FACTORS AFFECTING THE HERBICIDAL ACTIVITY OF N-(PHOSPHONOMETHYL) GLYCINE (GLYPHOSATE) ON QUACKGRASS [AGROPYRON REPENS (L.) BEAUV.] AND IN THE SOIL

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ABSTRACT

FACTORS AFFECTING THE HERBICIDAL ACTIVITY OF N-(PHOSPHONOMETHYL)GLYCINE (GLYPHOSATE) ON QUACKGRASS [AGROPYRON REPENS (L.) BEAUV.] AND IN THE SOIL

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Preplant applications of N-(phosphonomethyl)glycine (glyphosate) at 1.12 to 2.24 kg/ha prior to application of chemicals for annual weed control provided an effective system for control of quackgrass [*Agropyron repens* (L.) Beauv.] and annual weeds in corn (*Zea mays* L.), soybeans [*Glycine max* (L.) Merr.], and navy beans (*Phaseolus vulgaris* L.). Glyphosate more effectively controlled quackgrass 25 to 30 cm tall than quackgrass 15 to 20 cm tall. Late spring applications of 1.12 or 2.24 kg/ha provided season long quackgrass control. If the quackgrass was taller than 30 to 36 cm at the time of treatment, at least 2.24 kg/ha of glyphosate was necessary for effective control. Preplant applications of glyphosate caused no injury to agronomic crops.

In greenhouse studies, glyphosate, readily inactivated in the soil, was absorbed from the soil in small

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quantities by corn or soybeans. Although 1.2×10^{-4} M glyphosate causes phytotoxicity to wheat (Triticum aestivum L.) grown in nutrient solution, wheat grown in clay loam or muck soil treated with 56.0 kg/ha of glyphosate showed no injury. As pH and phosphate levels in the soil increased, the herbicide became more available for plant uptake. The herbicide does not bind to ethyl cellulose but does bind to charcoal and organic matter. Iron or aluminum-saturated muck and bentonite adsorbed more herbicide than calcium or sodium-saturated muck and bentonite. In the soil, glyphosate appeared to be rapidly bound with adsorption inversely related to the phosphate level in the soil. The herbicide was relatively immobile in the soil and was degraded to CO_2. For glyphosate, pKa values of < 2, 2.6, 5.6, and 10.6 were obtained.

The action, absorption, and translocation of glyphosate was studied. The type of adjuvant used had a significant effect on the initial rate of action. Iron or iron-nitrilotriacetic acid treatments did not affect its herbicidal activity on wheat. Absorption occurred rapidly in quackgrass with 66.7% of the ^{14}C absorbed moving to the rhizome and untreated shoots within 48 hours after treatment. In all species tested, the ^{14}C-label acted as a phloem-mobile compound moving to the areas of highest metabolic activity.

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A thin-layer chromatography procedure was developed to separate glyphosate, aminomethylphosphonic acid, glycine, and sarcosine.

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INTRODUCTION

From the time selective herbicides were first used to kill weeds, some weeds escaped control. At present, most of the herbicide or herbicide combinations used for annual weed control do not control perennial weeds. Quackgrass, [*Agropyron repens* (L.) Beauv.] a serious perennial weed problem in agronomic crop production in Michigan, competes effectively with crop plants for light (45), water (102), and nutrients (9, 75). Corn (*Zea mays* L.) is grown in rotation with soybeans [*Glycine max* (L.) Merr.], cereal grains, and other crops. Although 4.48 kg/ha of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine] in a single or in split applications controls quackgrass in corn (16), this herbicide is persistent enough to severely injure subsequent crops such as soybeans which are sensitive to atrazine residues. Thus, use of atrazine for quackgrass control requires that corn be grown for two successive years to avoid the residue problem (25).

A weed control system needs to be developed to provide adequate quackgrass control in crops as well as the versatility to grow any crop after the control of quackgrass without crop injury. A herbicide presently used, dalapon (2,2-dichloropropionic acid) controls quackgrass but requires a 4 week waiting period before susceptible crops such as corn or soybeans can be planted (14). Thus, dalapon does not provide an adequate means of quackgrass control in agronomic crop production in Michigan. If a system of complete weed control is developed, it also must control annual weeds and quackgrass without hazard to subsequent crops or the environment. The system may incorporate both chemical and cultural means to provide satisfactory control. If a herbicide was developed to selectively control quackgrass without injury to crop species, the problem could be solved. A second possibility is the application of a nonselective foliar-applied herbicide before plowing the land which controls quackgrass and does not injure crop plants. In this era of environmental concern, the biodegradability and the safety in use of this compound must be proven.

A nonselective herbicide, N-(phosphonomethyl)glycine (glyphosate) was reported to be toxic to quackgrass and to have no available residue in mineral soils (6). The purposes of this study were to (1) investigate the factors affecting the utility of glyphosate for quackgrass control in present agronomic cropping systems, (2) discover the factors affecting its inactivation and persistence in the soil, and (3) study the absorption, translocation, and action of glyphosate in quackgrass and other species.

CHAPTER 1

LITERATURE REVIEW

Quackgrass [Agropyron repens (L.) Beauv.] Control

Quackgrass [*Agropyron repens* (L.) Beauv.), a serious perennial weed in the northeast and northcentral United States and southern Canada (25), grows well under conditions of moderate temperature and adequate rainfall (52). Quackgrass spreads by seeds (52, 106) as well as by rhizomes (25, 52). It is cross pollinated and exhibits various morphological differences (25) as well as differential responses to herbicide treatment (17). Rhizomes produce lateral buds (25) capable of producing a shoot and root system (52). A field with a heavy infestation may contain 13,440 kg/ha of rhizomes and roots (60). Meyer and Buchholtz (67), studying bud dormancy, found that the optimum temperature for bud activity and shoot growth was 20 to 27 C. Bud activity of quackgrass decreased from mid-April to early June (52). During June, July, and August, an increase in osmotic pressure was observed (67, 103). Rhizomes exhibit a second type of dormancy known as apical dominance, a characteristic of the intact rhizome, where most of the buds except the apical one remain inactive during the entire life of the rhizome unless the rhizome is broken (52). This may be altered chemically with naphthalene acetic acid (NAA) which reduces the bud activity of quackgrass whereas 2,3,5-triiodobenzoic acid (TIBA) stimulates bud activity in intact rhizomes (66).

The ability of quackgrass to reduce yield has been attributed to the competition for light (45), water (102), and nutrients (9, 75). However, high levels of fertilization with nitrogen and potassium did not overcome the effects of quackgrass competition (9). Oxvold (75) suggested that quackgrass rhizomes might be producing a substance toxic to other plants. In greenhouse studies, the aqueous extracts of all plant parts gave inhibitory effects in the growth of several crop species (55, 58, 74). Although no evidence was obtained for a phytotoxic substance exuded from living rhizomes or roots (73), addition of high rates of nitrogen did not completely reverse the adverse effects of the past quackgrass infestation (56).

For years, quackgrass control methods revolved around the reduction of carbohydrates in the rhizomes and the desiccation of the rhizomes. Timely tillage with a field cultivator has been fairly successful in controlling quackgrass but its success is dependent upon periods of high temperature and low humidity to kill the rhizomes by desiccation (62). Vengris (97) found that one-bud rhizome cuttings produced shorter shoots than five-bud rhizome cuttings and did not recover as well from deep planting which explains why plowing followed by repeated disking was successful in controlling quackgrass (62).

Three herbicides are presently used for quackgrass control for agronomic crop production. Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] applied preplant, preemergence, or postemergence to corn provides the most consistent quackgrass control (25). With preplant treatments, late summer to fall applications are the most effective. Buchholtz (16) reported good control with atrazine at 2.24 kg/ha while others (31, 65) did not get consistent control with this rate. The most effective treatment was a split application of 2.24 kg/ha of atrazine prior to plowing followed by 2.24 kg/ha preemergence. Effectiveness of control depends on soil type (14), rainfall (14), and proximity (97) of the herbicide to the rhizomes. Due to the slow action of atrazine, preemergence or postemergence applications are less successful than preplant applications. However, atrazine applied after corn planting may provide reasonable control of light quackgrass infestations on sandy soils if adequate rainfall follows treatment to leach the herbicide downward (25). Unfortunately, atrazine may be persistent enough to injure subsequent crops (14, 64). Where atrazine was applied one year at 2.24 kg/ha, oats planted the following year was injured in half the tests (14). The amount of atrazine residue in the soil depends on rainfall, tillage methods, air temperature, and time of application (16). Since

4.48 kg/ha of atrazine are needed for consistent quackgrass control, corn should be grown for two successive years to avoid the residue problem (25).

Dalapon (2,2-dichloropropionic acid), absorbed by both leaves and roots (101), has long been used for quackgrass control (17). The best control is obtained when dalapon is applied to actively growing quackgrass which is 15 to 20 cm tall and the area is tilled 2 weeks after treatment (19). A number of factors influence the effectiveness of dalapon on quackgrass. Buchholtz (17) found that dalapon is less effective on some ecotypes of quackgrass while high rates of dalapon appear to severely burn the foliage thus preventing extensive translocation into the rhizomes (32). In the soil, dalapon is readily leached (54, 101) and rapidly degraded (54). A waiting period is needed after treatment before most crops can be planted in the treated soil (65). Potatoes, a tolerant crop, can be planted 7 to 10 days after treatment (50) whereas less tolerant crops as corn, soybeans, and other crops should not be planted for at least 4 weeks after treatment (15).

Amitrole (3-amino-*s*-triazole) plus ammonium thiocyanate, a foliar-applied herbicide, has given erratic control of quackgrass (23, 65). Quackgrass control with this herbicide combination is dependent on application at the proper stage of growth so that sufficient quantities of herbicide are absorbed and translocated into the rhizomes (63). Amitrole has a short soil residue period which is

dependent on soil type (85), adsorption, chemical reaction with ions, and microbial activity (2, 30). This herbicide combination can only be used on non-cropland areas (25).

In recent years, quackgrass and other perennials are becoming more prevalent in minimum tillage crop production systems (27, 28, 90, 105). The reasons for this are more apparent after a description of the various minimum tillage systems. The stale seedbed, a minimum tillage technique used in soybeans, consists of preparing a seedbed 3 to 5 weeks prior to planting, incorporating a herbicide for grass control, planting the soybeans, and applying a contact herbicide (78, 79). The no-till system, a system used for corn production, consists of applying a contact herbicide to kill the weed foliage and a residual herbicide for annual weed control followed by planting corn in the untill area (90). These systems are dependent on herbicides for both annual and perennial weed control without cultivation (27, 79, 105). Unfortunately, the compounds used are not effective on established quackgrass. In no-till corn, atrazine is often used but may fail to control quackgrass due to insufficient rainfall or to inadequate rate used. For maximum effectiveness of the no-tillage systems, a more effective chemical is needed to control quackgrass and other perennials.

Quackgrass Control with Glyphosate

Glyphosate [*N*-(phosphonomethyl)glycine] introduced in 1971 as a nonselective herbicide without active residues in the soil, appeared to be translocated to the underground portions of perennials and provides control (8). This foliar-applied herbicide provided season long control of quackgrass (8, 82) and was more effective than amitrole plus ammonium thiocyanate (81). However, rain within 8 hours after treatment reduced herbicidal activity (6, 93).

A number of physical factors affect the herbicidal activity of glyphosate (8). In most tests, 1.12 to 3.36 kg/ha of glyphosate gave satisfactory control of quackgrass during the first season after treatment (6, 7, 8, 10, 81, 82). Although higher rates did not appear to increase control the first season after application (8, 24), 4.48 kg/ha gave greater control the second season after application than 2.24 kg/ha (10). The herbicide must be used with a surfactant at a concentration of 1/4 to 1% by volume (93) to obtain maximum herbicidal activity (8, 81). Under field conditions, low gallonage application (10 gpa) showed greater herbicidal activity than a higher gallonage application (90 gpa) of diluent (93).

The physiological activity, stage of growth, and time of treatment of quackgrass also influenced herbicidal activity. Glyphosate was more effective when applied to actively growing quackgrass at the 4 to 6-leaf stage than than 1 1/2 to 2-leaf stage (6, 13, 93). Quackgrass in the

2 to 4-leaf stage was readily controlled with glyphosate (82). In greenhouse studies, a slight decrease in activity was noted at the 9-leaf stage (93). The time of treatment for best control has not been clearly delineated (10, 13, 82). Some researchers find that fall treatment is more effective than spring treatment (13). Researchers at Michigan State have shown that fall treatment are more effective than early spring treatments but late spring treatments are most effective (82). Others have found either fall or spring application provides excellent control (8, 93).

