CONTROLLED-RELEASE PREEMERGENCE HERBICIDE FORMULATIONS FOR ANNUAL GRASS CONTROL IN KENTUCKY BLUEGRASS TURF

BY

DAVID ROBERT CHALMERS

B.S., Michigan State University, 1974
M.S., Virginia Polytechnic Institute and State University, 1978

THESIS

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WE HEREBY RECOMMEND THAT THE THESIS BY

DAVID ROBERT CHALMERS

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Chairman

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February 1, 1983
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Walter Splitttoser
Departmental Representative
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I. INTRODUCTION

Commercial formulations of preemergence herbicides are applied in an available form. Normal dosage concentrations are above that needed to control germinating annual grasses (the threshold concentration for efficacy [TCe]) but below a level that causes turf injury (the threshold concentration for phytotoxicity [TCP]). The time period which the herbicide concentration remains above the TCe is termed the effective period of control (EPC). The EPC for a specific herbicide will depend on its biological activity. Biologically active herbicides, applied using conventional methods, can be depleted through volatilization, leaching, sorption by organic matter, adsorption by plants and chemical, photochemical and microbial degradation (25, 27). Reductions in herbicide activity with time decrease the EPC. Using a preemergence herbicide can necessitate either the use of repeat applications before the initial application is reduced to concentrations below the TCe or the application of the herbicide at elevated rates to compensate for depletion. These practices usually result in increased labor costs from the former, while increasing the application rate may cause turf injury.

An alternate method of extending the herbicide activity is to regulate the bioavailability of the active ingredient through the use of controlled-release preemergence herbicide formulations. Lewis and Cowsar (31) defined a controlled-release formulation as a combination of biologically active agent and an excipient, usually a polymer, arranged to allow the delivery of the agent to the target at controlled
rates over a specific period. Controlling the bioavailability also controls, to some extent, those avenues through which biologically active compounds can lose their effectiveness. Controlled-release formulations therefore have the potential of reducing the phytotoxic effects of marginally safe materials while eliminating the need for repeat applications of short-lived compounds.

Research was conducted to evaluate the performance of various preemergence herbicide formulations of two categories of controlled-release materials (methanol activated sludge: dialdehyde starch and starch xanthide) for potential use in annual grass control in turfgrass sites.
II. LITERATURE REVIEW

Preemergence Herbicides: Control in Turfgrass Sites

Preemergence herbicides are applied to established turf to control annual grassy weeds such as crabgrass (*Digitaria* sp.), goosegrass (*Eleusine indica* (L.) Gaertn.) and annual bluegrass (*Poa annua* (L)). These weeds are best controlled through the use of preemergence herbicide applications prior to the anticipated period of weed seed germination. The extent of control depends on the activity of the herbicide for a specific weed as well as how long the compound maintains herbicidal activity. Crabgrass is a summer annual and germinates during the spring of the year. Peters and Dunn (36) reported large crabgrass (*Digitaria sanguinalis* (L.) Scop.) can germinate under Connecticut conditions when average temperatures for the two week period prior to germination ranged from 12.2 to 13.1°C. Goosegrass will characteristically begin to germinate in mid-spring to mid-summer depending upon location. However, annual bluegrass is predominantly thought of as a winter annual in the United States and germinates in the fall of the year. It is a summer weed in Northern Europe.

In situations where crabgrass, goosegrass, and annual bluegrass are all problems, single yearly applications of preemergence herbicides are ineffective in controlling all three due to the inability of available preemergence herbicides to persist long enough to account for the different periods of germination. Bingham and Shaver (2) evaluated the effect of preemergence herbicides, applied in April or
May for crabgrass control and in June for goosegrass control on the subsequent control of fall infestations of annual bluegrass. Oxadiazon [2-tert-butyl-4(2,4-dicloro-5-isopropoxyphenyl)-Δ^2-1,3,4-oxadiazolin-5-one] applied in August completely controlled annual bluegrass but was ineffective when the last treatment occurred in June. Butralin [4-(1,1-dimethylethyl)-N-(1-methylpropyl)-2,6-dinitrobenzenamide], benefin (N-butyl-N-ethyl-α,α,α-triflouro-2,6-dinitro-p-toluidine), bensulide [0,0-diisopropyl phosphorodithioate S-ester with N-(2-mercaptoethyl) benzenesulfonimide] and DCPA (dimethyl tetrachloroterephthalate) showed little if any increase in annual bluegrass control over a September only application from April + June + September or June + September applications, indicating minimal herbicide carry-over from earlier treatments. In a related study Johnson (23) found DCPA, profluralin [N-(cyclopropyl-methyl)-α,α,α-triflouro-2,6-dinitro-N-propyl-p-toluidine], benefin, prosulfalin (N-[[4-(dipropylamino)-3,5-dinitrophenyl]sulfonyl]-S,S-dimethylsulfylimine) and napropamide treatments applied during the previous spring and summer to be ineffective in controlling winter annuals.

Preemergence herbicide effectiveness in controlling annual grassy weeds will vary according to herbicide, rate of application, formulation and application timing. Johnson (22) compared DCPA, oxadiazon, butralin, terbutol (2,6,di-tert-butyl-p-tolyl methylcarbamate) and benefin at three Georgia locations using four application dates (mid-February, March, April or May). Full season control (FSC) of large crabgrass varied with location, herbicide and application date. Benefin or DCPA did not provide FSC at one site while only benefin was able to
produce FSC from April applications at another location. Control
differences were credited to soil type and temperature variations
that differed with each experimental site. When the same herbicides
were applied in the same manner for goosegrass control only the
oxadiazon and butralin treatments were able to provide FSC.

Herbicide performance as it relates to application timing has
also been reported under Rhode Island conditions (19). May appli-
cations of benefin and siduron (1-(2-methylcyclohexyl)-3-phenyl urea)
were found to increase the control of smooth crabgrass (Digitaria
ischaemum (Schreb.) Muhl.) when compared to March applications. The inves-
tigator suggested that the results indicate a short residual activity
for these materials. Therefore, application timing of relatively
short-lived preemergence herbicides is important for effective weed
control. Coville and Jagschitz (8) reported siduron and benefin to
be less effective than bensulide, butralin, DCPA, napropamide, oxa-
diazon, and prosulfalin in smooth crabgrass control. When the same
materials were tested for goosegrass control they ranked as follows
(greatest to least in control): butralin, DCPA, and oxadiazon > pro-
sulfalin > benefin, bensulide, and siduron. A similar study (51)
again reported benefin to provide poorer smooth crabgrass control
than did bensulide, butralin, DCPA, oxadiazon, prosulfalin and siduron.

Watschke et al. (57) compared April applications of eight pre-
emergence herbicides for smooth crabgrass control under Pennsylvania
conditions. Benefin was reported unable to provide acceptable (85%)
control in either Kentucky bluegrass (Poa pratensis (L.)) or red
fescue (Festuca rubra (L.)) turfs. However, increasing benefin
application rates from 2.24 kg/ha to 3.36 kg/ha increased control from 66 to 77% in Kentucky bluegrass and 77 to 90% in red fescue. These results indicate that the ineffectiveness of benefin in controlling crabgrass can be mediated by increased application rates.

