight after 48 hr.

Newsom and Woods (51) found dinitramine degraded with a half life of 10 minutes in a 1 ppm aqueous solution in sunlight. It also degraded in natural waters and on sand.

Plimmer and Klingebiel (62) photodegraded butralin in sunlight to a dealkylated nitroso compound and minor products. It was less photodegraded than other dinitroanilines. This, with the low photosusceptibility found by Parochetti as reported by Helling (35) for penoxalin and butralin on soil, indicates that amino group monosubstituted dinitroanilines will photodegrade less rapidly than those that are disubstituted.

Removal by Plants

Probst et al. (64) reported that dinitroanilines are not readily translocated from soil to the upper portions of plants. Those detectable degradation products that may be observed frequently reflect the same residues observed in soil but to a much lesser degree. This premise is supported by the microradio autographic investigations of Strang and Rogers (79).

Golab et al. (27) grew carrots in soil containing ^{14}C -trifluoromethyl labeled trifluralin. The radioactivity in the roots was 0.65 ppm distributed as 69% in the peel and 10% at the approximate junction of the phloem and xylem. Trifluralin constituted 84% of the radioactivity in the carrot extract. It was not determined if the compounds found in the carrot root were the result of degradation in soil or the result of biological conversion by carrot tissue. A trace of trifluralin was found in the carrot tops.

Golab et al. (28) investigated the metabolism of ^{14}C -ring labeled benefin in peanut (Arachis hypogaea L.) plants. Similar degradation products were found in roots, hulls, and soil. In order, stems, leaves, and meats contained fewer products in lesser amounts. These differences suggest the absorption of benefin and its degradation products from soil and translocation in the plant rather than the absorption of benefin and its metabolism in plants.

After reviewing literature discussing the degradation of dinitroanilines in plants, Probst et al. (64) concluded that the extensive studies of trifluralin, benefin, nitralin, dinitramine, isopropalin, and oryzalin reveal that these herbicides and their

degradation products observed in soil do not accumulate in the edible portions of crops tolerant to these herbicides. The literature on these compounds supports the thesis that there is little translocation of parent or degradation compounds into the raw agricultural commodity, except for certain root crops and these crops incorporate only a minor portion of the available parent compounds.

Persistence in the Field

In general, states Helling (35), the dinitroaniline herbicides are moderately persistent in soils. Newsom and Mitchell (50) found dinitramine to be over 90% degraded in 3 to 4 months and profluralin 70 to 80% degraded in 6 months. Benefin gave 4 to 5 months weed control, and trifluralin 4 to 6 months as listed in the third edition of the Herbicide Handbook (85). The same reference described most dinitroanilines as degrading to nonphytotoxic levels within a growing season when soil conditions were moist and warm.

Parka and Tepe (57) found no evidence of trifluralin buildup or leaching in soils treated annually for 1 to 4 years and collected from 107 locations. Newsom and Mitchell (50) described similar conclusions for trifluralin, benefin, and nitralin after 5 years of treatment. Phytotoxic residues persisted, however, more than 15 months and only nitralin was undetected 30 months after the last herbicide application.

Persistence is increased at lowered temperatures according to Smith (73) and Horowitz, Hulin, and Blumenfeld (37). Increasing the depth of incorporation increases persistence (48, 54, 70).

Dinitroanilines normally persist for a shorter time in moist soils. Little butralin was lost in dry soil, but 4.5 kg/ha was inactivated in 6 months of moist soil, according to McLane, Fosse, and Whitendale (46). Gagnon and Hamilton (21) found no loss of seven dinitroanilines during the initial 4 months after application when the soil was cold and dry.

The effect of soil organic matter on persistence is unclear. Bardsley et al. (9) concluded that organic amendments prolonged trifluralin bioactivity. A field survey by Savage (69) discovered trifluralin residue levels were negatively correlated with organic matter content.