The density of the stand and time of mowing affect control. A dense stand of quackgrass required more herbicide for effective control than a sparse stand (7). Mowing prior to treatment generally decreased control (7, 82). Mowing 1 day after treatment decreased activity while mowing 1 to 2 weeks after treatment had little influence on control (7).

Environmental conditions during and following application influenced the initial herbicidal activity as well as the longevity of control (8). With fall applications, initial burndown was slower than with spring applications (82). In greenhouse studies, temperature preconditioning at 16 , 24 , or 32 C had little effect on herbicidal activity. Herbicide response was greater when the temperature after treatment was 16 C than 24 or 32 C. Conversely, the rate of penetration was greater at 32 C than at 16 or 24 C (93). Under field conditions, the best control was obtained if the temperature for the first 10 days following treatment was below 24 C (10). Light intensity also affected the rate of response to the herbicide. With johnsongrass under two different light regimes, control was greater under the high light in 2 weeks after treatment. For the next 2 weeks, both treatments were kept under greenhouse conditions. Four weeks after treatment, the plants showed little difference in response to glyphosate (92).

Tillage, repeated applications, and residual herbicides can affect control with glyphosate (8, 81, 82). Plowing increased the effectiveness of fall and apring treatments (82). Plowing 1 day after treatment gave significantly better control than plowing the day of treatment (7). Glyphosate at 1.12 kg/ha applied in June followed 1 month later by a second application of 0.56 kg/ha was more effective than a single application of 1.12 kg/ha (81). Glyphosate at 1.12 kg/ha applied in the fall followed by 1.12 kg/ha in the spring was more effective than 2.24 kg/ha applied in the spring (8). Addition of other herbicides may enhance the long term control (1, 82). Glyphosate plus residual herbicides appeared to have an additive effect (1). Combinations of glyphosate and simazine [2-chloro-4,6-bis (ethylamino)-s-triazine] were superior to glyphosate alone (76). The combination of glyphosate plus atrazine appeared to be no more effective than glyphosate alone (82).

Glyphosate has great potential for the control of quackgrass for agricultural and industrial uses (8). Glyphosate is useful for quackgrass control prior to the production of corn, soybeans, navy beans, cereal grains, and turf (24, 36, 82). Glyphosate was utilized to control quackgrass under several species of fruit trees without causing injury (76) and also has potential for use at industrial sites. In most situations, residual herbicides must be utilized to provide season long control of annual weeds (36, 76, 82).

Glyphosate successfully controls a variety of weed species (8). Annual weeds such as common lambsquarter (*Chenopodium album* L.) and yellow foxtail [*Setaria glauca* (L.) Beauv.] are effectively controlled at rates of 1.80 kg/ha or less (8, 76). At higher rates, glyphosate controls johnsongrass (8), Canada thistle [*Cirsum arvense* (L.) Scop.] (8), bermudagress [*Cynodon dactylon* (L.) Pers.] (24), field bindweed (*Convolvulus arvensis* L.) (76) and woody species (76).

Glyphosate Translocation and Mode of Action

Studies of several foliar-applied, phloem-mobile herbicides have been made (49, 63). Hull (40) thought that effectiveness of a foliar-applied herbicide on perennials depends on its basipetal translocation. Phloem-mobile herbicides such as dalapon and amitrole move toward regions of high metabolic activity such as young shoots and rhizome apices (49, 63). Dalapon or amitrole applied to a 10 to 15 cm shoot moved only within the shoot and seldom into the attached rhizome. Both compounds followed the normal source-to-sink relationships (63). Repeated defoliation of johnsongrass did not increase translocation of dalapon to the rhizomes (49). The quantity of parent compound transported to the underground parts and its stability in the plant determine in part whether the perennial was killed. In most cases, dalapon did not appear to be metabolized in the plant (33). Glyphosate, like dalapon and amitrole, kills the rhizomes of quackgrass. It is likely that glyphosate is phloem-mobile and acts similarly to dalapon and amitrole.

The mode of action of glyphosate appears to be the inhibition of chorismate mutase or prephenate dehydratase. With duckweed (*Lemma gibba*), L-phenylalanine reversed the growth inhibition of the herbicide. Tyrosine induced the same injury symptoms to *Lemma* as the herbicide. However, the toxicity symptoms could not be reversed by the addition of metal ions (51).

Soil Adsorption of Herbicides

The chemical and physical properties of the soil are controlled by constituents with reactive surfaces. The colloidal fraction, having the most reactive surface, can be divided into the organic matter and clay fraction (3). The humic acid portion contains carboxyl and phenolic hydroxyls (83). The cation exchange capacity of humic acid is 200 to 400 meq/100 g. Humic acid directly affects the binding of cationic and anionic pesticides (3). The clays can be divided into two main structural groups on the basis of the ratio of silicate to aluminum layers (89). Montmorillonite, a 2:1 type structure, is characterized by having a large surface area and a high exchange capacity. Illite, a non-expanding 2:1 type structure, has a lower cation exchange capacity. Kaolinite, a 1:1 structure, has the lowest surface area and cation exchange capacity.

The oxides and hydroxides of silica, iron, and aluminum, generally characterized by low surface area and low surface charge, may occur in separate phases or as coatings on surfaces of the layer silicates (3).

Soil type affects herbicide inactivation as it relates to adsorption, chemical degradation, and microbial degradation. Adsorption is dependent on the type of herbicide adsorbed and the type of clay (3). Cationic herbicides can be adsorbed by montmorillonite in quantities equivalent to the exchange capacity of the clay (100). Anionic herbicides as 2,4-D[(2,4-dichlorophenoxy)acetic acid] are weakly bound by montmorillonite (4). Organic matter also affects herbicide adsorption. Talbert and Fletchall (87) found that organic matter was more adsorptive to *s*-triazines than clay. Upchurch *et al.* (95) found that the toxicity of a diverse group of herbicides was positively correlated with organic matter. The toxicity of paraquat

(1,1'-dimethyl-4,4'-bipyridinium ion) is related to the degree of binding of the compound to the soil aggregate (91).

The chemical character of the compound determines its chemical properties as solubility and acidity (3). Frissel (38) found that the pKa was important in determining the extent and ease of binding. 2,4-D and 2,4,5-T[(2,4,5-trichlorophenoxy)acetic acid] gave negative adsorption until the pH of the clay went below the pKa of the herbicides (39). For basic compounds such as the triazines, the dissociation constant of the adsorbent is very important in determining the extent of adsorption (5).

Various environmental factors such as temperature, pH, and phosphorus content can influence adsorption (26, 39, 87). Adsorption of atrazine and simazine decreased as temperature increased (87). Herbicide adsorption generally increases with a decrease in pH (39). The binding of 13 s-triazines increased with a decrease in pH (98). High levels of phosphate in the soil also affect the phytotoxicity of herbicides (26, 94). Although phosphorus interacted with chloramben (3-amino-2,5-dichlorobenzoic acid) and atrazine to produce phytotoxicity, the root uptake of chloramben was not increased by the presence of phosphate (26).

Anionic herbicides such as bentazon (3-isopropyl-1H-2,1,3-benzothiadiazin-(4)3H-one 2,2-dioxide), chloramben, dicamba (3,6-dichloro-o-anisic acid), and picloram (4-amino-3,5,6-trichloropicolinic acid) are readily leached from the soil (1, 18, 44, 88). Leaching of chloramben is dependent on the solubility of the salt (88). Adsorption of dicamba and picloram is greatest at low pH (18, 44). Bentazon is not readily adsorbed by clay or cation exchange resins (1). Picloram and bentazon are adsorbed by anion exchange resins and charcoal (1, 44). Chloramben and dicamba are readily adsorbed by kaolinitic clay (18, 88).

Pesticides are inactivated in the soil by microbial and chemical degradation (69, 99). Amitrole was readily degraded in non-sterile soil (2). Conversely, paraquat did not undergo microbial degradation when bound to montmorillonite (99). Copper promoted the hydrolysis of certain organic phosphate pesticides in a pH range where they were usually stable (69).

Adsorption of Glycine and Phosphate

Glyphosate, a substituted glycine, has no apparent herbicidal activity in the soil (8). Since the herbicide consists of glycine and a phosphate group, both possibilities for adsorption should be pursued.

Glycine can be adsorbed both as a cation and as a zwitterion below its isoelectric pH of 2.57. In the cationic form, the amino acid is adsorbed on sodium or calcium montmorillonite with the resultant displacement of Na^+ or Ca^{++}. When the adsorption is by ion exchange as previously discussed, glycine resists displacement by water but can be displaced by salt solutions. A second means of cation adsorption is protonation of the amino acid at the adsorbent surface. The protons are available from exchangeable H^+ or from water associated with highly electronegative cations. In this case, glycine is not lost by washing with water (43). The zwitterion adsorbs to montmorillonite by physical forces and is easily removed by washing with water (37).

Other methods of amino acid adsorption have been proposed. The dipoles of amino acids and the exchangeable cation may interact with dispersive forces between the surface and the amino acid (43). This type of adsorption could occur near the isoelectric pH without proton transfer or cationic exchange (42). Adsorption apparently involves salt formation between a polyvalent metal ion and a functional group of the amino acid (20). Greenland (41) proposed a similar theory where polyvalent cations bridge between the amino acid and the clay.

With development of various adsorption mechanisms, exchangeable cations are important since they determine proton availability, coordination of carboxyl or amino groups to the cation, and bridging of the polyvalent cation where the clay neutralizes a charge while the amino acid neutralizes the other. The proposed mechanisms still apply to the amino acids at pH or below their isoelectric points (69). Therefore, the amino and carboxyl groups may not contribute significantly to their binding under normal soil pH conditions.

The phosphate group on the glyphosate molecule is potentially the most important in soil inactivation. To understand its possible reaction, phosphate adsorption must be reviewed.

Phosphate in the soil is present in both organic and inorganic forms (47). Inorganic phosphate may be bound by the soil in several different ways (89). Phosphate often combines with aluminum or iron to form crystalline precipitates (21, 48). The solubility of phosphate compounds decrease with time (89). The minimum solubility of Al-P is at pH 6 (84). Under laboratory conditions, crystallization of Al-P and Fe-P in water solution took 40 days at 105 C. Colloidal precipitates of Al-P and Fe-P are available to plants while crystallization makes them unavailable to plants (53). The minimum quantity of phosphate to cause precipitation of iron and aluminum phosphates is 0.1 to 1 ppm (86). For extensive precipitation to occur, 5 to 7 ppm of phosphate must be present in the soil solution (29). If iron and aluminum are removed from the clay surface, only one-half as much phosphate is adsorbed. Montmorillonite adsorbs more phosphate than kaolinite (22). The anion exchange capacity of kaolinite is one-half the cation exchange capacity (57). Black (11) claims that aluminum is responsible for adsorption in montmorillonite while iron and aluminum is responsible for adsorption of phosphates in illite. Phosphorus adsorbs to the surface of iron and aluminum oxides on the surface of kaolinite clay (12).

Iron and aluminum oxides and hydroxides also bind inorganic phosphate (34, 89).

Clay minerals can bind phosphate without exchangeable aluminum or iron present (61, 71, 80). The hydroxyl group from the broken edge of the aluminum layer may be displaced and replaced by phosphate (71, 80). Conversely, the phosphate may lose a hydroxyl and bind to the oxygen on the clay (29). In general, 1:1 type clays have more hydroxyl groups exposed than 2:1 type clays. At low pH, the hydroxyl would be most easily lost (72). Upon grinding, kaolinite binds larger quantities of phosphate than before grinding (68).

Divalent cations were thought to form absorbent-cation-phosphate linkages or cationic bridges in the soil (77). Levesque and Schnitzer (59) found that phosphates form a fulvic acid-metal-phosphate complex. Others thought that divalent cations could form clay-cation-phosphate bridges (77). Calcium-saturated clay adsorbs more phosphate than sodium-saturated clay. With any clay, the mechanism of cationic bridging most likely exists at a pH of 6.5 (89). One investigator found that when iron or aluminum was available, a clay adsorbed the same quantity of phosphate whether the ions were bound or displaced from the clay. The exchangeable cation effect was found with both monovalent and divalent cations (104).

A number of anions such as arsenate, hydroxyl oxalate are competitive with phosphate ions for binding in the soil (89).