Similar herbicide variability in controlling crabgrass in Kentucky bluegrass and red fescue turfs has been reported by Watschke et al. (56). Acceptable control with DCPA, butralin, and prosulfalin in both Kentucky bluegrass and red fescue turfs was obtained while napropamide only controlled crabgrass in Kentucky bluegrass.

The use of split applications has also been shown to have potential in increasing preemergence herbicide performance. Hall (14) used split applications of oxadiazon, butralin, and benefin to increase the control of goosegrass populations in Maryland, over single applications of each herbicide. Watschke et al. (55) reported split applications of prosulfalin (1.68 + 1.68 kg/ha) and DCPA (8.4 + 5.6 kg/ha) applied one month apart (May + June) to control smooth crabgrass as well as single applications on both Kentucky bluegrass and red fescue turf. Split application of siduron (8.96 + 6.72 kg/ha) provided control equal to that of its single application in red fescue but not in Kentucky bluegrass.

Preemergence Herbicides: Turfgrass Injury

Factors that can affect weed control (i.e., herbicide, application rate, formulation, application timing, and turfgrass susceptibility) can also have an effect on the severity of turfgrass injury sustained from preemergence herbicide applications.
Turgeon et al. (53) evaluated repeated annual applications of seven preemergence herbicides over an eight year period for their influence on clipping yield, root growth, thatch accumulation, and carbohydrate reserves of 'Merion' and 'Kenblue' Kentucky bluegrass and 'Pennlawn' red fescue stands. Bandane (polychlorodicyclo-pentadiene) applications acted to decrease turf quality, inhibit rooting, and increase susceptibility to stripe smut (Ustilago striiformis West. Niesel). Siduron, terbutol and bensulide reduced clipping yields in 'Pennlawn' red fescue while siduron and terbutol were also reported to reduce 'Kenblue' Kentucky bluegrass root growth. Thatch accumulation was less in benefin treated 'Merion' Kentucky bluegrass, bandane, benefin, bensulide and terbutol treated 'Kenblue' Kentucky bluegrass and in bandane, calcium arsenate, and terbutol treated 'Pennlawn' red fescue. Throughout the study the injurious herbicidal effects were found to vary from year to year with the most severe effects in turfgrass quality being observed during periods of summer drought and high temperature stress.

Gaskin (12) reported DCPA, trifluralin (α,α,α-triflouro-2,6-dinitro-N,N-dipropyl-p-toluidine) and bandane acted to reduce rhizome number, and the length and number of 'Merion' Kentucky bluegrass tillers. The lateral growth of 'A-20' Kentucky bluegrass plugs was also severely reduced from field applications of benefin and bensulide (48). However calcium arsenate and DCPA did not inhibit 'A-20' plug establishment.

Smith and Callahan (47) produced reductions in the rerooting of Kentucky bluegrass sod plugs when transplanted to 10 month old soil
residues and soils freshly treated with simazine [2-chloro-4,6-bis (ethylamino)-s-triazine] bensulide, terbutol, trifluralin, and atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine).

Differential turfgrass tolerance to preemergence herbicides can dramatically influence the relative competitive ability of individual grass species in a mixed turfgrass stand. Klingman and Murray (30) reported a population shift in the composition of a Kentucky bluegrass-red fescue stand that was apparently caused by preemergence herbicide applications. In test plots treated with benefin, butralin, DCPA, and profluralin there was shift in the amount of Kentucky bluegrass in the stand from an initial average of 3% to 30 to 45% following three consecutive years treatment. Watschke et al. (56) found napropamide injury most severe on creeping red fescue turf at high rates (4.48 kg/ha) and the early application date (March 21 when compared to April 28). Other results included greater injury from DCPA applications to red fescue than Kentucky bluegrass while prosulfalin produced greater injury to Kentucky bluegrass than red fescue. Coats et al. (6) studied the effect of spring applications of benefin and DCPA on cool season grasses overseeded into bermudagrass (Cynodon dactylon (L.) Pers. 'Tifdwarf') and maintained as a putting green. Results showed rough bluegrass (Poa trivialis L. 'Danish Common') and Italian ryegrass (Lolium multiflorum Lam. 'Gulf') to be injured more by benefin and DCPA than were creeping bentgrass (Agrostis palustris Hud. 'Pencross'), 'Dawson' red fescue or perennial ryegrass (Lolium perenne L. 'Medalist II').
The type of preemergence herbicide formulation used has also been reported to influence turf injury (8). This study, conducted in Rhode Island, showed granular formulations of DCPA injured a predominantly red fescue turf more than did the sprayable formulations tested.

The timing of preemergence herbicide application is also important. Torello and Jagschitz (51) found March applications of benefin to injure a red fescue turf greater than May applications while the reverse was true for oxadiazon. Watschke et al. (56) found naproamide injury to a red fescue turf to be greater from March rather than April applications.

Increasing herbicide application rates in an effort to increase control can also result in increased turf injury as was shown by Watschke et al. (57). Increasing benefin rates from 2.24 to 3.36 kg/ha caused a subsequent increase in injury to red fescue turf while Kentucky bluegrass remained unaffected.

Where injury is likely from either the use of marginally safe compounds or having a slightly susceptible turfgrass species some benefit may be derived from applying reduced rates of the preemergence herbicide in two or three split applications. This technique was used (57) in a Pennsylvania study which compared single and split applications of prosulfalin, DCPA, and siduron with single applications of bensulide, benefin, and butralin. None of the herbicides were observed to injure Kentucky bluegrass. Benefin and DCPA and butralin were found to injure red fescue. However, injury was reduced when DCPA was applied in split applications (8.4 to 5.6 kg/ha) one
month apart. In a similar study, Hall (14) reported split applications of oxadiazon and bensulide to be ineffective in reducing the injury to Kentucky bluegrass resulting from single applications.

Persistence of the Dinitroaniline Herbicides

Kearny (26) lists the ideal herbicide as one that: 1) will control weeds; 2) is non-toxic to non-target organisms; 3) is degraded to ecologically acceptable products within a reasonable amount of time; 4) remains at the site of application; 5) does not adversely interact with other pesticides; and 6) has a low potential for bioaccumulation. The manner in which a herbicide performs is greatly influenced by its interactions with the environment. Weber (58) divides herbicide-environmental interactions into degradation and transfer processes. Degradation processes are those that act to change the structure of the herbicide molecule and include biological decomposition, chemical decomposition and photodecomposition. Transfer processes on the other hand will act to physically influence the availability or positioning of the herbicide molecule and include adsorption and exudation by plants, microorganisms or other soil organisms, retention in vegetation, adsorption by soil components and movement through volatilization, surface runoff or leaching. Once a herbicide is altered from its active state or its concentration is depleted below a level needed to gain weed control its usefulness is reduced.