Analyses of 250 fields in the Mississippi delta conducted by Savage (69) showed a significant, inverse correlation between trifluralin and nitralin residue levels and soil pH. After modifying soil pH in the greenhouse, nitralin was the most persistent in an acid soil. Trifluralin was unaffected.

The role of microorganisms in the normal field dissipation of trifluralin is still tenuous (35).

A comparative persistence study by Palmer et al. (55) found trifluralin persisting longer in a Texas clay soil than nitralin. Gagnon and Hamilton (21) concluded that both profluralin and trifluralin were more persistent in Arizona than dinitramine. Dinitramine was, in turn, more persistent than butralin and nitralin.

Weed control declined from 95% to 20% when incorporation of nitralin was delayed 15 days stated Ogle, Stepp, and Loadholt (53). Smith and Wiese (75) found trifluralin to require incorporation within

24 hr to avoid herbicide loss. Dunster (17) decided butralin could be delayed 48 hr, although measurable loss of weed control occurred with a delay of only 2 hr. Savage and Barrentine (70) concluded profluralin, one of the more readily volatilized dinitroanilines, should be incorporated within 4 hr. Helling (35) summarized that incorporation, usually by mechanical tilling, is a practical and necessary means of controlling persistence.

Herbicide Bioassays

According to Santelmann (68), an herbicide bioassay is a quantitative measurement of the biologically active concentration of an herbicide. He indicated qualitative analyses are possible although difficult. Chemical and physical assays are other methods used, but, according to Santelmann, the bioassay has the added assurance that the phytotoxic activity of the herbicide molecule is what is being measured. It is not generally necessary to extract the herbicide from the substrate, thus circumventing the problems involved with extraction procedures that are often needed for chemical assays. Bioassays are more economical, less difficult, and do not require expensive equipment. Many bioassays are highly sensitive and accurate determinations are possible with some herbicides at concentrations as low as .00075 ppm.

Problems listed by Santelmann are several. First, plant growth is directly influenced by ambient environmental conditions such as light intensity, temperature, water level and method of delivery, and humidity. Steps should be taken to minimize these factors, checks should be used, and the conditions monitored. Second, there is a

possibility of individual plant variation within the species of indicator plant. Bioassay procedures allowing selection for individual plant uniformity increase reproducibility and reliability. Third, a time time requirement beginning with the sampling procedure and terminating with the final analysis of the bioassay may be sufficiently long to allow additional herbicide degradation which can enter additional error into the assay. Fourth, soils may tie up some of the herbicide present. No solutions were offered to minimize the final two problems.

Bioassay species should be sensitive enough to detect small amounts of herbicide. They should exhibit a gradual increase in susceptibility with increasing herbicide concentration. Healthy seedlings must be produced when not in presence of the herbicide and the species should be specific for the herbicide being tested.

Several species, concluded Santelmann, have been used as indicator species for dinitroaniline herbicides, including barley (Hordeum vulgare L.), cucumbers (Cucumis sativus L.), and sorghum.

MATERIALS AND METHODS

The data and conclusions extended in this thesis are based on field research conducted between June, 1976, and February, 1977. The experimental farmland and facilities are located in Tucson, Arizona, and belong to The University of Arizona.

At the Casa Grande Highway Experimental Farm, two borders of flood irrigated farmland were each subdivided into four experimental blocks. Each block contained ten field plots 4 m in width and 7 m in length. These plots were situated end to end, five plots in depth and two plots wide in the blocks. The borders were 175 m long. At each end of the two borders, 15 m were left untreated to serve as a buffer zone against irrigation irregularities, especially uneven water distribution at the upper end and excessive flooding at the lower end. Chemical treatments were assigned to the plots using a randomized complete block design. Treatments were replicated four times in each border.

As the objective of the experiment was to determine the soil persistence of nine dinitroaniline herbicides under fallow and irrigated conditions, one border was placed on a cotton irrigation schedule while the other was fallow.