In alkaline soil, calcium phosphate precipitates are readily formed. As the pH increases, the phosphates are precipitated into various calcium phosphate compounds. High pH and high calcium activity increases the rate of calcium phosphate precipitation. As pH increases, calcium phosphate compounds become more insoluble. Under high pH conditions, soils with free calcium carbonate cause the precipitation of phosphate on its surface (89).

After studying phosphate fixation, researchers found that fixation initially occurs rapidly and then slows. The fast fixation is the reaction of phosphate with the available iron and aluminum. The slow fixation appears to be the reaction of phosphate with the iron and aluminum released from minerals (46).

Large quantities of organic phosphates are present in the soil from the incorporation of plant and animal residues (89). One source of organic phosphate is phytin, the insoluble salts of inositol phosphate (47). Nucleic acids are also found in the soil. Adsorption of nucleic acids decreases with increasing pH and increases with the cation exchange capacity. Adsorption is reversible in that inositol phosphate or citrate decreases the binding of nucleic acids to bentonite or kaolinite. Adsorption of nucleic acids to calcium or magnesium-saturated clays are

greater than adsorption to a sodium or potassium-saturated clay. Microbial degradation of nucleic acid appears to be retarded by adsorption (40).

In summary, inorganic and organic phosphates are bound tightly in the soil by a wide variety of mechanisms.

CHAPTER 2

SYSTEMS FOR QUACKGRASS CONTROL IN AGRONOMIC CROP PRODUCTION

Abstract

Preplant applications of glyphosate [*N*-(phosphonomethyl)glycine] provide effective quackgrass [*Agropyron repens* (L.) Beauv.] control in agronomic crops without crop injury. In corn (*Zea mays* L.), glyphosate at 1.12 or 2.24 kg/ha gave more effective control of 25 to 30 cm (3 to 4-leaf) tall quackgrass than 15 to 20 cm (2 to 3-leaf) tall quackgrass. Older stages of growth required at least 2.24 kg/ha of glyphosate for control. Fall and spring applications are equally effective. Glyphosate plus atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine], 1.12 + 2.24 kg/ha or 1.12 + 3.36 kg/ha gave 90% or greater control. Late spring applications of glyphosate at 1.12 or 2.24 kg/ha gave 88 to 98% control of quackgrass subsequently planted in soybeans [*Glycine max* (L.) Merr.] and navy beans (*Phaseolus vulgaris* L.)

Introduction

Quackgrass, a serious perennial weed in the northeast and northcentral United States (8), produces both seeds and rhizomes but propagation by rhizomes is the most important means of dissemination in field crops (7). A field with a heavy quackgrass infestation may contain 13,440 kg/ha of rhizomes and roots (8).

The capacity of quackgrass to reduce yields has long been known. Although yield reductions were attributed to competition for light (6), nutrients (7, 10), and water (13), additions of nitrogen and potassium under favorable growing conditions failed to overcome the entire yield reduction attributed to competition (2). Osvold (10) found that quackgrass rhizomes produced a substance phytotoxic to plants.

Amitrole (3-amino-s-triazole) plus ammonium thiocyanate (NH_4SCN), dalapon (2,2-dichloropropionic acid) and atrazine have been used for quackgrass control in agronomic crop production. The utility of amitrole and dalapon, two foliar-applied herbicides, is determined by their effectiveness for quackgrass control and their soil residue. The stage of growth, season of treatment, and time of tillage affect the quackgrass control with amitrole or dalapon (5, 9, 11). The stage of growth influences the extent of translocation of dalapon and amitrole into the rhizomes (9). Fall application of dalapon at a given rate was more effective than spring application (11). Tillage within 2 weeks after dalapon application increased quackgrass control (5). At best, dalapon and amitrole plus NH_4SCN gave incomplete control. The presence of a soil residue toxic to crop plants has limited the use of dalapon and amitrole plus NH_4SCN for quackgrass control in agronomic crops. With dalapon, susceptible crops as corn and soybeans should not be planted for at least 4 weeks after treatment (4). At present, amitrole cannot be used on cropland areas. Atrazine can provide effective control of quackgrass in corn. A single preplant application of 2.24 kg/ha gave inconsistent quackgrass control whereas split applications of 2.24 kg/ha prior to plowing followed by 2.24 kg/ha preemergence gave effective quackgrass control (4). Adequate quackgrass control with atrazine depended on the time of application and the proximity of the herbicide to the rhizomes (4, 12). Atrazine residues are often toxic to subsequent crops. Buchholtz (3) found that 2.24 kg/ha applied one year produced injury to one-half of the oat plots the following year.

In 1971, glyphosate was introduced as a nonselective herbicide active on perennial weeds and had no apparent soil residue in mineral soils (1). With these properties, the herbicide could be used to control quackgrass a week prior to the planting of agronomic crops.

The purpose of this study was to determine: (a) the effect of rate, tillage, stage of quackgrass growth, and time of glyphosate application on quackgrass control, and (b) the feasibility of using glyphosate for quackgrass control for corn, soybeans, and navy beans.

Materials and Methods

Field studies during 1971, 1972, and 1973 were conducted at several locations in southern Michigan. Plots were 3.1 by 12.2 m or 3.1 by 15.2 m and the treatments were replicated three or four times. The herbicides were applied with a tractor-mounted sprayer at 2.11 kg/cm^2 pressure and 215 L/ha. In 1971, the mono(dimethylamine) salt of glyphosate formulated as a 1.48 kg/L water soluble concentrate was used and 0.8% (v/v) of MON 0027[1] surfactant was added. In 1972 and 1973, the formulation[2] of glyphosate used contained 0.89 kg/L of glyphosate as the isopropylamine salt and 0.45 kg/L of surfactant. Quackgrass and annual weed control were visually rated on a percentage basis where 0 equals no control and 100 equals complete control. The two middle rows (152 cm) of each four row plot were rated.

[1] MON 0027 is a non-ionic surfactant produced by Monsanto Company, St. Louis, Missouri.

[2] The MON 2139 formulation was used in 1972 and contained non-ionic MON 0818 surfactant. In 1973, the commercial formulation known as Roundup^R was used. These are produced by Monsanto Company, St. Louis, Missouri.

The first field experiment (Tables 1 to 4) was conducted to determine the effect of time of application and time of plowing on quackgrass control with glyphosate and atrazine and their combinations. The plots were arranged in a split-plot design with three replications. In 1971, glyphosate was applied to 15 to 25 cm (3 to 4-leaf) tall quackgrass at rates of 0.28 to 4.48 kg/ha on September 27. Spring applications of the same rates were made on May 3, 1972 to 10 to 15 cm (2 to 3-leaf) tall quackgrass. The plots were fall-plowed on October 15, 1971 and spring-plowed on May 20, 1972. The area was disked twice and planted to 'Michigan 400' corn on May 22, 1972 and cyanazine [2-[[4-chloro-6-(ethylamino)-s-triazin-2-yl] amino]-2-methylpropionitrile] plus alachlor [2-chloro-2', 6'-diethyl-N-(methoxymethyl)acetanilide], 1.12 + 2.24 kg/ha was applied preemergence to the entire area. Preemergence treatments of atrazine were applied on May 26, 1972. The quackgrass control with fall application was rated 6, 13, and 25 days after treatment. The fall-treated plots were again evaluated on May 20, 1972 while all plots were evaluated on July 5, 1972. In the second year of the study, 15 to 25 cm (3 to 4-leaf) tall quackgrass was treated on October 2, 1972 with glyphosate. Spring applications were made on May 10, 1973 to 20 to 28 cm (3 to 4-leaf) tall quackgrass. The area was fall-plowed on October 16, 1972 and spring-plowed on May 20, 1973. After disking, 'Michigan 396' corn was planted on June 1, 1973. The preemergence treatments of atrazine were applied and cyanazine plus alachlor, 1.12 + 2.24 kg/ha was broadcast on June 2, 1973. The plots were evaluated 6, 13, and 25 days after fall treatment and again evaluated on May 20 and July 30.

The next experiment was done to compare glyphosate and other herbicides for quackgrass control (Table 5). The herbicides were applied to 25 to 30 cm (4 to 5-leaf) tall quackgrass on June 17, 1971 and to 25 to 50 cm (4 to 6-leaf) tall quackgrass on June 5, 1973. The plots were evaluated in 1971 on July 23 and in 1973 on August 2. No preemergence herbicides or tillage were used for annual weed control.

Late spring applications of glyphosate were used to control quackgrass prior to planting soybeans (Table 6). In 1972, 25 to 30 cm (4-leaf) tall quackgrass was treated with 1.12 or 2.24 kg/ha of glyphosate on May 15. The area was plowed on May 24 and planted to 'Anoka' soybeans on June 7. Preplant incorporated and preemergence herbicides were applied on June 7 for annual weed control. The plots were visually evaluated on July 14. In 1973, 1.12 or 2.24 kg/ha of glyphosate was applied to 20 to 25 cm (3 to 4-leaf) quackgrass on May 17. After plowing on May 24, the plots were planted to 'Hark' soybeans on May 26. Preplant incorporated and preemergence herbicides were applied on May 26 and the area was rated on August 2.

Spring applications of glyphosate were used to control quackgrass prior to planting navy beans (Table 7). Various preplant incorporated and preemergence herbicides

were used to determine the compatibility of the systems of weed control. In 1972, 1.12 and 2.24 kg/ha of glyphosate were applied to 25 to 30 cm (3 to 4-leaf) tall quackgrass on May 15. The area, plowed and disked 9 days later, was treated on June 7 with preplant incorporated or preemergence herbicides for annual weed control and was planted to 'Gratiot' navy beans the same day. The area was visually rated on July 14. In 1973, two rates of glyphosate were applied to 20 to 30 cm (3 to 4-leaf) tall quackgrass on May 10 and the area was plowed on May 20. On June 1, the preplant incorporated or preemergence herbicides were applied and the 'Sanilac' navy beans were planted. The plots were rated on August 1 for quackgrass and annual weed control.

Results and Discussion

Fall applications of glyphosate gave relatively rapid kill with the higher rates tested (Table 1). The initial control was more rapid in 1972 than in 1971. At rates of 1.12 kg/ha and above, control of quackgrass was complete in 25 days. Tillage after fall application may increase control (Table 2). In 1972, tillage increased quackgrass control at 0.56 kg/ha from 48% to 84% while with higher rates control was not affected. In 1973, tillage did not appear to increase control.

Four possible combinations or systems of fall or spring treatment and fall or spring plowing were compared

Table 1.--Control of quackgrass shoots with time after fall application of glyphosate.

Glyphosate	Days after application[b]					
	6		13		25	
	1971	1972	1971	1972	1971	1972
(kg/ha)	(% control)[a]					
0.56	17 a	23 a	23 ab	50 c	37 b-d	92 e
1.12	27 a-c	32 b	53 d	72 d	97 f	97 f
1.68	50 d	37 b	77 e	78 d	97 f	100 g
2.24	47 cd	37 b	80 e	78 d	100 f	99 g

[a] Means of each year's data with common letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] The herbicide was applied in 1971 on September 27 and in 1972 on October 3.

Table 2.--The effect of tillage on quackgrass control 6 months after fall applications of glyphosate.

Glyphosate	Tillage[b]			
	Fall plowed		No plowing	
	1972	1973	1972	1973
(kg/ha)	(% control)[a]			
0.28	23 ab	67 a	17 a	63 a
0.56	84 c	82 b	45 b	82 b
1.12	95 c	86 bc	89 c	92 c
1.68	94 c	89 bc	96 c	91 bc
2.24	98 c	91 bc	94 c	88 bc

[a] Means of each year's data with common letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] In 1971, the herbicide was applied on September 27 and the plots plowed on October 15. In 1972, the herbicide was applied on October 3 and the plots plowed on October 16. The plots were evaluated the following spring on May 20 both years.

(Table 3). In 1972, fall treatment followed by fall plowing was most effective with glyphosate at 1.68 kg/ha giving 92% control. Fall treatment followed by spring plowing was consistently less effective with 1.68 kg/ha showing 87% control. Spring application were less effective than fall application. Spring treatment followed by spring plowing gave 83% control. The least effective treatment was fall plowing followed by spring application where 1.68 kg/ha of glyphosate gave 50% control. The same conclusion can be drawn from observing the overall trend of control with increasing rate in each of the various systems. In 1973, fall applications followed by fall plowing or spring application followed by spring plowing gave nearly equivalent control. At rates between 0.28 and 1.68 kg/ha, the fall application was superior to spring application. At the higher rates, there was little difference in control between the two treatments except at the two highest rates. Fall application followed by spring plowing or fall plowing followed by spring application was less effective than two previous treatments. In comparing these two treatments, the fall application was more effective than spring application at rates above 2.24 kg/ha. No crop injury was observed.