Herbicide persistence in the environment is related to the edaphic climate as well as herbicide structural properties (26). Kearney (26) lists the relative order of decreasing herbicide
persistence by class as: urea, triazine and pichloram herbicides
> benzoic acid and amide herbicides > phenoxy, toluide and nitrile
herbicides > carbamates and aliphatic acid herbicides.

One group of herbicides that have been the object of a great
number of investigations concerning their biological activity has been
the dinitroaniline herbicides. Herbicides in this class are prac-
tically immobile in soil, possess low water solubility, and are subject
to varying degrees of loss via volatilization and photodecomposition
(10,16,58,59). Results obtained with dinitroaniline herbicides have
found herbicide persistence to vary greatly with herbicide, cropping
system and environmental and soil conditions.

Harvey (15) compared soil incorporated treatments of twelve
dinitroaniline herbicides for velvetleaf (Abutilon theophrasti Medic.)
and giant foxtail (Setaria faberii Herrm.) control in soybeans [Glycine
max (L.) 'Corsoy'] under field conditions. Herbicide persistence was
reported to increase as application rates increased but was reduced by
increased rainfall when test years were compared. Miller et al. (32)
could find no evidence of accumulation of trifluralin, benefin and
nitratin [4-methylsulfonyl)-2,6-dinitro-N,N-dipropylaniline] from
annual soil incorporated treatments for weed control in cotton (Gos-
sypium hirsutum L. 'Acala SJ-1') during a five year period. However,
15 months after the final application herbicide residues were high
enough to injure fieldgrown sorghum [Sorghum bicolor (L.) Moench] 46%,
43%, and 25% for trifluralin, nitratin and benefin, respectively.

Herbicide persistence has also been studied in perennial cropping
systems where the herbicide cannot be soil incorporated and must be
surface applied. Johnson (24) reported increased crabgrass control in turf when benefin applications were repeated 2 and 2 plus 4 months after the initial application. This report indicates that while single applications of benefin did not persist for the time period needed to achieve full season control of crabgrass this lack of persistence can be offset by repeat applications.

Stewart et al. (49) compared herbicide persistence based upon the period of time required for bioassay or residue analysis to reach a level of 90% herbicide loss of those concentrations derived from commonly recommended application rates. Approximate persistence levels in soils based on this criteria for four dinitroaniline herbicides were: benefin 120-150 days; isopropalin (2,6-dinitro-N,N-dipropyl-cumidine) 150 days; profluralin 320-460 days; and trifluralin 120-180 days. This method of analysis is mainly concerned with the potential of herbicide carryover to injure succeeding crops and not with the soil concentrations at which herbicides become ineffective in controlling weeds.

A large portion of the literature concerning the dinitroaniline herbicides examines the environment-herbicide interactions that can affect the ultimate fate and/or persistence of these herbicides. Areas of major importance in determining the fate of the dinitroanilines in the environment include potential loss or inactivation through volatilization, photodecomposition, adsorption by soil components, chemical decomposition, microbial decomposition and plant adsorption.
Dinitroaniline herbicide volatility is influenced by soil moisture, soil texture, soil organic matter content, soil and air temperature, air movement and time and method of herbicide incorporation (10). Ellis and Norton (10) classified dinitroaniline herbicides with the following volatilization potentials: oxyzalin (3,5-dinitro N\(^4\),N\(^4\)-dipropylsulfanilamide), and nitralin - relatively nonvolatile; dinitramine (N\(^4\),N\(^4\)-diethyl-\(\alpha,\alpha,\alpha\)-trifluoro-3,5-dinitrotoluene-2,4-diamine) - slightly volatile; isopropalin, fluchloralin [N-(2-chloroethyl)-\(\alpha,\alpha,\alpha\)-trifluoro-2,6-dinitro-N-propyl-p-toluidine], penoxalin [N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine] and benefin - moderately volatile; and trifluralin and profluralin - highly volatile.

Kennedy and Talbert (28) reported losses of nitralin, butralin, dinitramine, fluchloralin, penoxalin, trifluralin, profluralin, benefin, and isopropalin to greatly increase from three or more days delay in herbicide soil incorporation. Laboratory analysis determined profluralin, benefin and trifluralin to be most volatile of the group tested with losses of 35%, 25%, and 18% respectively occurring at 30°C in a 24 hour period. Increasing soil moisture to 33% increased the severity of loss. Moisture content has been reported to influence volatilization of trifluralin to a greater extent than soil type (29).

In this study soils kept at 75% field capacity moisture content had greater losses than those that remained dry. In a similar study Savage (40) reported trifluralin and ethafluralin [N-ethyl-N-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl) benzenamine] volatilized more during an eight day period when soil moisture levels were kept at field capacity rather than air dried or flooded.
Jacques and Harvey (21) used an oat (*Avena sativa* L. 'Dal') primary root bioassay to compare soil residues of eight dinitroaniline herbicides having existed under growth chamber, greenhouse and field conditions. Herbicides were found to remain biologically active longer under dry and cool soil conditions. Wet soils resulted in more rapid dissipation rates when compared to dry soil in greenhouse testing.

Parochetti and Hein (35) found increasing temperatures and raising soil moisture content from air dryness to field capacity increased volatility loss. He reported vapor losses at 50°C from a Lakeland loamy sand soil at field capacity to be 24.5% and 12.5%, respectively for trifluralin and benefin. Trifluralin vapor loss was less from a granular formulation than when applied as a spray. However, vapor losses were similar from granular and spray formulations of benefin. Excessive surface moisture was found by Parochetti et al. (34) to decrease the volatility losses of benefin, profluralin, and trifluralin from approximately 23 percent to 10, 13 and 17.5 percent respectively.

The rate or extent of volatility loss has been reported to be influenced by soil components (17, 34, 35, 41). Savage and Jordan (41) found initial loss rates from surface applied trifluralin, fluchlorin and pendimethalin [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] to be rapid in the first five days. However, the initial rate of loss was less from a clay soil than in a silt loam soil. Rainfall on the first day accelerated the initial rate of herbicide loss. Parochetti and Hein (35) reported trifluralin volatility to decrease
as the cation exchange capacity (CEC) of the soil increased. However, a similar study by Parochetti et al. (34) compared the volatility levels of benefin, profluralin and trifluralin from three soils containing varying cation exchange capacities and could not find a correlation between volatility and soil CEC.

Adsorption of the dinitroaniline herbicides in the soil system appears to be more readily influenced by organic matter than by clay content. Hollist and Foy (17) reported the relative order of effectiveness of soil components in reducing phytotoxicity as steamed organic matter >> organic matter >> steamed montmorillonite > steamed kaolinite ~ kaolinite ~ montmorillonite. Steaming the organic matter more than doubled its anion exchange capacity which the authors concluded to be a better parameter than CEC for estimating the potential of soil components to reduce herbicide phytotoxicity.