During the test, all treatments received $2911 \text{ m}^3/\text{ha}$ of rainfall and the irrigated treatments received $5495 \text{ m}^3/\text{ha}$ of water from basin irrigations between the months of June through September. A total of $8406 \text{ m}^3/\text{ha}$ of combined rainfall and irrigation water were received on the irrigated border and a total of $2911 \text{ m}^3/\text{ha}$ on the fallow. Water

volumes received on the borders are tabulated on a monthly basis in Table 1.

Table 1. Rainfall received on the fallow border and rainfall and irrigation moisture received on the irrigated border.

Interval after treatment (months)	Fallow border (m^3/ha)	Irrigated border (m^3/ha)
0 to 1	127	2325
1 to 2	845	845
2 to 3	124	2322
3 to 4	944	2043
4 to 5	145	145
5 to 6	124	124
6 to 7	0	0
7 to 8	602	602
Total	2911	8406

The soil in each border was 60% sand, 24% silt, and 16% clay with an organic matter content of 0.64%.

Herbicides were hand applied on May 31, 1976, using a knapsack-type sprayer equipped with a K5 flooding nozzle tip. Treatments were applied in two directions to insure complete soil coverage. The herbicides were incorporated by disking to a depth of 10 cm immediately after application.

Butralin and oryzalin were applied at 2 kg/ha and dinitramine, ethalfluralin, fluchloralin, pendimethalin, profluralin, trifluralin, and prodiamine were applied at 1 kg/ha.

A biological assay procedure with sorghum as an indicator plant was used during the entire experiment and data were obtained from two parameters: shoot height, and shoot weight.

Soil in the plots was sampled 1 day prior to the herbicide application and bioassayed to determine the soil uniformity. Samples subsequent to application were taken at 1 day and at each month thereafter until the eighth month. Soil samples were obtained from four locations within each plot. A metal can 6.5 cm wide and 7 cm deep with a volume of 232 ml was used to obtain soil samples.

In the greenhouse, soil was sifted through a 0.63 cm hardware cloth to eliminate larger soil aggregates and to thoroughly mix the soil from within the sample. Four hundred ml of soil were placed in a 600 ml plastic container with perforations in the bottom to allow drainage of excess water and to allow access of irrigation water. One hundred sixty milliliters of water were then applied to the soil surface without disturbing the soil surface and allowed to percolate through the soil.

Twenty RS-610 sorghum seed were placed on the soil surface at least 1.3 cm from the edge of the container to insure roots of seedlings would not come in contact with the edge of the container.

One hundred milliliters of dry soil were added from the sample to cover the moist soil and seeds. This method of planting avoided forming a crust on the soil surface which would interfere with the emergence of the seedlings. Containers were placed on flat baking trays as close together as possible, to minimize possible variations due to temperature and wind current changes. Containers were irrigated by capillary action from water placed in the baking pans, and periodically the pans were rotated on the greenhouse bench. The light period varied with day length and the greenhouse was heated below 15 C and cooled above 30 C.

Between 7 and 12 days after planting, the number of coleoptiles above the soil surface were counted. Then, the seedlings were thinned to ten per container where necessary.

The growing period was a function of day length ranging from 13 to 18 days. When the average shoot heights in the check container were between 15 and 18 cm, the average shoot height in all containers was noted and the seedlings prepared to determine shoot weight. All seedlings in the container were carefully cut at soil level with a razor blade, placed into plastic sandwich bags of predetermined weight, and weighed.

The data on shoot weight and height were submitted to an analysis of variance and the means separated by Duncan's multiple range test.

RESULTS AND DISCUSSION

Data presented is in the form of shoot weight and height of sorghum seedlings. Grown as indicator plants in nine biological assays, these seedlings illustrate relative herbicidal persistence. Tables 2 and 3 list the treatment means of the above parameters in the fallow border. Similar data from the irrigated border are presented in Tables 4 and 5.

During the test, a total of 5495 m³/ha more water was received on the irrigated border than on the fallow border. No other variable was incorporated into the test.