The differences in control between fall and spring application may be explained by the stage of growth at the time of treatment. In 1972, the quackgrass treated in the fall was much larger than the quackgrass treated in the

Table 3.--The effects of fall or spring application and tillage on quackgrass control with glyphosate.

Glyphosate	Times of herbicide application and tillage[b]							
	Fall treatment, fall plowed		Fall treatment, spring plowed		Spring treatment, fall plowed		Spring treatment, spring plowed	
	1972	1973	1972	1973	1972	1973	1972	1973
(kg/ha)	(% control)[a]							
0.28	17 bc	57 b-d	10 ab	45 ab	3 a	53 bc	23 cd	38 a
0.56	37 d-f	77 e-i	33 de	66 c-e	33 de	59 b-d	47 e-h	65 c-e
1.12	77 i-k	91 j-m	60 g-i	74 e-g	67 h-j	75 e-g	63 g-j	87 g-l
1.68	92 k-n	90 j-m	50 e-h	70 d-f	87 k-n	82 f-j	84 j-m	82 f-j
2.24	96 l-n	91 j-m	57 f-i	74 e-g	92 k-n	76 e-h	83 j-m	90 i-m
2.80	97 mn	93 l-m	60 g-i	75 e-g	95 l-n	89 h-m	83 j-m	93 k-m
3.36	95 l-n	94 l-m	43 d-g	66 c-e	91 k-n	78 e-i	83 j-m	91 j-m
3.92	99 n	95 l-m	60 g-i	81 f-j	95 mn	94 l-m	81 j-l	83 f-j
4.48	96 l-n	96 m	53 e-h	83 f-j	93 k-n	90 j-m	87 k-m	83 f-k

[a] Means of each year's data with common letters are not significantly different at the 5% level of Duncan's Multiple Range Test.

[b] In the 1972 study, the plots were sprayed with herbicides in the fall of 1971 on September 27 or in the following spring on May 3. The area was fall-plowed on October 15, 1971 or spring-plowed on May 20, 1972. The plots were visually evaluated on July 5, 1972. In the 1973 study, the plots were sprayed with herbicides in the fall of 1972 on October 3 or the following spring on May 10. The area was fall-plowed on October 1, 1972 or spring-plowed on May 20, 1973. The plots were visually evaluated on July 30, 1973.

spring. The poorest treatment, fall plowing followed by spring application was ineffective because tillage had buried many rhizomes too deeply for the shoots to emerge by the time of treatment and the shoots which had emerged were too small for effective control. In 1973, fall and spring applications were made at the same stage of growth because spring treatments were made one week later than in 1972. As a result, there was little difference in control between fall and spring applications.

Combinations of atrazine and glyphosate were tested for quackgrass control (Table 4). The earlier studies, glyphosate at rates of 0.56 to 1.12 kg/ha often gave unsatisfactory control. Usually, atrazine at 2.24 kg/ha does not injure subsequent crops (4) but does provide reasonable quackgrass control. It was postulated that if the initial glyphosate application could significantly reduce the quackgrass infestation, preemergence applications of atrazine applied as part of the annual weed control program would nearly eradicate the quackgrass and still not injure subsequent crops. This practice might increase quackgrass control the first season as well as provide greater longevity of control. The initial control obtained from glyphosate usually determined the subsequent effectiveness of this combination. If the glyphosate does not provide at least 60 to 70% quackgrass control, the combination seldom results in 90% or greater control (Table 4).

Table 4.--The effects of time of herbicide application and time of tillage on quackgrass control with glyphosate, atrazine, and their combinations in corn.

Chemical	Rate	Times of herbicide application and tillage[b]							
		Fall treatment, fall plowed		Fall treatment, spring plowed		Spring treatment, fall plowed		Spring treatment, spring plowed	
		1972	1973	1972	1973	1972	1973	1972	1973
	(kg/ha)	(% control)[a]							
Glyphosate	0.56	37 ab	77 f-h	33 a	66 e-g	33 a	59 de	47 a-d	65 ef
Glyphosate	1.12	77 e-i	91 i-o	60 c-f	74 fg	67 d-h	75 f-h	63 d-g	87 h-l
Glyphosate	2.24	96 l-m	91 j-o	57 b-e	74 fg	92 i-m	76 f-h	83 g-l	90 i-n
Atrazine	2.24	70 e-h	30 ab	63 d-g	47 cd	30 a	28 ab	37 ab	25 a
Atrazine	3.36	60 c-f	42 bc	67 d-h	50 cd	40 a-c	42 bc	33 a	48 cd
Glyphosate + atrazine	0.56 + 2.24	77 e-i	95 l-o	67 d-h	66 e-g	70 e-h	92 j-o	67 d-h	80 g-j
Glyphosate + atrazine	1.12 + 2.24	95 l-m	97 no	74 e-i	77 f-h	92 i-m	93 k-o	92 i-m	95 m-o
Glyphosate + atrazine	2.24 + 2.24	96 l-m	97 no	83 g-l	80 f-i	95 k-m	93 k-o	94 k-m	96 l-o
Glyphosate + atrazine	0.56 + 3.36	86 h-l	94 k-o	77 e-i	79 f-i	87 h-l	95 l-o	80 f-k	89 h-m
Glyphosate + atrazine	1.12 + 3.36	98 m	93 k-o	77 e-j	84 h-k	93 j-m	98 o	83 g-l	95 l-o
Glyphosate + atrazine	2.24 + 3.36	99 m	97 no	83 g-l	90 i-n	99 m	96 l-o	92 i-m	95 l-o

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[a] Means of each year's data with common letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] In the 1972 study, the plots were sprayed with herbicides in the fall of 1971 on September 27 or in the following spring on May 3. The area was fall-plowed on October 15, 1971 or spring-plowed on May 20, 1972. The plots were visually evaluated on July 5, 1972. In the 1973 study, the plots were sprayed with herbicides in the fall of 1972 on October 3 or in the following spring on May 10. The area was fall-plowed on October 16, 1972 or spring-plowed on May 20, 1973. The plots were visually evaluated on July 30, 1973.

The glyphosate plus atrazine combinations, 1.12 + 2.24 kg/ha or 1.12 + 3.36 kg/ha respectively gave 90% or greater control in three of the four treatment-tillage systems. Increasing the rate of glyphosate to 2.24 kg/ha did not substantially increase quackgrass control.

Glyphosate was compared to several other post-emergence herbicides for quackgrass control (Table 5). In 1971 and 1973, maximum or near maximum control was obtained with 2.24 kg/ha of glyphosate. Dalapon at 11.2 kg/ha gave 70% or greater control both years. Amitrole plus NH_4SCN[3] at 2.24 kg/ha was equal or more effective than 1.12 kg/ha of glyphosate under the conditions of the experiment. Atrazine plus crop oil, 4.48 kg/ha + 9.36 L/ha was the most effective treatment used. Several things are apparent from the study. The quackgrass was too tall for maximum control with dalapon and amitrole. At the taller quackgrass height in 1973, 2.24 kg/ha was needed to give effective quackgrass control. In 1973, glyphosate at 2.24 or 4.48 kg/ha gave control nearly equivalent to 4.48 kg/ha of atrazine.

Glyphosate at 1.12 or 2.24 kg/ha gave 93% or greater control of quackgrass in soybeans (Table 6). The preplant

[3] The commerical formulation of amitrole plus NH_4SCN used in this study is sold as Amitrole-T by American Cyanamid Company, Princeton, New Jersey.

Table 5.--Quackgrass control with glyphosate and other herbicides.

Chemical	Rate	Control, %[a]	
		1971	1973
	(kg/ha)		
Glyphosate	0.56	47 a	23 a
Glyphosate	1.12	67 ab	38 b
Glyphosate	2.24	77 b	91 d
Glyphosate	4.48	67 ab	95 e
Amitrole	2.24	43 a	45 b
Dalapon	11.20	70 b	82 c
Atrazine + oil	4.48 + 9.35[b]	80 b	96 e

[a] Means with common letters within a column are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] The oil was applied in L/ha.

[c] The plots were treated in 1971 on June 17 and in 1973 on June 5. Visual evaluations were made in 1971 and in 1973 on July 23 and August 2, respectively.

Table 6.--A system for soybean weed control using spring applications of glyphosate for quackgrass control followed by preplant incorporated or preemergence compounds for annual weed control.

Glyphosate rate	Preplant incorp. or preemergence chemical	Rate	Crop injury, %[a]	Control, %					
				Quack-grass		Rag-weed		Grass	
			1972	1972	1973	1972	1973	1972	1973
(kg/ha)		(kg/ha)							
0	Chloramben........	3.36	8 ab	0 a	0 a	. .	83 bc	. .	84 bc
1.12		3.36	3 ab	93 b	95 b	80 b	83 bc	91 b	69 ab
2.24		3.36	18 b	94 b	96 b	83 b	95 c	88 b	68 ab
0	Trifluralin[c]......	0.84	0 a	0 a	0 a	. .	63 a-c	. .	64 ab
1.12		0.84	5 ab	97 bc	97 b	12 a	45 a	90 b	71 ab
2.24		0.84	12 ab	96 bc	98 b	15 a	57 ab	65 a	68 ab
0	Metribuzin........	0.56	8 ab	0 a	0 a	. .	100 c	. .	79 ab
1.12		0.56	5 ab	95 bc	94 b	60 b	100 c	85 b	54 a
2.24		0.56	8 ab	96 bc	95 b	78 b	100 c	93 b	60 a
0	Metribuzin + alachlor..........	0.28 + 2.24	12 ab	0 a	0 a	. .	85 bc	. .	98 cd
1.12		0.28 + 2.24	12 b	98 c	95 b	80 b	100 c	100 b	95 cd
2.24		0.28 + 2.24	10 ab	96 bc	95 b	78 b	89 bc	98 b	100 d

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[a] Means with common letters within a column are not significantly different at the 5% level of Duncan's Multiple Range Test.

[b] In the 1972 study, the plots were sprayed with glyphosate on May 15. The area was plowed on May 24, planted to soybeans on June 7, and sprayed for annual weed control on June 7. Plots were visually rated on July 14. In 1973, the plots were sprayed with glyphosate on May 17. The area was plowed on May 24, planted to soybeans on May 26, and sprayed for annual weed control on May 26. The plots were evaluated on August 2.

[c] The herbicide was preplant incorporated.

applications of glyphosate in combination with the preplant incorporated or preemergence herbicides used for annual weed control did not appear to cause any erratic weed control or increased crop injury over the herbicides used alone for annual weed control. The ragweed and grass control ratings remained constant with or without quackgrass control with glyphosate. Although the crop injury was variable, it did not appear to increase with increasing rates of glyphosate used. Spring applications of glyphosate can provide excellent quackgrass control in soybeans.

Glyphosate at 1.12 or 2.24 kg/ha gave 88% or greater quackgrass control in navy beans. The system using glyphosate for quackgrass control and the preplant incorporated or preemergence herbicides for annual weed control and did not appear to decrease quackgrass and annual weed control or increase crop injury (Table 7).

Glyphosate can be useful for quackgrass control in the production of corn, soybeans, and navy beans in Michigan. With corn, fall treatment of quackgrass may be the most practical. First, quackgrass does not grow tall enough to treat until mid-May while corn should be planted in early May. If a quackgrass-infested area is fall-treated, the quackgrass still must be actively growing and in the proper stage of growth at the time of treatment. The fall treatment may be limited by the steepness of land treated. If the land is likely to erode, complete vegetation control with glyphosate may cause significant loss of

Table 7.--A system for navy bean weed control using spring applications of glyphosate for quackgrass control following by preplant incorporated or preemergence herbicides for annual weed control.