Photodecomposition can also significantly reduce the concentrations of the dinitroaniline herbicides under certain conditions. Wright and Warren (60) reduced the biological activity of trifluralin after its application to glass surfaces and subsequent exposure to sunlight. However, the loss of activity was not as great when trifluralin applications were made to soil surfaces and exposed to sunlight. Parochetti and Dec (33) compared ten dinitroaniline herbicides applied to the soil surface in unfiltered solar radiation and in the dark. All herbicides were found to degrade more in the light than the dark. Percent photodecomposition values after seven days exposure were: isopropalin 8.2%; butralin 9.0%; pendimethalin 9.9%; benefin 17.1%; trifluralin 18.4%; oxyzalin 26.4%; fluchloralin 30.4%
nitralin 40.6%; profluralin 47.6%; and dinitramine 72.3%. Ellis and Norton (10) suggest that losses via photodecomposition have little effect on the initial activity of the dinitroaniline herbicides especially if they are soil incorporated. However in the absence of soil incorporation photodecomposition would become more of a factor in reducing dinitroaniline herbicide activity.

Dinitroaniline herbicides that enter the soil environment and are not depleted via volatilization or photodecomposition can be affected by microbial and chemical degradation. Evidence is limited pertaining to specific microorganisms associated with dinitroaniline herbicide breakdown (10). However, chemical and microbial breakdown has been differentiated as to their respective influence on the initial activity and the persistence of the dinitroaniline herbicides.

Probst et al. (37) reported soil microbes were more important in trifluralin persistence than in initial dissipation under aerobic conditions. Anaerobic degradation (soil moisture at 200% field capacity) occurred more rapidly than at lower soil moisture levels and was determined not to be associated with anaerobic soil microorganisms or soil texture but was found to increase with increasing temperatures. Golab et al. (13) found benefin to decompose more rapidly in soil flooded with water as compared with a moist soil. Only 4.6% benefin remained after 16 days under anaerobic conditions while in aerobic soils 47.4% and 10% benefin remained after 28 and 352 days respectively.

Savage (40) calculated half-lives of trifluralin, fluchloralin, and pendimethalin in autoclaved and non-autoclaved soils maintained at field capacity and flooded soil moisture content. Results showed
that autoclaving prior to treatment had no significant effect on the
dissipation rates of any of the herbicides tested at either soil
moisture regime, indicating the observed increased dissipation rates
under flooded conditions may be from a non-microbiological effect.
Half-lives for herbicides in the non-autoclaved soil for the three
herbicides ranged from 4 to 8 days under flooded conditions to 51
to 82 days in soils maintained at field capacity.

Herbicides can also be removed from the soil environment by plant
uptake. Businelli et al. (3) reported application of 1.3 and 1.9
kg/ha of benfluralin resulted in whole carrot (Daucus) benfluralin
residues of $210 \pm 18$ and $240 \pm 47$ ng/g respectively. Benefin has
been reported to accumulate in peanut (Arachis hypogaea L.) and alfalfa
(Medicago sativa L.) (13).

**Controlled-Release Formulations**

Controlled-release technology first received attention in the
1960's as an alternative method of delivering pesticides to the site of
action. Formulations that are controlled-release may restrict the
scale of loss of biologically active compounds into the environment.
Potential advantages from controlled-release formulations include:
1) the need for less active ingredient; 2) fewer applications; 3) more
effective control of the target organism; 4) reduced toxicity to
non-target organisms; and 5) reduced potential for environmental
pollution (46). Cardarelli (4) also suggests that controlled-release
formulations of non-persistent agents could be substituted for per-
sistent ones. Numerous controlled-release delivery systems have been
proposed in an attempt to control pesticide release rates (4,42). Starch xanthide and sludge polymer are two such formulations that have been developed and patented by chemists at the United States Department of Agricultural Northern Regional Research Center, Peoria, IL. (39,46).

Sludge polymer (SP) formulation techniques have been described by Roth (39). Synthesis involves crosslinking a heterogeneous mixture of polysaccharides contained in methanol activated sludge (MAS) with dialdehyde starch (DAS) in the presence of the active agent, thus entrapping the agent.

Experimental testing of SP pesticide formulations to examine their potential as a controlled-release pesticide carrier is limited. Foley and Wax (11) compared SP formulations of trifluralin, alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide], metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide], EPTC (S-ethyl dipropylthiocarbamate), vernolate (S-propyl dipropylthiocarbamate) and butylate (S-ethyl diisobutylthiocarbamate) under natural field conditions. Results were found to vary with treatment year. However, SP herbicide formulations were similar to their respective EC formulation in providing little or no residual control.

Clayton (5) applied SP formulations of benefin, bensulide, DCPA, oxadiazon, prosulfalin and siduron to Kentucky bluegrass and creeping bentgrass (Agrostis palustris Huds.) turf. SP preemergence herbicide treated turf experienced similar phytotoxic injury and crabgrass infestation as those areas treated with commercial herbicide formulations.
Shasha et al. (46) state that starch xanthide pesticide formulations are attractive as controlled-release carriers due to: 1) simplicity of the formulation procedure; 2) the availability of starch and its low cost; and 3) the carrier will biodegrade without leaving any residue in the environment.

The formulation of starch xanthide has been described by Shasha (45) and Doane et al. (9). Starch xanthide encapsulation of a pesticide begins by treating a water suspension of starch with carbon disulfide and an alkali metal hydroxide. Within 30 minutes approximately 70% of the carbon disulfide is converted to xanthate with limited additional conversion occurring. Each repeating anhydro-glucose unit of starch theoretically can possess 3 xanthate groups (a degree of substitution [D.S.] of 3). However, a D.S. of 0.1 to 0.35 has been found to be sufficient (9). The active agent in liquid form (or after having been mixed with a small amount of solvent) is thoroughly dispersed into the viscous slurry of starch xanthate. The pH is lowered to 4 to 5 with glacial acetic acid which is then followed by the addition of an oxidant or metal cations to crosslink the starch xanthate, physically encapsulating the pesticide. Shasha (45) has outlined the reaction sequences as follows:

\[ \text{Starch} - \text{OH} + \text{CS}_2 + \text{NaOH} \rightarrow \]

\[ \text{Starch-OCSNa} \xrightarrow{H^+[O]} \text{Starch-OCSSCO-Starch} \]

Variations in this formulation process have been found to produce starch xanthide carriers possessing different pesticide release properties (9,38,43,45).
In field situations starch xanthide composed of acid modified flour was found to release butylate faster than did mixtures of acid modified flour and starch which in turn released butylate faster than when starch alone was used (9). The same study revealed that percent recovery of the encapsulated agent is greatest when using only starch, least when using acid modified flour with mixtures of acid modified flour and starch being intermediate. Additions of latex to starch xanthate prior to crosslinking decreased the release of DBCP (1,2-dibromo-3-chloropropane) while release of butylate or EPTC remained unchanged with latex addition (45).

Selection of a crosslinking agent has been found to affect pesticide release (38,43). Schreiber et al. (43) discovered NaNO$_2$ crosslinked starch xanthides released butylate and EPTC at much faster rates than did H$_2$O$_2$ crosslinked materials. They also reported that release from a starch xanthide matrix appeared related to properties of the encapsulated active agent. Starch xanthide butylate formulations resulted in slower initial release with longer persistence when compared to similar starch xanthide formulations of EPTC.