No significant reduction of shoot weight or height occurred in soil from the fallow border during the pretreatment bioassay. Only soil from the plots designated for fluchloralin treatment in the irrigated border significantly reduced seedling growth prior to herbicide application. Treatment means calculated by averaging the four treatment values from the replications within the border revealed differences of 0.05 gm and 2.25 gm respectively between the maximum mean weight and height values of the check plots and the minimum mean values of the fluchloralin treated plots. The differences were judged to be minor and the soil of each border was considered uniform.

Soil sampled from the plots 1 day after herbicide application significantly reduced both shoot weight and height of seedlings. Symptoms of inhibition expressed by the indicator plants included severe stunting of shoot and root growth, reduction in secondary root number,

Table 2. Shoot weight of sorghum grown in soil from the fallow border at 9 sampling dates.

Treatment	Sampling dates ^a								
	Prespray (g)	0 months (g)	1 months (g)	2 months (g)	3 months (g)	4 months (g)	5 months (g)	6 months (g)	8 months (g)
Check	.20 a	.27 a	.30 a	.24 a	.32 a	.29 d	.23 a	.16 a	.26 a
Butralin	.17 a	.11 b	.16 bc	.18 bc	.25 bc	.27 ab	.17 bcd	.15 ab	.24 ab
Dinitramine	.20 a	.05 cd	.10 cde	.19 b	.29 ab	.30 a	.22 ab	.16 ab	.26 a
Ethalfuralin	.19 a	.05 cd	.07 de	.16 bcde	.34 bc	.24 abc	.18 abc	.14 abc	.24 ab
Fluchloralin	.19 a	.08 bc	.18 b	.17 bcd	.22 cd	.22 bcd	.16 cd	.13 abcd	.22 abc
Oryzalin	.19 a	.02 d	.06 de	.12 f	.15 ef	.17 d	.12 cde	.10 abcde	.19 c
Pendimethalin	.18 a	.04 cd	.10 cde	.13 ef	.17 de	.18 cd	.18 de	.8 cde	.18 c
Prodiamine	.19 a	.03 d	.04 e	.07 g	.10 f	.08 e	.07 e	.03 e	.08 d
Profluralin	.19 a	.07 bcd	.14 bcd	.13 cdef	.19 de	.19 cd	.16 cd	.09 bcde	.22 abc
Trifluralin	.20 a	.05 cd	.12 bcde	.14 def	.15 ef	.16 d	.12 cde	.07 de	.20 bc

^aValues within a column followed by the same letter are not significantly different at the 5% level of Duncan's Multiple Range Test.

Table 3. Shoot height of sorghum grown in soil from the fallow border at 9 sampling dates.

Treatment	Sampling date ^a								
	Pre-spray (cm)	0 months (cm)	1 months (cm)	2 months (cm)	3 months (cm)	4 months (cm)	5 months (cm)	6 months (cm)	7 months (cm)
Check	13.5 a	18.0 a	18.0 a	15.3 a	18.5 a	15.8 a	16.0 a	11.8 a	15.0 a
Butralin	13.0 a	7.3 B	12.3 B	12.0 bc	15.8 ab	15.3 ab	12.8 bc	12.0 ab	14.5 ab
Dinitramine	13.3 a	4.0 cd	5.8 c	12.8 b	16.8 ab	16.3 a	14.8 ab	12.8 a	15.8 a
Ethalfuralin	14.0 a	3.0 cde	4.8 c	9.5 cde	14.8 bc	14.5 ab	13.0 bc	11.8 ab	14.0 ab
Fluchloralin	13.5 a	5.5 bc	11.8 b	11.8 bcd	14.8 bc	13.3 bc	12.3 bc	9.8 abc	13.5 abc
Oryzalin	13.3 a	2.3 de	4.5 c	7.0 e	9.8 de	10.0 d	9.0 d	8.3 bcd	12.0 cd
Pendimethalin	13.8 a	2.3 de	6.0 c	7.5 e	10.8 d	10.8 d	8.8 de	7.0 cd	11.0 d
Prodiamine	14.3 a	1.0 e	3.3 c	4.0 f	7.3 e	6.5 e	6.3 e	4.3 d	6.3 e
Profluralin	13.3 a	4.5 bcd	8.5 bc	9.3 de	12.0 cd	11.5 cd	10.5 cd	7.0 cd	12.5 bcd
Trifluralin	13.8 a	3.0 cde	6.5 c	8.8 e	10.0 e	11.0 cd	8.5 de	6.3 cd	12.3 bcd