Glyphosate rate	Preplant incorp. or preemergence chemical	Rate	Crop injury, %[a]	Control, %					
				Quack-grass		Rag-weed		Grass	
			1972	1972	1973	1972	1973	1972	1973
(kg/ha)		(kg/ha)							
0	EPTC[c]	3.36	5 bc	0 a	39 a	. .	16 a-c	. .	99 de
1.12		3.36	10 c	92 b	98 c	20 b	23 bc	94 ab	98 c-e
2.24		3.36	10 c	95 b	96 c	20 b	20 a-c	83 ab	95 a-e
0	Trifluralin[c]	0.84	0 a	0 a	8 a	. .	0 a	. .	83 a
1.12		0.84	3 ab	93 b	93 c	3 a	0 a	85 ab	90 ab
2.24		0.84	3 ab	95 b	94 c	8 a	13 ab	85 ab	91 a-c
0	Alachlor	3.36	10 c	0 a	15 a	. .	41 c	. .	100 e
1.12		3.36	10 c	98 b	96 c	43 b	33 bc	100 b	99 de
2.24		3.36	10 c	97 b	97 c	33 b	30 bc	95 b	98 b-e
0	Chloramben	2.24	0 a	0 a	0 a	. .	86 d	. .	95 a-e
1.12		2.24	3 ab	89 b	88 c	45 b	84 d	68 a	91 a-d
2.24		2.24	0 a	97 b	90 c	43 b	85 d	88 ab	84 a

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[a] Means with common letters within a column are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] In the 1972 study, the plots were sprayed with glyphosate on May 15. The area was plowed on May 24, planted to navy beans on June 7, and sprayed for annual weed control on June 7. Plots were visually rated on July 14. In 1973, the plots were sprayed with glyphosate on May 10. The area was plowed on May 20, planted to navy beans on June 1, and sprayed for annual weed control on June 1. The plots were evaluated on August 1.

[c] The herbicide was preplant incorporated.

the topsoil. Spring treatment of quackgrass may only be useful if the area treated is planted to silage corn which can be planted as late as June 1. Glyphosate can be extremely useful in control of quackgrass prior to growing soybeans or navy beans. By May 15, quackgrass is usually large enough to obtain effective control with glyphosate. Within a week after treatment, the area can be plowed and readily planted to a crop. Since soybeans are usually planted in late May and navy beans are planted in early June, glyphosate will fit into the present cropping systems.

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CHAPTER 3

RAPID INACTIVATION OF GLYPHOSATE IN THE SOIL

Abstract

In greenhouse studies, soil applications of ^{14}C-methyl-labeled glyphosate [*N*-(phosphonomethyl)glycine] were not readily absorbed by corn (*Zea mays* L. 'Michigan 400') and soybeans [*Glycine max* L. Merr. 'Hark']. Wheat (*Triticum aestivum* L. 'Avon'), a sensitive bioassay plant, was used to detect the herbicide. Clay loam and muck rapidly inactivated 56 kg/ha of glyphosate. Autoclaving of the soil did not prevent the inactivation of glyphosate. In a sandy clay loam, application of 56 kg/ha decreased plant growth with increasing pH. Additions of 96 or 196 kg/ha of phosphate to the soil surface decreased glyphosate inactivation in the soil.

Introduction

Glyphosate, a nonselected postemergence herbicide introduced in 1971, has excellent herbicidal activity on a diverse group of herbaceous perennial weeds (2).

Applications of glyphosate at proposed use rated did not injure crops planted immediately after herbicide treatment (3). With these properties, the herbicide could be used for perennial weed control in agronomic and vegetable crops, in orchards, and in industrial areas. Since the herbicide has the potential for widespread use, it is necessary to determine the factors influencing its herbicidal activity in the soil. With most pesticides, chemical degradation, microbial degradation, and adsorption determine their availability to plants growing in the soil (1). The objective of this study was to determine the factors influencing the inactivation of glyphosate in the soil.

Materials and Methods

Greenhouse studies were conducted to determine if glyphosate was absorbed from the soil by crop plants. A 946-ml container was filled with Spinks sandy loam soil containing 1.2% organic matter with a pH of 5.7. Four seeds of soybeans or corn were planted 3 cm deep in the soil. After leveling the soil on the pot surface, 30 ml of water was evenly applied to each pot. Then, 5 ml of a 40-ml solution containing 1.6 μCi of ^{14}C-methyl-labeled glyphosate (spec. act. = 1.51 mCi/mM) and 0.032 g of technical grade glyphosate was evenly applied to the surface of each pot. This concentration was equivalent to a glyphosate application of 4.48 kg/ha. The pots were subirrigated and the plants grown in a greenhouse for 16 days at 23 to 27 C.

The plants were harvested and the roots were washed in a series of three distilled water baths. After freezing the plants in dry ice, they were freeze-dried, separated into shoot and root, cut into small pieces, and ground with a mortar and pestle. A representative sample of the plant material was combusted for radioassay by the method of Wang and Willis (4). The treatments were arranged in a completely randomized design with two replications.

A bioassay procedure was deemed desirable to detect glyphosate in the soil. Seven crop species were tested for suitability including flax (Linum usitatissimum L. 'B-5128'), 'Michigan 400' corn, 'Anoka' soybeans, 'Avon' wheat, barley (Hordeum vulgare L. 'Larker'), oats (Avena sativa L. 'Clintland 64') and cucumber (Cucumber sativus L. 'Wisconsin SMR 15'). The bioassay procedure consisted of filling a 946-ml container with 650 ml of sand and putting 10 seeds in each container. Two hundred ml of sand were placed in a 475-ml cup and sprayed at 935 L/ha and 2.11 kg/cm^2 pressure with several rates of glyphosate. The herbicide was thoroughly incorporated into the sand which was then poured over the seeds. The 946-ml container was set into a larger diameter 475-ml container which served as a water reservoir for the large container. The water level in the smaller container was kept high enough to permit optimal plant growth. Fifty ml of a modified no. 1 Hoagland's solution was added 8 and 13 days after planting. The plants were harvested and shoot height, shoot fresh weight, shoot dry weight and percent germination were measured. The treatments were in a completely randomized design with three replications.

A study was initiated to determine how readily wheat seedlings could absorb glyphosate from nutrient solution. Wheat plants were grown in vermiculite. Plants 12 to 16 cm tall were transplanted into 297-ml plastic containers. The plants were suspended in the containers with a sponge rubber disc and grown in 125 ml of modified no. 1 Hoagland's solution with various concentrations of glyphosate added. Only the roots were exposed to the herbicide solution. These plants were placed in the growth chamber at 25 C and 14 klux. After 50 hr, the wheat plants were transplanted to greenhouse soil and grown for 5 days. Fresh weights and dry weights were measured. The treatments were arranged in a completely randomized design with eight replications.

In the remaining experiments, the previously described bioassay procedure was used. Soil was substituted for the sand and 12 wheat seeds were planted per pot. The same sprayer system was used and the level of the water in the outter container was adjusted to promote optimum growth. The plants were grown under greenhouse conditions at 25C and 8 klux, harvested after 16 days, and shoot dry weights measured.

The effect of autoclaving on the soil inactivation of glyphosate was studied. Spinks sandy loam soil was autoclaved at 1.06 kg/cm^2 pressure for 30 minutes. After cooling, seeds were planted in the autoclaved and non-autoclaved soils. The dry weight of the 10 largest plants was measured. The experiment was arranged in a completely randomized design with five replications.

Another greenhouse study was initiated to examine the effect of soil type on glyphosate inactivation. Quartz sand, muck soil (81% organic matter), and a Toledo clay loam with a pH of 7.3 and 3.7% organic matter were used in this study. The average dry weight of the plants was measured. The treatments were arranged in a completely randomized design with four replications.

The effect of pH on the inactivation of high rates of glyphosate was investigated in a greenhouse study. Soil was collected from a field site of Hillsdale sandy loam containing 1.5% organic matter and with a pH which had been adjusted over a 15-year period with ammonium sulfate, calcium nitrate or calcium carbonate to 4.6, 5.1, 5.6, 6.1, and 6.7. The average dry weight of the plants was measured. The treatments were arranged in a completely randomized design with four replications.

Several experiments were initiated to study the effect of phosphate on the soil activity of glyphosate. The Spinks sandy loam was used because it has a low adsorption capacity. The bioassay procedure previously described was used and after rates of 0, 4.48, 11.2, and 56.0 kg/ha of glyphosate were applied, 0.45 or 0.89 g of

Ca $(H_2PO_4)_2 \cdot H_2O$ granules was evenly distributed on the surface of each pot. These phosphate rates were equivalent to 98 and 196 kg/ha of phosphate, respectively. The pots were subirrigated to keep the soil surface moist to solubilize the phosphate. The average dry weight of the plants was measured. Treatments were arranged in a completely randomized design with four replications.

The possible interaction of phosphate levels and pH was also investigated. A Spinks sandy loam soil with a pH of 5.7 was used. Fifty-ml of KH_2PO4, K_2HPO4, or their combination buffered to a pH 6.0 were added to the soil surface in rates equivalent to 98 and 196 kg/ha of phosphate. The average dry weight of the plants was measured. Treatments were arranged in a completely randomized design with four replications.

An experiment was initiated to determine the rapidity of breakdown of glyphosate. The soil bioassay procedure was used with rates of 0 and 56.0 kg/ha of glyphosate applied to the soil. Wheat seeds were planted at 0, 1, 2, 3, 4, and 6 weeks after glyphosate applications and phosphate in the form of $Ca(H_2PO4)_2 \cdot H_2O$ was applied at 0 and 198 kg/ha at these times. The average dry weight of the plants was measured. The treatments were replicated four times in a completely randomized design. All data presented are the means of two experiments with two or more replications per experiment.

Results and Discussion

Only small quantities of ^{14}C-glyphosate were taken up by both corn and soybeans after soil application of glyphosate (Table 1). In soybeans, more herbicide was found in the shoot than in the root while in corn, the quantity of herbicide in the shoot and root were not significantly different. The lack of plant uptake of glyphosate from the soil could be due to rapid microbial degradation, chemical degradation, adsorption to the soil, lack of plant absorption, or several of these factors combined.

Table 1.--Uptake of ^{14}C-methyl-labeled glyphosate by corn and soybeans from a Spinks sandy loam soil.

Species	Plant part	radioactivity	Uptake of total ^{14}C-glyphosate applied[a]
		(dpm)	(%)
Soybean	Shoot	175	0.55b
	Root	34	0.11a
Corn	Shoot	248	0.78b
	Root	154	0.49ab

[a] Means with common letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

The sensitivity of various plants to glyphosate in sand culture was determined. Glyphosate did not affect the germination of corn, soybeans, or wheat (Table 2).

Table 2.--The effect of glyphosate applied in sand culture on the growth of 16-day-old crop plants.

Glyphosate[c]	Crop species					
	Wheat		Corn		Soybeans	
	Germination[a]	Dry wt.	Germination	Dry wt.	Germination	Dry wt.
	(%)	(mg/plant)	(%)	(mg/plant)	(%)	(mg/plant)
0	93 a	33 e	95 a	125 d	100 a	110 d
0.56[b]	98 a	15 c	100 a	47 c	96 a	33 c
1.12[b]	93 a	9 bc	100 a	19 b	93 a	20 b
2.24[b]	95 a	5 ab	98 a	17 b	98 a	11 ab
4.48[b]	93 a	2 a	98 a	4 a	98 a	6 a
0.8% MON 0027 surfactant	93 a	28 d	93 a	102 d	97 a	95 d

[a] Means with common letters within a column are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] 0.8%(v/v)Mon 0027 surfactant added, product of Monsanto Company, St. Louis, Missouri.

[c] Mono(dimethylamine) salt of glyphosate.

The added surfactant caused a significant reduction in shoot dry weight of wheat but no significant reduction in shoot dry weight of corn or soybeans. As the rate of glyphosate increased, the shoot dry weight decreased such that 4.48 kg/ha gave a 93, 94, and 96% reduction in the shoot dry weight of wheat, soybeans, and corn, respectively. If all seven crop species are compared for sensitivity to glyphosate using the parameters of plant height, shoot fresh weight, and shoot dry weight, a wide spectrum of sensitivity to glyphosate was noted (Table 3). Flax appeared to be most sensitive of all species used. Corn, soybeans, and wheat were less sensitive than flax while barley, oats, and cucumber were the least sensitive of all. Although wheat was not the most sensitive to glyphosate, it was the bioassay plant of choice. The more sensitive species caused several problems. The flax seeds germinated poorly while the large seeded plants as corn and soybeans were not as likely to provide a uniform assay for the herbicide. Therefore, wheat was used in the remaining studies as the bioassay plant. Glyphosate inhibited wheat shoot elongation but not seed germination. As a result, shoot fresh weight, shoot dry weight and plant height were useful parameters to measure plant inhibition by glyphosate. Glyphosate caused stunting and failure of the wheat leaves to unfold at 0.56 kg/ha. With increasing concentrations, shoots often failed to emerge and sometimes upon emerging showed chlorotic stripping similar to zinc deficiency.

Table 3.--The effect of 0.56 kg/ha of glyphosate[c] applied in sand culture on the growth of several crop species.