Raboy and Hopen (38) reported similar results in laboratory studies with various encapsulated formulations of chloramben (3-amino-2,5-dichlorobenzoic acid). Chloramben release from starch xanthide proved to be a function of crosslinking agent as well as the form of chloramben encapsulated. Release rates of chloramben acid were greater than that of the chloramben ester, while crosslinking agents ranked as follows (from fastest to slowest release) Ca$^{2+}$ > H$_2$O$_2$ > Fe$^{3+}$.

The process of double encapsulation (adding another layer of xanthate to that which has already been crosslinked and crosslinking as before) has reportedly produced slower release rates than single encapsulation (45).
Particle size of the starch xanthide granule has been found to affect pesticide release rate. Trimmell et al. (52) reported release of trifluralin from starch xanthide into hexane over a seven day period to increase as particle size decreased.

These variables have the potential of altering pesticide release rates from starch xanthide granules. Pesticide release rates from starch xanthide carrier can be varied to fit field needs. However, the design challenge is in being able to predict how a particular starch xanthide formulation will release a specific pesticide, and matching that activity with the predicted activity of the pest to achieve maximum control over the desired time period.

Evaluations of starch xanthide herbicide formulations are limited, however, field, greenhouse and laboratory comparisons with commercially available formulations have been made. Initially starch xanthide (SX) encapsulation was studied as a means by which thiocarbamate herbicide performance could be increased by reducing volatility losses.

Schreiber et al. (43) applied SX EPTC and SX butylate formulations to an air dried silt loam in the greenhouse after which he periodically seeded robust purple foxtail (Setaria viridis (L.) Beau. var. robusta-purpurea Schreiber) as a bioassay species. SX EPTC formulations produced control equal to the emulsifiable concentrate (EC) at initial seeding dates. At subsequent seeding dates SX EPTC formulations provided significantly better control than the EC except at the highest herbicide concentration. SX butylate formulations were found to have slower initial release but provided greater extended control when compared to similar formulations of EPTC.
Coffman and Gentner (7) compared SX and EC trifluralin formulations in an effort to improve trifluralin performance by reducing photodegradation and volatility losses. Treatments were applied to flats of sand, in the greenhouse, at four rates (1.1, 2.2, 4.4 and 8.8 kg/ha) and were seeded at weekly intervals with Italian ryegrass (Lolium multiflorum Lam.). SX trifluralin formulations were observed to be significantly less herbicidal at the initial seeding than the EC but after two weeks SX formulations were significantly more active than the EC. The herbicidal activity was extended for all formulations by increasing application rates. SX trifluralin formulations also possessed herbicide activity which proved equal to that obtained with twice the rate of the EC.

Coffman and Gentner (7) conducted a similar study on a silt loam soil under field conditions using the same parameters. Results showed SX formulations were less herbicidal than the EC initially but were superior 2 weeks after application. A concern was expressed that SX trifluralin formulations are too slow in initially releasing the trifluralin. Suggested measures for improved control from SX trifluralin formulations included the modification of the SX formulation or using SX formulations with higher initial release rates in combination with slower releasing SX formulations.

SX chloramben formulations have been studied in an effort to reduce leaching losses that are common when the herbicide is formulated as the NH$_3$ salt of the benzoic acid, and as a possible means of reducing microbial degradation of the CH$_3$ ester of the benzoic acid formulation (38). Raboy and Hopen (38) compared SX chloramben
formulations against their soluble concentrate (SC) for weed control in pumpkin [Cucurbita moschata (Puich.) Poir.] at two Illinois locations. At one location applications were made to a Flanagan silt loam soil while at the other a Plainfield sandy soil was used. Results showed no advantage in using SX chloramben of the SC chloramben formulation on the Flanagan silt loam soil. However there was a slight advantage to using the SX chloramben on the Plainfield sand soil which contains less than 1% organic matter.

Clayton (5) starch encapsulated benefin, bensulide, DCPA, oxadiazon, prosulfalin, and siduron to assess their potential in preemergence control of crabgrass and the reduction of herbicide injury in a Kentucky bluegrass turf. Only SX formulations of benefin and prosulfalin controlled crabgrass better than commercially available formulations. Injury inherent to the granular commercial formulation of oxadiazon and the wettable powder (WP) commercial formulation of prosulfalin was found to decrease when encapsulated in starch xanthide.

Foley and Wax (11) found SX trifluralin to be more active, compared to the EC formulation, as incorporation was delayed from 0 to 2 or 20 hours. SX trifluralin also possessed greater residual activity than its EC while this advantage was only slight for SX EPTC and SX butylate formulations. SX EPTC and SX vernolate formulations were found to be less safe for use in corn (Zea mays L. 'Pioneer 3535') and soybeans [Glycine max (L.) Merr. 'Wells'] than EC formulations that included the crop protectant R-29148 [3-dichloroacetyl]-2,2,5-tri-methylloxadiazoline].
II. MATERIALS AND METHODS

All starch xanthide (SX) and sludge polymer (SP) formulations used in this research were provided by the United States Department of Agriculture, USDA formulation chemists B. Shasha and W. Roth, from the Northern Regional Research Center, Peoria, Illinois, USA 61604.

Field Experiments

All field experiments were conducted at the Ornamental Horticulture Research Center, University of Illinois, Urbana, Illinois. The turf was a 'Kenblue' common Kentucky bluegrass \textit{(Poa pratensis (L.)]} mowed biweekly at a mowing height of 3.81 cm in 1978 and 1979 and 2.54 cm in 1980. The soil classification for all field sites was a fine, montmorillonitic, mesic aquatic argiudoll (Flanagan silt loam). All studies were fertilized with a 10-6-4 (N:P\sub{2}O\sub{5}:K\sub{2}O) water soluble fertilizer and irrigated when necessary to prevent wilting of the untreated control plots.

Data were collected periodically during the growing season to evaluate weed control and phytotoxic injury to the turf.

Experiment 1: The Evaluation of Starch Xanthide and Sludge Polymer Formulations of Benefin, Oxadiazon and Prosulfalin for Crabgrass Control in Kentucky Bluegrass Turf

Benefin (N-butyl-N-ethyl-\(\alpha,\alpha,\alpha\)-triflouro-2,6-dinitro-p-toluidine), oxadiazon [2-tert-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazoline-5-one], and prosulfalin (N\[4-Dipropylamino)-3,5-dinitrophenyl)sulfonyl]-S,S-dimethylsulfililmine) were formulated into various SX granules and SP matrices to evaluate their performance in the control of large crabgrass \textit{(Digitaria sanguinalis (L.) Scop.)}. 
SX formulations were prepared using pilot plant procedures described by Stout et al. (50) and varied in crosslinking agent, degree of substitution (D.S.) and the base used in the xanthation process. The technical grade of each herbicide was added in the formulation process to yield an SX granule containing 2.9 ± 0.3% active ingredient by weight. All SX formulations were sieved to produce SX granules passing a 20 but not 40 mesh screen (841 to 425 microns). SX formulations used in this study are listed in Table 1.