^a Values within a column followed by the same letter are not significantly different at the 5% level of Duncan's Multiple Range Test.

Table 4. Shoot weight of sorghum grown in soil from the irrigated border at 9 sampling dates.

Treatment	Sampling dates ^a								
	Prespray (g)	0 months (g)	1 months (g)	2 months (g)	3 months (g)	4 months (g)	5 months (g)	6 months (g)	8 months (g)
Check	.22 a	.29 a	.26 a	.19 a	.24 a	.19 ab	.18 a	.23 a	.26 a
Butralin	.20 ab	.12 b	.21 abc	.18 ab	.25 a	.17 ab	.15 a	.19 a	.27 a
Dinitramine	.19 ab	.04 cd	.21 ab	.18 ab	.26 a	.19 ab	.18 a	.22 a	.25 a
Ethalfuralin	.21 ab	.07 cd	.13 bcd	.15 abc	.24 a	.20 a	.16 a	.19 a	.24 a
Fluchloralin	.17 b	.07 cd	.17 bcd	.17 ab	.23 a	.19 ab	.17 a	.22 a	.25 a
Oryzalin	.19 ab	.04 cd	.12 cd	.18 ab	.26 a	.19 ab	.17 a	.22 a	.26 a
Pendimethalin	.19 ab	.08 bc	.12 d	.16 abc	.21 ab	.18 ab	.18 a	.18 a	.25 a
Prodiamine	.20 ab	.03 d	.13 bcd	.11 c	.13 b	.11 c	.10 b	.09 b	.14 b
Profluralin	.18 ab	.12 b	.18 bcd	.14 abc	.23 a	.15 b	.16 a	.19 a	.24 a
Trifluralin	.20 ab	.07 cd	.15 bcd	.13 bc	.25 a	.18 ab	.19 a	.19 a	.24 a

^aValues within a column followed by the same letter are not significantly different at the 5% level of Duncan's Multiple Range Test.

Table 5. Shoot height of sorghum grown in soil from the irrigated border at 9 sampling dates.

Treatment	Sampling dates ^a								
	Prespray (cm)	0 months (cm)	1 months (cm)	2 months (cm)	3 months (cm)	4 months (cm)	5 months (cm)	6 months (cm)	8 months (cm)
Check	14.5 a	17.8 a	18.3 a	14.8 a	15.5 a	15.0 a	14.5 a	15.5 a	15.3 a
Butralin	13.8 abc	8.5 b	15.8 ab	12.5 abc	16.3 a	14.3 a	12.0 ab	14.5 a	15.3 a
Dinitramine	13.3 abc	2.3 c	14.8 ab	13.5 ab	16.0 a	14.8 a	14.0 a	15.0 a	15.0 a
Ethalfuralin	13.8 abc	5.0 c	11.8 bc	12.0 abc	15.3 a	14.3 a	13.5 a	13.8 a	14.8 a
Fluchloralin	12.3 c	5.0 c	11.3 bc	10.5 bc	15.3 a	14.5 a	13.8 a	14.8 a	15.0 a
Oryzalin	13.8 abc	2.3 c	6.8 c	13.0 abc	16.5 a	14.0 a	13.8 a	16.0 a	14.5 a
Pendimethalin	13.8 abc	2.8 c	8.0 c	11.3 bc	13.5 a	13.5 a	12.0 ab	13.0 a	14.0 a
Prodiamine	14.3 ab	2.5 c	7.0 c	7.0 d	9.0 b	8.8 b	8.8 b	8.3 b	9.8 b
Profluralin	13.8 abc	7.8 b	12.5 abc	9.8 cd	15.5 a	13.5 a	12.8 a	12.3 a	14.5 a
Trifluralin	14.3 ab	4.5 c	12.8 abc	10.0 cd	15.3 a	13.8 a	13.0 a	14.3 a	15.0 a