Species	Percent of control[ab]		
	Plant ht.	Shoot fresh wt.	Shoot dry wt.
Flax	14 a	21 a	20 a
Corn	35 b	48 bc	45 b
Soybeans	36 b	42 ab	33 ab
Wheat	56 c	55 bc	52 b
Barley	68 d	72 cd	71 c
Oats	82 e	116 d	100 c
Cucumber	75 de	69 cd	86 c

[a] Means within a column with common letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] The control is the treatment where 0.8% surfactant was applied to the sand.

[c] Mono(dimethylamine) salt of glyphosate.

In the bioassay system, a reduction in growth or plant moisture content was indicative of lack of glyphosate inactivation in the soil.

Glyphosate was readily absorbed from nutrient solution by wheat seedlings (Table 4). Concentrations of 1.2×10^{-4} M caused a significant reduction in plant moisture content compared with the control. As the concentration increased, the moisture content of the plant decreased. Thus, the absence of glyphosate soil activity was not due to the failure of the plants to absorb glyphosate via the roots.

Glyphosate, a substituted amino acid, might possibly be degraded by microbes before germinating plants could absorb sufficient quantities to produce injury. However, the shoot dry weight of wheat plants grown in autoclaved soil treated with 4.48 kg/ha of glyphosate was not significantly different from the shoot dry weights of the control plants grown in autoclaved soil (Table 5). Autoclaving the soil had not prevented glyphosate inactivation. The dry weight of the plants grown in nonautoclaved soil treated with 4.48 kg/ha was not significantly different from the dry weight of the control plants grown in nonautoclaved soil. The release of nutrients from autoclaving resulted in a significantly greater shoot dry weight for the plants grown in autoclaved soil. In addition, the process of autoclaving significantly reduced the microbial population for at least the first 3 to 4 days afterwards. If the

Table 4.--Root uptake of glyphosate by 7-day-old wheat seedlings from nutrient solution.

Glyphosate[b] (moles/L)	Plant moisture content[a] (%)
0	87.8 e
2.9×10^{-5}	86.6 de
5.9×10^{-5}	84.0 cde
1.2×10^{-4}	81.9 c
1.8×10^{-4}	82.4 cd
2.4×10^{-4}	81.3 bc
3.5×10^{-4}	77.4 ab
4.7×10^{-4}	75.6 a
5.9×10^{-4}	76.3 a

[a] Means with common letters are not significantly different at the 5% level of Duncan's Multiple Range Test.

[b] Mono(dimethylamine) salt of glyphosate.

Table 5.--Effect of autoclaving and soil application of glyphosate on the growth of 16-day-old wheat plants in Spinks sandy loam soil.

Soil	Treatment	Dry wt.[a] (mg/plant)
Non-autoclaved soil		
	Control	34.5 a
	Glyphosate,[b] 4.48 kg/ha, surface applied	33.8 a
	Glyphosate, 4.48 kg/ha, incorp.	37.8 a
Autoclaved soil		
	Control	64.8 b
	Glyphosate, 4.48 kg/ha, surface applied	62.2 b
	Glyphosate, 4.48 kg/ha, incorp.	65.1 b

[a] Means with common letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] Mono(dimethylamine) salt of glyphosate.

microbial numbers were low, glyphosate would not have been degraded very rapidly during this time. The wheat also germinated and emerged during the initial 3 to 4 days after planting. If the initial inactivation of glyphosate resulted from microbial degradation alone, the wheat plant would probably have shown glyphosate injury symptoms during growth. From the results of this experiment, it is evident that the rapid soil inactivation of glyphosate was not due to rapid microbial degradation.

The data shown in Table 6 indicates a possible role of soil adsorption in the inactivation of glyphosate. Soil applications of glyphosate at 56.0 kg/ha did not reduce the dry weight of plants grown on a Toledo clay loam or a muck soil. Under field conditions, the proposed application rates are 1.12 to 2.24 kg/ha. This indicates that glyphosate was rapidly inactivated in the soil at rates twenty-five times the proposed use rates.

The pH of the soil had an influence on the inactivation of glyphosate in Hillsdale sandy clay loam (Table 7). At any pH assayed, glyphosate at 4.48 or 11.2 kg/ha did not significantly reduce the dry weight of wheat plants. Glyphosate at 56 kg/ha showed differences due to soil pH. At pH values of 4.6 or 5.1, no significant difference in dry weight between 0 and 56 kg/ha was noted. At pH 5.6, there was a significant difference in dry weight between the treated and the control. As pH increases, the

Table 6.--Effect of glyphosate in sand culture and in the soil on the growth of 16-day-old wheat plants.

Soil type	Glyphosate[b]	Dry wt.[a]
	(kg/ha)	(mg/plant)
Quartz sand....................	0	43.8 b
	4.48	7.0 a
	11.20	6.9 a
	56.00	0.0 a
Toledo clay loam...............	0	54.6 c
	4.48	54.4 c
	11.20	55.3 c
	56.00	51.0 bc
Muck...........................	0	53.9 c
	4.48	51.9 bc
	11.20	58.0 c
	56.00	50.1 bc

[a] Means with common letters are not significantly different at the 5% level of Duncan's Multiple Range Test.

[b] Mono(dimethylamine) salt of glyphosate.

Table 7.--The effect of glyphosate on the dry weight of 16-day-old wheat plants following incorporation into Hillsdale sandy clay loam at several pH levels.

pH	Glyphosate[b] (kg/ha)			
	0	4.48	11.2	56.0
	(mg/plant)[a]			
4.6	20 ab	15 a	19 ab	16 ab
5.1	40 de	39 de	42 de	37 cd
5.6	44 e	43 e	44 e	32 c
6.1	43 de	43 de	43 de	21 b
6.7	40 de	40 de	40 de	18 ab

[a] Means with common letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] Isopropylamine salt of glyphosate.

dry weight decreased indicating that more glyphosate was bound to the soil at the lower pH.

Phosphate also influenced the binding of glyphosate to the Spinks sandy loam soil (Table 8). Glyphosate applied at 11.2 kg/ha with 98 kg/ha of phosphate gave a significant reduction in plant dry weight while 11.2 kg/ha of the herbicide had no effect. The interaction between glyphosate and phosphate was more pronounced at higher rates. From the rates necessary to obtain this response it is apparent that this is not likely to be a problem in the field. The data indicates that the initial glyphosate binding to the soil was reversible with phosphate anions competing with glyphosate for binding sites. It also appears likely that glyphosate was bound through the phosphate group of the herbicide. Since glyphosate in the soil interacted with phosphate to produce a greater reduction in plant dry weight than glyphosate alone, it is apparent that glyphosate became more available and had not been completely degraded. Thus, the initial inactivation of glyphosate in the soil was not due to its rapid chemical degradation.

Surface applications of $Ca\ (H_2PO4)_2$ reduce the pH of Spinks sandy loam soil. A study was designed to determine how pH and phosphate might interact to reduce glyphosate adsorption. Addition of KH_2PO_4 or K_2HPO_4 altered soil pH, however, adjusting the pH to 6.0 elucidated the same phytotoxic response (Table 9). It appears that pH in

Table 8.--The effect of glyphosate on the dry weight of 16-day-old wheat plants following incorporation into Spinks sandy loam soil and surface application of several levels of phosphate.

Glyphosate[b]	Phosphate rate (kg/ha)		
	0	98	196
(kg/ha)		(mg/plant)[a]	
0	45 de	46 e	44 de
4.48	44 de	43 de	41 d
11.2	44 de	36 c	35 c
56.0	18 b	13 a	12 a

[a] Means with common letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] Isopropylamine salt of glyphosate.

Table 9.--The effect of pH and phosphate levels on the availability of soil-applied glyphosate in Spinks sandy loam soil as measured by the dry weight of 16-day-old wheat plants.

Phosphate source	Rate	pH	Glyphosate (kg/ha)[b]	
			0	56
	(kg/ha)		(mg/plant)[a]	
Control	0	5.7	50 d	29 c
KH_2PO_4	98	5.4	51 d	11 ab
KH_2PO_4	196	5.4	51 d	9 ab
K_2HPO_4	98	6.1	53 d	13 b
K_2HPO_4	196	6.3	49 d	6 a
K_2HPO_4+KH_2PO_4(pH 6.0)	98	5.5	49 d	11 ab
K_2HPO_4+KH_2PO_4(pH 6.0)	196	5.6	51 d	9 ab

[a] Means with common letters are significantly different at the 5% level by Duncan's Multiple Range Test.

[b] Isopropylamine salt of glyphosate.

the range of 5.4 to 6.3 did not have a significant effect on binding (Table 9). From this experiment, it is more apparent that glyphosate and phosphate may be competing for the same binding sites.

In comparing two rates of glyphosate without added phosphate, the dry weight of wheat planted one week after application was no longer significantly different from the control (Table 10). In comparing glyphosate at 0 and 56.0 kg/ha with 196 kg/ha phosphate added, the dry weight of the wheat plants was reduced for 0, 1, 2, and 4 weeks after treatment. After 6 weeks, glyphosate or glyphosate and phosphate did not reduce the dry weight of wheat plants from the control. This indicated that glyphosate degrades in the Spinks sandy loam soil even when extremely high rates are applied. Furthermore, either the rate of binding was slow for high rates or the inactivation occurring with the elapse of time involved microbial degradation of glyphosate not inactivated by binding to soil.

In summary, glyphosate was rapidly inactivated in the soil. Corn and soybean plants grown for 16 days absorbed only very small quantities from the soil. However, glyphosate could be absorbed by the wheat seedling from nutrient solution. The initial inactivation of glyphosate was not the result of its rapid microbial degradation in the soil. However, the rapid inactivation of large quantities of glyphosate by organic and mineral soils

Table 10.--The effect of soil[c] application of glyphosate and subsequent phosphate application on the dry weight of 16-day-old wheat plants seeded at various time intervals after herbicide application.

Phosphate	Glyphosate[b]	Time after applications (wk)					
		0	1	2	3	4	6
(kg/ha)	(kg/ha)				(mg/plant)[a]		
0	0	45 j	26 c-e	34 f-i	32 e-i	36 hi	34 f-i
	56	21 bc	21 bc	27 c-f	29 d-g	32 e-i	34 f-i
196	0	45 j	25 cd	38 i	35 g-i	38 i	32 e-i
	56	12 a	17 b	29 d-g	25 cd	22 bc	31 d-h

[a] Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] Isopropylamine salt of glyphosate.

[c] Spinks sandy loam soil.

indicates that the herbicide was adsorbed to the soil. Soil adsorption was reversible with phosphate competing with glyphosate for binding sites. Thus, chemical degradation is not the means of the rapid inactivation of glyphosate in the soil. Furthermore, glyphosate was still detected in the soil 4 weeks after large quantities of the herbicide had been applied. Glyphosate at the high rates did not cause injury to wheat seeded 6 weeks after herbicide application indicative of microbial or chemical degradation of glyphosate in the soil.

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CHAPTER 4

ADSORPTION, MOBILITY, AND MICROBIAL DEGRADATION OF GLYPHOSATE IN THE SOIL

Abstract

Glyphosate [N-(phosphonomethyl)glycine] was bound to charcoal and muck but not to ethyl cellulose. Iron and aluminum-saturated clays and organic matter adsorbed more glyphosate than sodium or calcium-saturated clays and organic matter. The herbicide was readily bound to kaolinite, illite, and bentonite. In the soil, most of the herbicide in solution was bound in the first hour. With increasing levels of phosphate in the soil, ^{14}C-glyphosate adsorption decreased. Soil mobility was affected by pH, phosphate level, and soil type. The ^{14}C-glyphosate was degraded in soil to $^{14}CO_2$ by means of cometabolism by the native microbial population. Potentiometric titrations of the compound gave pKa values of < 2, 2.6, 5.6, and 10.6.

Introduction

Foliar applications of glyphosate at 1.12 to 4.48 kg/ha control many perennial weeds without causing injury to the crops planted a few days after application (2). Although the herbicide is absorbed by wheat (*Triticum aestivum* L.) from nutrient solution, crop plants do not readily adsorb the herbicide from mineral soils. Soil applications of glyphosate at 56.0 kg/ha did not injure wheat plants grown in clay or much soils (13). Glyphosate, a substituted glycine may be bound to soil in a manner similar to glycine and/or phosphate.

Glycine, with pKa values of 2.2 and 9.6 (1), can be adsorbed on clay as a cation, a zwitterion, or by salt formation. As a cation, glycine is adsorbed by ion exchange with the displacement of other cations (5). The zwitterionic form of glycine, existing between pH 3.3 and 8.9 (1), may be protonated at the clay surface after adsorption. In either case, glycine is not lost by washing with water. However, the zwitterion of glycine is adsorbed to montmorillonite but is readily removed by washing with water. When glycine is adsorbed as a cation or zwitterion, it can be removed by washing with salt solutions. Another possible mechanism for glycine binding to soil is salt formation between a polyvalent metal ion with the amino and carbonyl groups of glycine (5).