Table 1. SX preemergence herbicide formulations used in field experiments 1 and 2.

<table>
<thead>
<tr>
<th>Formulation Number</th>
<th>Herbicide</th>
<th>Xanthation Base</th>
<th>Degree of Substitution</th>
<th>Crosslinking Agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>SX&lt;sub&gt;1&lt;/sub&gt;</td>
<td>benzin</td>
<td>NaOH</td>
<td>0.17</td>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
</tr>
<tr>
<td>SX&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td>NaOH</td>
<td>0.30</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>SX&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td>KOH</td>
<td>0.30</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>SX&lt;sub&gt;1&lt;/sub&gt;</td>
<td>oxadiazon</td>
<td>NaOH</td>
<td>0.10</td>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
</tr>
<tr>
<td>SX&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td>NaOH</td>
<td>0.30</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>SX&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td>KOH</td>
<td>0.30</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>SX&lt;sub&gt;1&lt;/sub&gt;</td>
<td>prosulfalin</td>
<td>NaOH</td>
<td>0.17</td>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
</tr>
<tr>
<td>SX&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td>NaOH</td>
<td>0.30</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>SX&lt;sub&gt;3&lt;/sub&gt;</td>
<td></td>
<td>NaOH</td>
<td>0.30</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

SP formulations were prepared using procedures described by Roth (39). Three SP formulations of each preemergence herbicide varied only in the weight ratio of methanol activated sludge (MAS) to the dialdehyde starch (DAS) crosslinking agent. The weight of MAS was held
constant for each formulation while the DAS was varied to yield MAS:DAS ratios of 1:4, 1:1, and 4:1 on a dry weight basis.

The percent solids in the MAS varied between spring and fall applications in 1978 being 2.5 and 1.7% respectively. However, formulations were standardized by incorporating a quantity of MAS equivalent to 5.3 g per liter. The DAS crosslinking agent had a concentration of 10% dry weight solids in both spring and fall formulations.

Herbicides used in the SP formulations were obtained from a 2 lb per gallon emulsifiable concentrate (EC) formulation of oxadiazon, a 1.5 lb per gallon EC formulation of benefin and a 50 percent wettable powder (WP) formulation of prosulfalin.

SX, SP and commercial formulations (CF) of benefin, oxadiazon and prosulfalin were applied to 1.83 by 2.43 m plots at a rate of 3.36 kg/ha active ingredient on May 10, 1978. Commercial formulations included a 2.5% granular form of benefin, a 2.0% granular form of oxadiazon and a 50% WP form of prosulfalin. The 1 liter SP formulations were diluted with 1 liter of water and were applied, along with the CF of prosulfalin, with a small plot sprayer (54) calibrated to deliver 266.5 l/ha. SX and granular commercial formulations were weighed per individual plot and applied out of small paper bags in a "salt shaker" fashion. Each treatment plus an untreated control were replicated three times in a randomized complete block design. Treatments were randomly re-applied in a stripped fashion to either the top or bottom half of each replication on September 1, 1978 to evaluate their potential for controlling Poa annua. In 1979 the SP formulations and repeat
fall applications were deleted from the experiment. SX and commercial formulations were applied once on May 5, 1979 to each 1.83 x 2.43 m plot.

In 1978 and 1979, before intitial herbicide application, the entire plot area was cultivated with a turf spiker designed to produce narrow perforations in the soil 0.64 to 1.27 cm in depth. Immediately following cultivation large crabgrass was overseeded at a rate of 24.4 kg/ha. Large crabgrass was again overseeded at 24.4 kg/ha once and twice more in 1978 and 1979 respectively. Annual bluegrass (Poa annua) was overseeded on August 29, 1978 at a rate of 12.20 kg/ha.

Data were collected periodically through the growing season. Raw data were subjected to an analysis of variance for each collection date and treatment means were compared using Duncan's multiple range test. Crabgrass data is expressed as the percentage of crabgrass in the untreated control controlled by treatments. Phytotoxicity data taken on September 26 and October 26, 1978 following the September 1 treatment, and data on Poa annua infestation were analyzed as a split-plot in strips due to the repeat application sub-treatment being stripped across each replication.

Experiment 2: The Influence of Granule Size on the Performance of Starch Xanthide Formulations of Benefin, Oxadiazon and Prossulfalin in the Control of Crabgrass in Kentucky Bluegrass Turf

Coarse textured (840 μ to 1410 μ) and fine textured (250 μ to 425 μ) SX granules of benefin, oxadiazon and prosulfalin identical in formulation to those SX compounds listed in Table 1, were selected to ascertain the influence of particle size on the performance of SX preemergence herbicide formulations. SX formulations were weighed for
individual plots and applied out of small paper bags in a "salt shaker" fashion to 0.91 by 1.52 m plots at a rate of 3.36 kg/ha (active ingredient) on May 10, 1978 and May 5, 1979. Each treatment plus untreated control were replicated three times in a randomized complete block design.

In 1978 and 1979 the plot area was spiked and overseeded with crabgrass as in the first experiment.

Data were collected periodically on turf phytotoxicity and percent crabgrass infestation. Raw data were subjected to an analysis of variance for each collection date and treatment means were compared using Duncan's multiple range test. Crabgrass data is expressed as the percentage of crabgrass in the untreated control controlled by treatment.

Experiment 3: The Evaluation in Six Starch Xanthide Benefin Formulations for Crabgrass Control in Kentucky Bluegrass Turf

Technical grade (95% active ingredient) benefin was formulated into six SX benefin compounds to determine how SX formulation variables might influence benefin performance. Formulation variables included the use of Fe$^{3+}$ and H$_2$O$_2$ as crosslinking agents on starch xanthates possessing degrees of substitution of 0.30 and 0.17. One formulation used acid modified flour in place of cornstarch (xanthation process) and one SX formulation contained a higher concentration of benefin.

All SX benefin formulations contained 1.8 ± 0.4% and 2.5 ± 0.4% benefin in 1979 and 1980 respectively except one SX formulation which contained 7.0 ± 0.2% benefin. SX formulations were sieved to yield
granules 425 to 841 microns in size. SX benefin formulations used in this study are listed in Table 2.

All SX benefin treatments were weighed per individual plot and applied out of small paper bags in a "salt shaker" fashion to 1.83 by 3.05 m plots at rates of 2.24 and 4.48 kg/ha on May 7, 1979 and May 1, 1980. Each SX benefin treatment plus an untreated control were replicated three times in a randomized complete block design where the rate/ha factor was arranged in strips across the top or bottom half of each replication.

The experimental area was overseeded in 1979 with large crabgrass at a rate of 24.4 kg/ha on April 30, June 25, July 31, and December 1. In 1980 large crabgrass was overseeded at a rate of 48.8 kg/ha on April 26 and May 10. A turf spiking machine and a Ryan Renothin verticutter were used at the time of initial overseeding in 1979 and 1980 respectively, 2 to 4 days prior to treatment applications. Tillage was used to provide a more favorable environment for crabgrass germination and growth. In both years all subsequent overseedings were applied without tillage.