^aValues within a column followed by the same letter are not significantly different at the 5% level of Duncan's Multiple Range Test.

and dark red coloration of leaves. These symptoms were most pronounced during the first bioassays conducted. In later bioassays, symptoms became less pronounced and finally disappeared.

The growth of seedlings in soil from irrigated plots of butralin and dinitramine could not be significantly separated from growth of seedlings in check plots by weight after 1 month. After 2 months, trifluralin and prodiamine alone reduced seedling growth and at 3 months only prodiamine continued to show activity.

With few exceptions, height data from the irrigated border provided similar results. The growth of seedlings influenced by butralin, dinitramine, trifluralin, and profluralin could not be separated from the growth of sorghum in the check plots at 1 month. At 2 months, butralin, dinitramine, ethalfluralin, and oryzalin did not reduce sorghum growth. However, at the third month, prodiamine alone restricted sorghum growth. The failure of trifluralin and profluralin to restrict growth during the first month bioassay was not necessarily the result of herbicide decomposition, especially in light of the second month results. More likely, the variation was due to sampling error.

In the fallow border all treatments significantly reduced sorghum growth through the second month; however, fluchloralin, butralin, dinitramine, and ethalfluralin inhibited growth less than the other treatments.

After 3 months, seedlings grown in soil treated with dinitramine could not be distinguished by weight or height from seedlings grown in soil from the check plots. In addition, height data alone indicated

that butralin influenced seedlings were not significantly different from check seedlings.

The fourth month bioassay revealed three treatments no longer restricting sorghum growth. Ethalfluralin, butralin, and dinitramine treated soil failed to significantly reduce sorghum weight and height.

After the sixth month, butralin, dinitramine, ethalfluralin, and fluchloralin treatments did not affect sorghum growth. Oryzalin treated soil reduced sorghum shoot height but not weight.

The last bioassay was performed at the end of the eighth month. In both the irrigated and fallow border, prodiamine continued to show more biological activity than any other dinitroaniline tested. In the fallow border, trifluralin, oryzalin, and pendimethalin reduced both sorghum height and weight. Profluralin reduced only shoot height. Butralin, dinitramine, ethalfluralin, and fluchloralin did not affect sorghum growth.

Dinitramine injury to the indicator plants could not be significantly measured in the fallow border after 3 months and after 1 month in the irrigated border. It was the least persistent dinitroaniline tested.

Butralin persistence was similar to that of dinitramine. In the fallow border, butralin no longer affected sorghum growth after 3 months and in the irrigated border after 1 month. However, butralin was more closely aligned statistically with the more persistent herbicides than dinitramine and was slightly more persistent than dinitramine.

Ethalfluralin and fluchloralin reduced sorghum growth through the sixth month in the fallow plots. Ethalfluralin did not inhibit

sorghum growth in the irrigated plots after 1 month, but fluchloralin affected sorghum through the third month.

Oryzalin, pendimethalin, profluralin, and trifluralin demonstrated similar persistence patterns. Each reduced sorghum growth through the eighth month in the fallow border. They were not detected in the irrigated border after the third month.

Prodiamine was the most persistent dinitroaniline. Active through the eighth month in both the fallow and irrigated border, it was different from all other herbicides tested.

A comparison has been drawn in Figure 1 of the relative persistence patterns of dinitramine, the least persistent; trifluralin, intermediately persistent; and prodiamine, the most persistent.