The poly-α-aminomethylphosphonic acids form stable complexes with alkaline earth metals which are bound by 2 to 3 aminomethylphosphonate groups (9). If an ethyl group is substituted for an aminomethylphosphonate group, the stability constant for a particular metal ion decreases.

For instance, the stability constants for Ca^{++} complex of ethyliminodi(methylenephosphonic acid) is 3.36 compared to the Ca^{++} complex of diethylaminomethylphosphonic acid which is 1.28 (3). Although a single phosphonic acid group may be a poor chelating agent, a complex may be formed between the carbonyl and the phosphonic acid moieties of glyphosate making the phosphonic acid moiety potentially important for soil inactivation.

If the phosphonic acid group does not act as a complexing agent, glyphosate may bind to the soil similar to inorganic phosphate. At low phosphate concentrations, phosphate adsorbs to clays and iron and aluminum oxides and hydroxides (15). Phosphate binds to clay minerals through exchangeable iron and aluminum as well as through the hydroxyl group on the broken edges of clays (10). At a higher concentration of 5 to 7 ppm, precipitation occurs rapidly[1] forming iron and aluminum phosphates which become insoluble with increases in time and pH (7). Another possible mechanism of binding is the formation of adsorbent-cation-phosphate linkages. Levesque and Schnitzer (8) found that phosphates form fulvic acid-metal-phosphate complexes while others (11) thought clay-calcium-phosphate linkages were formed. In alkaline soils, calcium phosphate

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[1] Ellis, B. G. Michigan State University, personal communication.

precipitates and becomes more insoluble with time. In the soil, anions such as arsenate, hydroxyl, and oxalate compete with phosphate for binding sites (15).

The soil adsorption of nucleic acids, an organic phosphate, decreases with increasing pH and decreasing cation exchange capacity. Clays saturated with calcium or magnesium have greater adsorption for nucleic acids than clays saturated with potassium or sodium. Although the adsorption of nucleic acids on clay can be reversed with citrate or inositol phosphate, microbial degradation appears to be retarded by adsorption (4). Glyphosate, which is in fact an organic phosphate herbicide, may be bound to the soil in a manner similar to natural organic phosphate compounds.

The objective of this study was to investigate some of the factors affecting the adsorption, mobility, and degradation of glyphosate in the soil.

Materials and Methods

For the greenhouse studies, a bioassay procedure using white quartz sand allowed comparison of the various adsorbents. In this bioassay procedure, 850 g of sand were added to a 946-ml container, saturated with a modified Hoagland's no. 1 nutrient solution, and planted with 'Avon' wheat seeds. The various adsorbents were incorporated into enough sand to make 300 g and glyphosate at 0 and 4.48 kg/ha was applied at 935 L/ha and 2.11 kg/cm^2 pressure.

The herbicide was thoroughly incorporated into the sand and the mixture poured over the seeds. Although 50 ml of water was added to the surface, the pots were subirrigated to promote optimum plant growth. After 16 days, fresh and dry weights of the wheat plants were measured. All treatments were arranged in a completely randomized design with four replications. The data presented are the means of two experiments.

In the first experiment, ethyl cellulose, charcoal, or muck soil (81% organic matter) at 5 or 10% (by dry weight) was added to the surface 300 g. of sand. In the other two experiments, clay and organic matter were saturated with cations. With the organic matter, 15 g of muck was put in a Buchner funnel fitted with a Whatman No. 5 filter paper and leached with 200 ml of 0.5 M $CaCl \cdot 2H_2O$, $MgCl_2 \cdot 2H_2O$, $AlCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $ZnCl_2$ or NaCl. The muck was washed with 400 ml of water to remove excess ions and used in the above bioassay. The Na^+-saturated Wyoming bentonite, with a cation exchange capacity of 102 meq/ 100 g, also had to be saturated with the cations of the salts used above. The clay was saturated with the appropriate cations by repeated treatment with their chloride salts and washed free of chlorides with distilled water. For the bioassay, the clay was dried, ground fine with a mortar and pestle, and put in the surface sand in 15 g portions. For the radiotracer study, the clay was centrifuged, the supernatant removed, and the clay freeze-dried for later use.

For the radiotracer adsorption studies, ^{14}C-methyl-labeled glyphosate (sp. act. = 1.51 mCi/mmole) was converted from the acid to the isopropylamine salt by the addition of isopropylamine to 2.26 mg of acid. One-half ml of water and 0.8% MON 0818[2] (v/v) were added to the above to give 0.2 µCi/5 µL. This stock solution was kept frozen between the times of use. Adsorption of ^{14}C-glyphosate was determined using slight modifications of the adsorption procedure developed by Talbert and Fletchall (14). With the soil, 0.4 g, previously dried and later screened through a 1 mm sieve, was weighed into a 15-ml centrifuge tube and 6 ml of 0.04 µCi/6 ml solution of ^{14}C-glyphosate was added. The tube was stoppered with a polyethylene-covered rubber stopper since aluminum foil adsorbed the herbicide. Each sample was equilibrated for 4 hr at 25 C in a horizontal shaker reciprocating at 120 strokes per minute. The stopper was removed and the sample was centrifuged at 12,000 x g for 20 minutes. A 0.5 ml sample of the supernatant was removed and placed in 15 ml of a scintillation solution consisting of 0.1 g of 1,4-<u>bis</u>[2-(4-methyl-5-phenyloxazoyl)]-benzene (dimethyl-POPOP), 5.0 g of 2,5-diphenyloxazole (PPO), 50 g of naphthalene, 380 ml of toluene, 380 ml of

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[2] MON 0818 is a non-ionic surfactant produced by Monsanto Company, St. Louis, Missouri.

1,4-dioxane, and 240 ml of absolute ethanol. The samples were counted for 10 minutes and glyphosate adsorption was determined by comparing the radioactivity in a sample with soil to a sample of solution without soil. The difference was considered to be the quantity of herbicide bound and was expressed in nanomoles (nM) of herbicide bound/g of adsorbent. Initial adsorption studies were conducted at concentrations between 0.43 and 3.8 ppm and conformed to Freudlich adsorption isotherm. Data presented in the tables are the means of two experiments. The treatments were replicated three times in a completely randomized design. The above general procedure was used in all the adsorption studies with few minor modifications.

In the two experiments involving cation-saturated bentonite, illite, kaolinite, and hydroxides the following procedure was followed. The concentration of clay solutions was 0.5 g/100 ml of water and the concentration of iron and aluminum hydroxides were 3.81 g/100 ml and 4.48 g/100 ml of water, respectively. A 5.9 ml portion of these adsorbent solutions was placed in a 15-ml centrifuge tube with 0.1 ml containing 0.04 µCi of ^{14}C-glyphosate. The solutions were shaken for 4 hr and handled as previously described in the general radioisotope adsorption procedure.

A Spinks sandy loam soil was studied to determine the length of time required for glyphosate to equilibrate between the soil and aqueous phase of the suspension. The general procedure was modified by adding 3 ml of glyphosate containing 0.02 µCi/3 ml to 0.2 g of soil. The samples were equilibrated for 1, 2, 4, 8, 24, 48, and 96 hr, centrifuged, and radioassayed.

In the soil experiments comparing the adsorption of the various soil types, the general radioactive adsorption procedure originally described was used. Several soils with differing clay and organic matter contents were used. The Toledo clay loam originally containing 15 kg/ha of available phosphate was taken from plots where 0 and 240 kg/ha of phosphate had been applied 3 months prior to the collection of the soil sample.

For the experiment on herbicide mobility, the soil thin-layer chromatography procedure described by Helling (6) was used. Soil thin-layer plates 20 cm by 20 cm were coated with a 500-µm thick layer of each of the soils using a thin-layer chromatographic spreader. The plates were allowed to dry and then spotted 2 cm from the bottom with 0.01 or 0.05 uCi of ^{14}C-glyphosate in 5 µL of solution. The plates were allowed to equilibrate for 30 minutes and chromatographed ascendingly 15 cm above the origin. However, the plates coated with the Toledo clay loam were only chromatographed to height of 10 cm. The plates were air-dried for 24 hr and radioautographed. The treatments were replicated twice.

The ionization constants of glyphosate were determined by potentiometric titration. The pH meter was standardized with buffers at pH 4, 7, and 10 at room temperature. A 250-ml portion of 0.00123 M solution of 98.5% pure technical grade glyphosate was titrated from pH 2.4 to pH 11.0 with 0.2 N NaOH and back titrated to pH 2.4 with 0.2 N HCl. The two isoelectric points, were determined by finding the points of most rapid pH change. Since the compound has four pKa values, the pKa between the isoelectric points could be determined by finding the pH where one-half of an equivalent of OH^- had been added. The pKa values below and above the isoelectric points were determined by finding when one-half an equivalent of H^+ or OH^- had been added. If the pKa was below pH 4 or above pH 9, corrections were made for the H^+ or OH^- concentrations necessary for pH change. The remaining H^+ was attributed to dissociation of the herbicide. The titration was repeated several times with similar results.

Glyphosate degradation in the soil was investigated in the following way. Soils from southern Michigan were collected in June and stored in a closed plastic bag overnight in the refrigerator. A 25 g portion of soil was placed in a 300-ml flask. Most of the soils received 5 ml of 6.3×10^{-4} M NH_4NO_3 while the sodium azide treated soils received 5 ml of 6.3×10^{-4} M NH_4NO_3 plus 3.9×10^{-2} M NaN_3. A 1-ml portion of radioactive glyphosate (0.6 μCi of ^{14}C-glyphosate/30 ml of water) was added to each flask. A small 2-ml plastic beaker containing 1 ml of 1 M KOH was suspended in the flask to collect the $^{14}CO_2$. The flask was sealed with a rubber stopper and placed in a room at

23 to 27 C under low light intensity. The flasks were sampled at 1, 3, 5, 7, 9, 11, 14, 21, and 28 days after treatments. At sampling time, the contents of the 2-ml beaker were dumped into a vial containing 15 ml of 1:1 (v/v) CAB-O-SIL^{R} solution:60 g naphthalene, 4 g PPO, 0.2 g POPOP, 100 ml methanol, 20 ml ethylene glycol filled to a liter with p-1,4-dioxane. The contents of the vials were shaken to assure even distribution and radioassayed by scintillation spectrometry. The treatments were replicated times in a completely randomized design. The data presented was the mean of two experiments.

Results and Discussion

In the bioassay study, a reduction in fresh weight indicated that glyphosate was not bound by the adsorbent. Table 1 illustrates the relative adsorption of glyphosate by two rates of several organic adsorbents. Glyphosate at 4.48 kg/ha in quartz sand reduced the fresh weight of wheat plants indicating the lack of glyphosate inactivation. The presence of 5 or 10% ethyl cellulose in the sand did not inactivate glyphosate as the reduction in fresh weight due to glyphosate was not significantly different from the above. However, charcoal or muck inactivated glyphosate, as the treatments did not cause the reduction in fresh weight obtained in glyphosate-treated quartz sand. All adsorbents themselves significantly reduced the fresh

Table 1.--Binding of glyphosate by several organic matter sources as measured by the fresh weight of 16-day-old wheat plants.

Organic matter sources	Glyphosate (kg/ha)[b]	
	0	4.48
	(mg/plant)[a]	
Quartz sand	571 f	128 ab
5% Ethyl cellulose	473 e	68 a
10% Ethyl cellulose	460 de	163 b
5% Muck	403 cd	414 cde
10% Muck	364 c	380 c
5% Charcoal	395 cd	408 cde
10% Charcoal	358 c	356 c

[a] Means with common letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] Mono(dimethylamine) salt of glyphosate.

weight of the plants when compared to the quartz sand control without glyphosate.