Data were collected periodically throughout the growing season on turf phytotoxicity and percent crabgrass infestation. Raw data were subjected to an analysis of variance for split-plot in strips experimental design. For each data collection date treatment means were compared using Duncan's multiple range test. Crabgrass data is expressed as the percentage of crabgrass in the untreated control controlled by treatment.
Table 2. SX benefin formulations

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Crosslinking Agent</th>
<th>Degree of Substitution</th>
<th>% Benefin 1979</th>
<th>% Benefin 1980</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid modified flour</td>
<td>Fe^{3+}</td>
<td>0.30</td>
<td>1.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Corn starch</td>
<td>Fe^{3+}</td>
<td>0.30</td>
<td>1.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Corn starch</td>
<td>Fe^{3+}</td>
<td>0.17</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Corn starch</td>
<td>H_2O_2</td>
<td>0.30</td>
<td>1.9</td>
<td>2.6</td>
</tr>
<tr>
<td>Corn starch</td>
<td>H_2O_2</td>
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<td>1.4</td>
<td>2.9</td>
</tr>
<tr>
<td>Corn starch</td>
<td>H_2O_2</td>
<td>0.17</td>
<td>7.2</td>
<td>7.0</td>
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Experiment 4: The Performance of Starch Xanthide and Commercial Benefin Formulations Applied Individually and in Combination in the Control of Crabgrass in Kentucky Bluegrass Turf

Research was conducted to determine if weed control could be enhanced through combining a readily available commercial-type formulation of benefin with an SX benefin formulation possessing controlled release characteristics.

Technical grade benefin was formulated into a SX benefin compound with a D.S. of 0.17, oxidatively crosslinked with H_2O_2 and containing 2.0 and 2.3% benefin in 1979 and 1980, respectively. SX benefin granules were sieved to produce granules ranging from 425 to 841 microns in size. A specially formulated 0.5% granular commercial-type formulation of benefin (formulated and supplied by the Elanco division of Eli Lilly Company, Greenfield, Indiana, USA) was also used in this experiment.
The SX benefin and CF benefin compounds were applied individually in a "salt shaker" fashion out of small paper bags to 1.52 by 1.83 m plots on May 7, 1979 and May 1, 1980. Benefin was applied at rates of 2.24, 3.36, and 4.48 kg benefin/ha in active ingredient weight ratios of 4:0, 3:1, 1:1, 1:3 and 0:4 (SX benefin:CF benefin). Herbicide treatments plus an untreated control were replicated three times and arranged in a randomized complete block design.

The experimental area was overseeded in 1979 with large crabgrass at a rate of 24.4 kg/ha on April 30, June 25, July 31, and December 1. Large crabgrass was overseeded in 1980 at a rate of 48.4 kg/ha on April 26 and May 10. A turf spiking machine and a Ryan Renothin verticutter were used in 1979 and 1980 respectively at the time of initial overseeding, 2 to 4 days prior to treatment applications, to provide a more favorable environment for crabgrass seed germination and growth. In both years subsequent overseedings were applied without tillage.

Data were collected periodically throughout the growing season on turf phytotoxicity and percent crabgrass infestation. Raw data were subjected to an analysis of variance for each collection date and treatment means were compared using Duncan's multiple range test. Crabgrass data is expressed as the percentage of crabgrass in the untreated control controlled by treatment.

Experiment 5: The Evaluation of Split Applications of Benefin for the Control of Crabgrass in Kentucky Bluegrass Turf

A specially formulated 0.5% granular commercial-type benefin formulation (Elanco Division of Eli Lilly and Company) was applied at a rate of 4.48 kg benefin/ha in six treatment regimes to 1.52 by 1.83 m
plots in an effort to define the requirements of a controlled release preemergence herbicide system. Initial treatments were applied on May 7, 1979 and May 1, 1980. The six treatment regimes are listed in Table 3. The six treatments plus an untreated control were replicated three times and arranged in a randomized complete block design.

The experimental area was overseeded in 1979 with large crabgrass at a rate of 24.4 kg/ha on April 30, June 25, July 31 and December 1. Large crabgrass was overseeded in 1980 at a rate of 48.4 kg/ha on April 26 and May 10. A turf spiking machine and a Ryan Renothin verticut-cutter were used at the time of initial overseeding in 1979 and 1980 respectively, 2 to 4 days prior to initial treatment applications, to provide a more favorable environment for crabgrass seed germination and growth. In both years subsequent overseedings were applied without tillage.

Data were collected periodically throughout the growing season on turf phytotoxicity and percent crabgrass infestation. Raw data were subjected to an analysis of variance for each collection date and treatment means were compared using Duncan's multiple range test. Crabgrass data is expressed as the percentage of crabgrass in the untreated control controlled by treatment.
Table 3. Benefin application timing regimes

<table>
<thead>
<tr>
<th>Initial application*</th>
<th>Weeks after initial application</th>
<th>Total applied benefin</th>
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</tr>
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<td>0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00</td>
<td></td>
</tr>
</tbody>
</table>

*Initial application dates were May 7, 1979 and May 1, 1980.

Greenhouse Experiment

Evaluation of the Controlled Release Performance of Four Starch Xanthide Benefin Formulations on Two Soil Types Under Greenhouse Conditions

SX benefin compounds and a 0.5% benefin commercial-type granular formulation (Elanco Division of Eli Lilly and Company) were compared under greenhouse conditions for preemergence herbicide activity on germinating large crabgrass seedlings.

Technical grade benefin was encapsulated into four SX granules containing all combinations of two crosslinking agents (H₂O₂ and Fe³⁺) and two degrees of substitution (0.17 and 0.3). All SX benefin formulations contained 2.0 ± 0.2% benefin and ranged in particle size from 425 to 841 microns.
Two naturally occurring soils, a fine, montmorillonitic, mesic aquic argiudoll (Flanagan silt loam) and a mixed, mesic, typic udipsomments (Plainfield Sand) were placed in 10.16 cm diameter plastic pots with drainage holes for adequate drainage. The soil was allowed to equilibrate under a mist system for two weeks prior to herbicide application. On September 29, 1980, the SX benefin and commercial-type benefin treatments were surface applied with a salt shaker at 2.24 and 4.48 kg benefin/ha. Benefin treatments plus an untreated control were applied to a total of four groups of pots which were replicated five times and arranged in a randomized complete block design. Following application the treatments were watered in using an overhead mist system.

Large crabgrass seed, tested to be approximately 20% viable was sown 100 seeds to a pot on one-fourth each of the pots 1, 21, 42 and 63 days respectively, following herbicide treatment. To keep the crabgrass seeds in place a light 5 cc topdressing of sand was applied to just barely cover the seeds. Seeds were kept moist by an overhead mist system operating for 15 seconds at 10 minute intervals for 2 to 3 hours per day. Greenhouse temperatures ranged from 33/21°C (day/night) at the beginning of the experiment to 27/21°C (day/night) at the conclusion.