Figure 1 shows the persistence pattern of dinitramine and prodiamine in the irrigated border. Dinitramine inhibited growth to 15% of the check while prodiamine decreased growth to 14% in soil sampled 1 day following herbicide application. After 1 month, dinitramine lowered sorghum growth to 80% of the check. Prodiamine reduced growth to 38%. At 3 months, dinitramine was 103% of the check and prodiamine was 58%. After 8 months, prodiamine was still inhibiting growth to 63%.

Trifluralin persistence as shown in Figure 1 was similar to the pattern of dinitramine, except that trifluralin was intermediate between dinitramine and prodiamine and persisted 2 months longer than dinitramine, reaching 98% of the check growth at 3 months.

Studies similar to this have presented varied results. Probst et al. (63) and Axe, Mathers, and Wiese (6) found trifluralin residues of only 15% after 2 months and 14% after 3 months, respectively. Smith

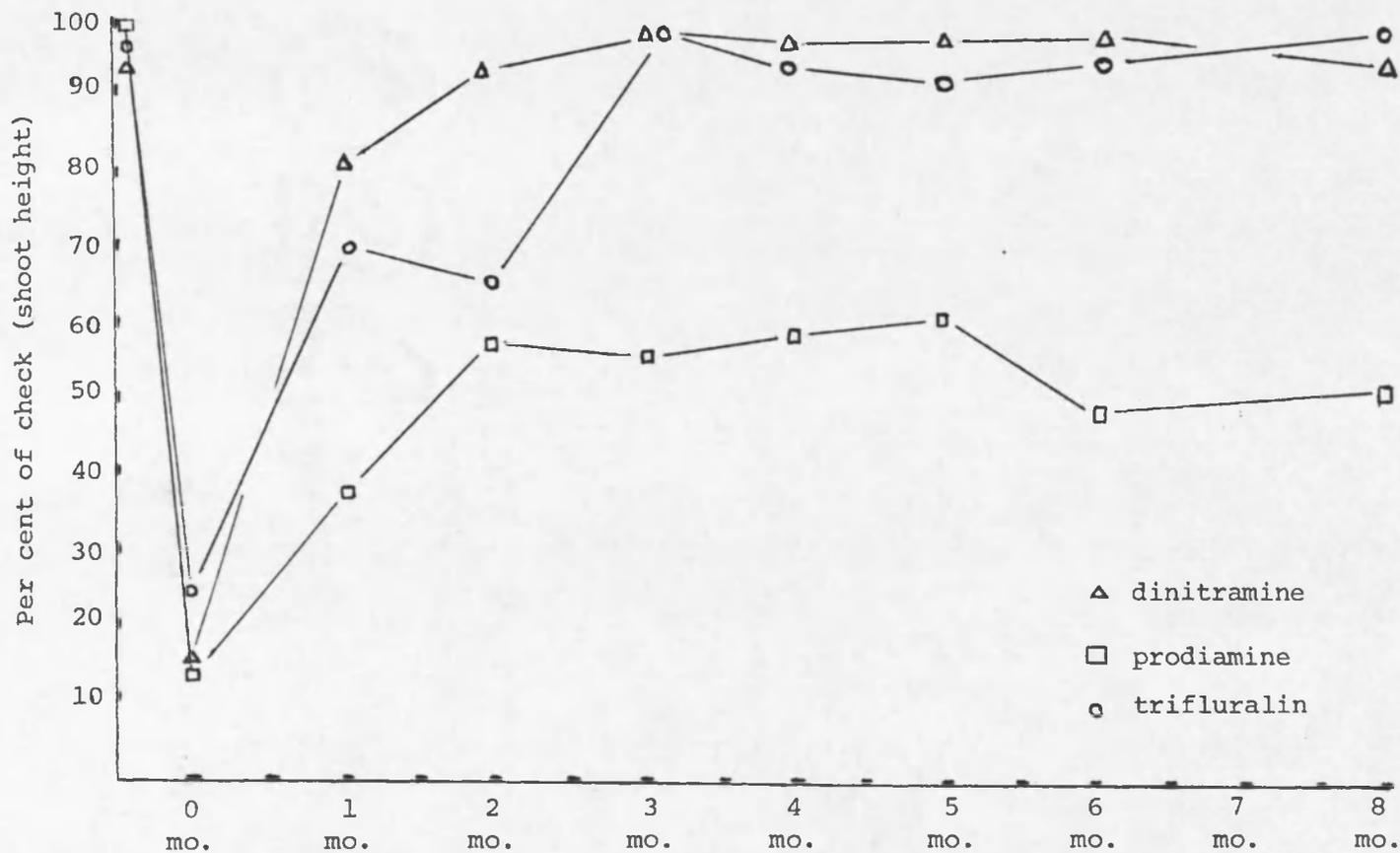


Figure 1. Shoot height of sorghum expressed as per cent of check grown in soil treated with dinitramine, prodiamine, and trifluralin, in the irrigated border.

(72) found only 10 to 20% of trifluralin in soil after 5 months. Rahman and Ashford (65) tested trifluralin and dinitramine treated soils by bioassay to determine field persistence. Residues phytotoxic to the indicator plants persisted between October and May, but declined more rapidly thereafter. In Texas, Menges and Hubbard (47) discovered the half-life of trifluralin to be 3 weeks and no phytotoxicity remained by 7 months. Horowitz et al. (37) and Smith (73) found increased dinitroaniline persistence at lower temperatures. In dry soil, according to McLane et al. (46), little butralin was lost but 4.5 kg/ha was inactivated in 6 months in moist soil. Gagnon and Hamilton (21) detected no loss of seven dinitroanilines during the initial 4 months after application when the soil was cold and dry.

The present study found the relative persistence of eight dinitroanilines to be 3 months or less under irrigated conditions and hot temperatures. Gagnon and Hamilton (21) applied herbicides in October during a cool, dry season. As long as the climate remained cool and dry, little loss of herbicide was noted. However, as temperature and moisture increased, herbicide persistence decreased. Similar results were reported by Rahman and Ashford (65), Horowitz et al. (37), and Smith (73).