Data were collected on the basis of the number of germinating crabgrass plants developing to the two leaf stage and beyond 3 to 4 weeks after seeding. Raw data were subjected to an analysis of variance for each seeding date and treatment means were compared using Duncan's multiple range test. Data is expressed as percent control of germinating crabgrass seed as compared to the untreated control.
Laboratory Studies

Physical Examination of the Granule Structure of Starch Xanthide Dinitroaniline Herbicide Formulations

SX granule structural characteristics were examined by both scanning electron and light microscopy to determine if any correlation existed between experimentally observed herbicide release characteristics and the structural integrity of selected SX formulations.

All SX prosulfalin formulations (Table 1) were coated with gold and paladium while separate samples of SX₂ and SX₃ prosulfalin formulations were placed in 50% ethanol and through a dehydration series of ethanol-water to absolute alcohol before using critical-point drying procedures as described by Anderson (1) and Horrige and Tamm (18). Following critical-point drying, samples were coated with gold and paladium. All samples were observed with a Cambridge Mark II scanning electron microscope.

All SX benefin formulations (Table 1) were placed into a cryostat (manufactured by International Equipment Company), immersed in distilled water and immediately frozen to -10°C. Sections approximately 20μ thick were cut from each SX benefin granule using a freezing microtome. Sections were immediately place upon a glass microscope slide, covered with Harleco resin and glass cover slide without external treatment and observed under a light microscope.

The Influence of Granule Size, Water Absorption, Solvent and Temperature on Benefin Release from a Starch Xanthide Matrix under Laboratory Conditions

SX benefin and a commercial-type benefin formulation were tested to evaluate factors affecting herbicide availability. Benefin ring
labelled with 14-C (supplied by Eli Lilly and Company, Indianapolis, Indiana 46206 USA) and containing a specific activity of 4.03 microcuries per mg was combined with unlabeled benefin and encapsulated into \( \text{H}_2\text{O}_2 \cdot 0.17 \) (crosslinking agent - D.S.) SX granules. The commercial-type 2.0% granular benefin formulation contained 0.75 microcurie per mg from 14-C benefin and was supplied by the Eli Lilly and Company.

Granules were placed inside a circular stainless steel wire and nylon basket strainer with 50 mesh (356 μ) openings (Delavan-Delta Inc., Lexington, TN 38350). The basket was then lowered into a 14 mm inside diameter glass column equipped with a stopcock at the bottom. A pledget of glass wool protected the stopcock.

Reagent grade acetone or an acetone:distilled water mixture was directed through plastic tubing and allowed to flow onto and through the sample at a rate of 2.0 ± 0.2 ml per minute. The eluate entered a 5.5 ± 0.2 ml volumetric siphon device which discharged into 15 ml volumetric test tubes which were immediately covered with parafilm. After collection of ten fractions the granules were removed from the column and allowed to air dry under a fume hood for 30 minutes.

A 0.2 ml sample was taken from each fraction and pipetted into 15 ml of a scintillation fluid composed of 5.5 g of permablend III (a mixture of 2,5 diphenyloxazole and p-bis-(0-methylstyryl)-benzene) and 120 g of naphthalene dissolved in 1,4-dioxane and brought to a 1 liter volume. All chemicals were of scintillation grade and supplied by the Packard Instrument Company, Inc., Downer's Grove, Illinois 60515, USA.
The radioactivity in each sample was counted using a Packard Model 2425 scintillation counter. The amount of radioactivity in each sample was determined using the following calculations:

\[
\text{counts per minute (CPM) - an external standard \times percent counting efficiency} \times \text{volume correction} = \text{total disintegrations per minute (DPM)}
\]

\[
\frac{\text{total DPM}}{\text{the number of mg in original sample}} = \text{DPM/mg recovered in each fraction}
\]

The percent counting efficiency was obtained using a set of prepared standards containing a known amount of radioactivity with various degrees of quenching. The observed percent counting efficiency (CPM observed/known DPM in standard) was plotted versus the automatic external standard ratio (A.E.S.) to form a quench curve from which percent counting efficiency could be determined.

Granules were transferred from the wire baskets, after 30 minutes of drying, to a 7 cm diameter filter paper disc (Whatman No. 42, ashless) that was folded around the granules. A second filter disc was folded around the first. The entire granular residue was converted into a cylindrical pellet using a pelletizer (the Parr Instrument Co.). The granular residue samples were then oxidized using a Packard Model 306 radioactive sample oxidizer. Radioactivity in each sample was counted using a Packard Model 2425 scintillation counter. The amount of radioactivity contained in each sample was determined by the following calculation:

\[
\frac{\text{CPM \text{percent counting efficiency}}}{\text{DPM in sample \text{mg granules in sample}}} = \text{DPM per mg of granules}
\]
In this instance percent counting efficiency was determined by the addition of a known amount of 14-C toluene (supplied by the Packard Instrument Company Inc.) into a blank sample of scintillation fluid from the oxidizer and then counting the sample. Observed CPM/known DPM equaled the percent counting efficiency.

Percent recovery of oxidized samples was determined by introducing a known quantity of 14-C hexadecane (supplied by the Packard Instrument Company, Inc.) onto a blank filter paper pellet, immediately oxidizing it, and then comparing the recovered radioactivity with samples containing a blank oxidizer scintillation cocktail and an identical amount of 14-C hexadecane.

Experiment 1. SX 14-C benefin granules were separated into coarse (840 to 1190 μ) and fine (420 to 590 μ) particles and compared to 14-C CF benefin granules to determine whether the availability of SX encapsulated benefin could be influenced by granule size. The approximately 100 mg (dry) samples were eluted with 100% acetone.

Experiment 2. Coarse SX 14-C benefin granules in approximately 50 mg quantities were subjected to a 12 hour soak (at 22.0°C) in 5 ml of distilled water while inside of the glass columns. Pre-soaked granules were compared to dry SX 14-C benefin granules by eluting with 100% acetone to evaluate if SX granule imbibition of water could alter benefin release from the SX matrix.

Experiment 3. Coarse SX 14-C benefin granules in approximately 50 mg quantities were subjected to a 12 hour distilled water soaking treatment (22.0°C) as in Experiment 2. After twelve hours the distilled water was eluted from the columns and samples were then eluted
with a 3:1, 1:1, and 1:3 solvent mixture (H₂O:Acetone, v/v) to determine what effect solvent mixture has on the release of benefin from a water soaked SX matrix.

Experiment 4. Coarse SX 14-C benefin granules in approximately 50 mg quantities were subjected to a 12 hour distilled water pre-soak treatment at temperatures of 8 and 37°C to determine the effect of temperature on benefin release from SX matrices. After 12 hours the distilled water was eluted off the columns and samples were then eluted with 100% acetone.

In all experiments radioactivity contained in each fraction and residual activity remaining in association with the granules were evaluated in three (experiments 1, 3 and 4) or four replications (experiment 2) and data were subjected to an analysis of variance.