Moisture did not change the relative pattern of herbicide disappearance; however, it did influence the rate of persistence. Between irrigated and fallow conditions, moisture increased the rate of degradation as much as 2 months. This observation parallels the results of a similar study conducted by Gagnon (20). Temperature, too, appears to play an important role in the length of herbicide persistence. This

study agrees well with other studies similar to it and lends strength to the understanding of the effect of moisture and temperature on dinitroaniline persistence.

SUMMARY

The purpose of the study was to determine the effect of moisture on the persistence of nine dinitroaniline herbicides over an 8-month period.

Nine herbicides, butralin, dinitramine, ethalfluralin, fluchloralin, oryzalin, pendimethalin, prodiamine, profluralin, and trifluralin were applied to two borders of farmland. One border was irrigated by a normal cotton irrigation schedule. The other border was held fallow. A randomized complete block design was employed. There were four replications per border.

Soil from the plots was removed prior to herbicide application, 1 day after treatment, and each month for 8 months. Samples were subjected to a sorghum bioassay in the greenhouse. Shoot height and weight of seedlings grown in treated soils compared with the seedlings grown in soil from the check plots measured herbicide persistence.

Prodiamine was the most persistent herbicide and dinitramine persisted least. Butralin, ethalfluralin, and fluchloralin persisted longer than dinitramine but less than oryzalin, pendimethalin, profluralin, and trifluralin.

Moisture levels in the soil influenced dinitroaniline persistence. Herbicides in the fallow border remained in the soil longer than those in the fallow. Comparison of earlier studies with the present revealed that temperature can play an important role in determining the length of dinitroaniline persistence.

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