Since glyphosate contains a phosphate group, metal ions may be important in determining its relative affinity for organic matter. Levesque and Schnitzer (8) found the formation of fulvic acid-metal-phosphate complexes. The adsorption of cation-saturated organic matter was compared between the adsorbent above and the herbicide-treated adsorbent (Table 2). Na^+ and Mg^{++}-saturated organic matter gave a significant reduction in plant fresh weight indicating little glyphosate adsorption. Zn^{++}-saturated organic matter caused a smaller reduction in plant fresh weight but the adsorbent alone was toxic to plants. The fresh weight of wheat plants grown in Ca^{++}, Mn^{++}, Fe^{+++}, and Al^{+++}-saturated organic matter treated with glyphosate was not significantly reduced. All of the cation-saturated organic matter alone caused some reduction in plant fresh weight since some of the ions such as Zn^{++} caused a alteration in the physical properties of the muck. If the controls of the first two experiments are compared (Tables 1 and 2), glyphosate gave a 76% reduction in plant fresh weight while the same treatment in the second experiment gave a 94% reduction in fresh weight. The mono(dimethylamine) salt used in the first experiment had degraded so that the usual reduction of 90 to 95% in fresh weight was not achieved. All other experiments using other samples of glyphosate did not show any loss of herbicide activity with time.

Table 2.--The effect of cations on glyphosate binding to organic matter as measured by the fresh weight of 16-day-old wheat plants.

Organic matter	pH	Glyphosate (kg/ha)[b] 0	Glyphosate (kg/ha)[b] 4.48
		(mg/plant)[a]	
Quartz sand control		511	31 a
Na^+	6.5	399 g	152 b
Mg^{++}	6.0	398 g	151 b
Muck	5.7	392 fg	305 de
Ca^{++}	5.8	340 efg	312 de
Zn^{++}	5.4	276 d	217 c
Mn^{++}	5.1	378 fg	363 efg
Fe^{+++}	3.2	335 ef	360 efg
Al^{+++}	3.8	339 efg	342 efg

[a] Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] Isopropylamine salt of glyphosate.

The cation-saturated clays showed great differences in adsorption of glyphosate (Table 3). In the bioassay study, all the clays tested gave significant reduction in plant growth in comparison with the sand control. If a comparison is made between the glyphosate treatments and the significance of their differences, the relative adsorption of the clays can be determined. The control, the Na^+, the Ca^{++}, and the Mg^{++}-saturated clay all allowed only poor plant growth indicating little glyphosate adsorption. The Zn^{++}-saturated clay allowed greater growth of the wheat plants. The fresh weights of the wheat plants grown in Mn^{++}, Al^{+++}, and Fe^{+++}-saturated clay treated with glyphosate were not significantly different from their controls. With ^{14}C-glyphosate, the control and the Na^+-saturated bentonite showed no glyphosate adsorption. Glyphosate adsorption to the various cation-saturated bentonite clays increased as follows: $Ca^{++} < Mn^{++} < Zn^{++} < Mg^{++} < Fe^{+++} < Al^{+++}$. The strong adsorption to Al^{+++} and Fe^{+++} indicates that phosphate could be involved in adsorption. Phosphates may be precipitated or bound to the clays. Iron and aluminum rapidly form colloidal phosphates which are somewhat available to plants. Crystalline phosphates, unavailable to plants, form slowly from colloidal iron and aluminum phosphates. Precipitation of phosphate occurs rapidly at concentrations of 5 to 7 ppm. At lower concentrations, phosphate is adsorbed to clay, organic matter, and hydroxides. Thus, it is possible that glyphosate might

Table 3.--Effect of cations on the adsorption of glyphosate by bentonite clay as measured by the fresh weight of 16-day-old wheat plants and radiotracer technique.

Bentonite clay	pH	Glyphosate (kg/ha)[a] 0	Glyphosate (kg/ha)[a] 4.48	^{14}C-Glyphosate adsorption[b]
		(mg/plant)		(nM/g of clay)
Control	6.0	551 i	38 a	0 a
Na^+	8.1	510 h	49 ab	0 a
Ca^{++}	6.5	459 g	82 b	169 b
Mg^{++}	6.3	456 g	76 ab	260 e
Zn^{++}	6.7	253 d	207 c	201 d
Mn^{++}	5.7	365 e	369 e	193 c
Al^{+++}	4.2	446 fg	404 ef	516 g
Fe^{+++}	5.4	425 fg	361 e	505 f

[a] Means with similar letters within an experiment are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] Isopropylamine salt of glyphosate.

be precipitated or more likely adsorbed through the phosphate group. An alternate hypothesis is that glyphosate may form an adsorbent-cation-herbicide complex with clay and organic matter.

In comparing several types of clays and adsorbents, kaolinite adsorbed more herbicide than illite or Na^+-saturated bentonite (Table 4). The iron and aluminum hydroxides also adsorbed small quantities of glyphosate. The cation exchange capacities decrease as follows: bentonite > illite > kaolinite > iron and aluminum hydroxides. Therefore, binding does not seem to be related to the cation exchange capacity of clays but is more related to the cation on the clay. With kaolinite, glyphosate probably binds through the broken edges of the clay while iron and aluminum hydroxide probably adsorb glyphosate by replacement of a hydroxyl group.

After studying the adsorption of glyphosate to various soil substituents, glyphosate adsorption by the soil was investigated. Although most of the adsorption occurs within the first hour, the binding of glyphosate increased with time (Table 5). Soil type often affected the adsorption of glyphosate in the soil (Table 6). A sandy loam soil adsorbed less glyphosate than a clay loam soil. It appears that phosphate might be the most important factor in determining the quantity of glyphosate adsorbed. As the quantity of phosphate in the soil increased, glyphosate

Table 4.--Adsorption of ^{14}C-glyphosate by several clays and hydroxides.

Adsorbent	pH	Glyphosate adsorption[a]
		(nM/g of soil)
Kaolinite	6.9	498.1 d
Illite	7.3	276.3 c
Na^+-bentonite	8.1	4.0 a
Iron hydroxide	10.8	39.7 b
Aluminum hydroxide	3.8	6.6 a

[a] Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

Table 5.--^{14}C-glyphosate adsorption to Spinks sandy loam soil after various time intervals.

Time after treatment	Glyphosate adsorption[a]
(hr)	(nM/g of soil)
1	28.0 a
2	29.0 ab
4	31.9 ab
8	32.9 b
24	30.1 ab
48	30.0 ab
96	41.8 c

[a] Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

Table 6.--The effect of soil type and phosphate level on the soil adsorption of ^{14}C-glyphosate.

Soil type	Clay	Organic matter	pH	Phosphate	Glyphosate adsorption[a]
	(%)	(%)		(kg/ha)	(nM/g of soil)
Spinks sandy loam	21.7	2.0	6.1	330	16.5 a
Conover sandy clay loam	29.7	2.7	5.7	76	27.3 c
Toledo clay loam	71.7	3.8	7.4	15	27.1 c
Toldeo clay loam	69.7	3.8	7.6	249	22.3 b

[a] Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

adsorption decreases while pH did not seem to affect adsorption.

Glyphosate moved slightly on the various soil thin-layer plates used, achieving Rf values of 0.04 to 0.20. Increasing the concentration of glyphosate from 0.01 to 0.05 µCi increased movement. At either concentration, glyphosate moved less in the Spinks sandy loam soil than in the Toledo clay loam. In the Toledo clay loam, mobility increased with an increase in the phosphate level of the soil. As pH increased, the Rf values on the soil thin-layer plates also increased. Although glyphosate is a very water soluble compound, it is bound tightly having only low mobility in the soil.

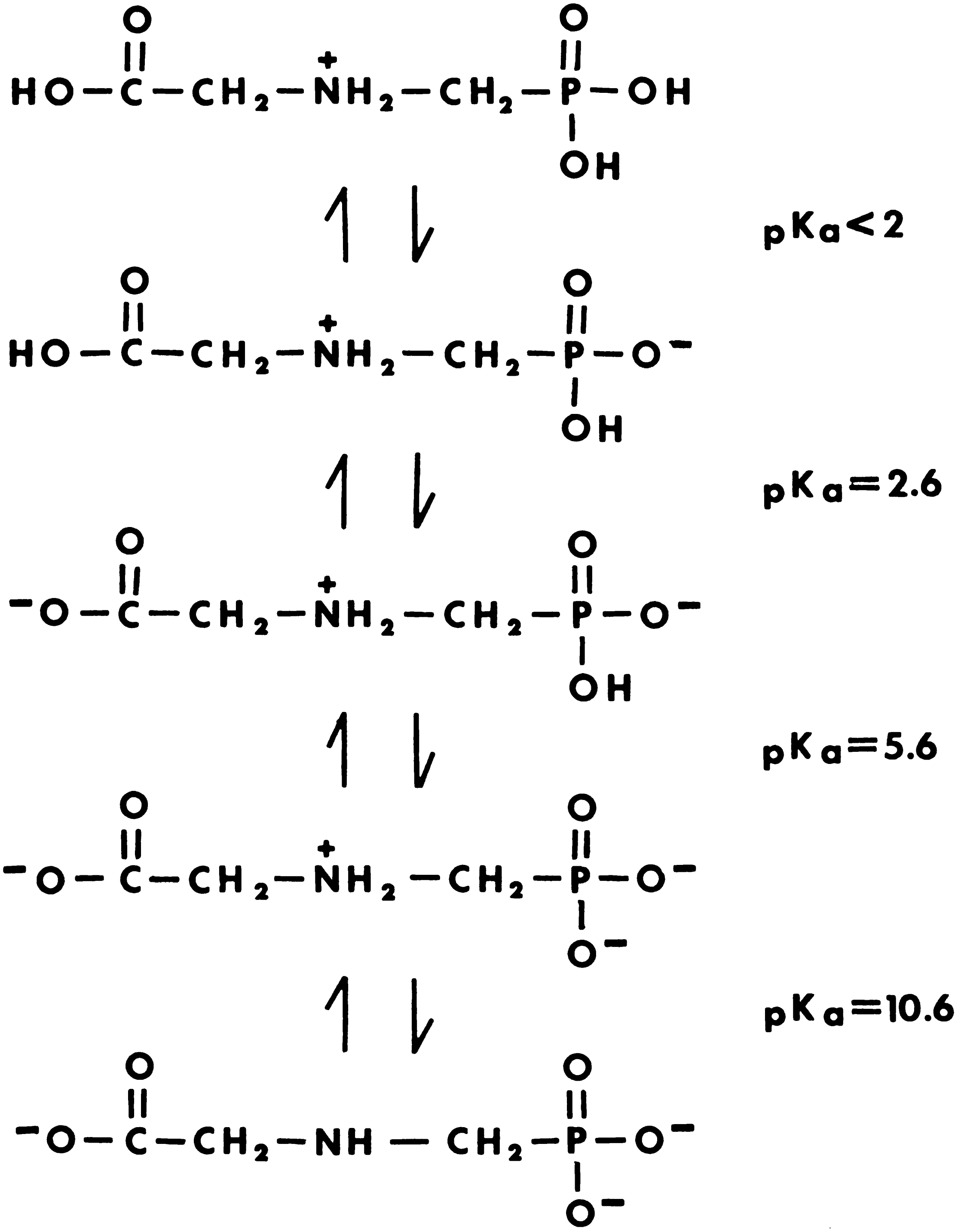
Glyphosate can lose up to 4 equivalents of H^+ per mole (Figure 1). The titration of glyphosate from pH 2.43 to pH 11 required 3 equivalents of hydroxide and did not account for all the H^+ potentially released. Possibly one pKa value was lower than pH 2.43. The two isoelectric points of this titration curve were at pH 4.1 and 8.1. Evaluation of similar compounds aided in the assignment of pKa values to the proper functional groups (Figure 1). The pKa_1 of glycine for the carboxyl group is 2.2 to 2.6 (1) while the pKa_1 of methylphosphonic acid is 2.7 (12). Addition of an electron-donating group to the methylphosphonic acid lowered the pKa_1 value. For example, ethylphosphonic acid has a pKa_1 of 2.1 (12) while phenylphosphonic acid has a pKa_1 of 1.83 (1). Since the amino group

Table 7.--The effect of soil type, pH, and phosphate on the mobility of ^{14}C-glyphosate on soil thin-layer chromatography plates.

Soil type	Organic matter	pH	Phosphate	Rf values[a] Glyphosate conc. (µCi/spot) 0.01 µCi	0.05 µCi
	(%)		(kg/ha)		
Spinks sandy loam	2.0	6.1	330	0.04 a	0.14 d
Toledo clay loam	3.8	7.4	15	0.07 c	0.15 de
Toledo clay loam	3.8	7.6	249	0.13 d	0.20 g
Hillsdale sandy clay loam	1.5	4.6	240	0.04 a	0.14 d
Hillsdale sandy clay loam	1.3	5.6	123	0.06 bc	0.17 ef
Hillsdale sandy clay loam	1.5	6.7	131	0.08 c	0.18 f

[a] Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

Figure 1. Proposed dissociation diagram and ionization constants for glyphosate.


pKa<2
pKa=2.6
pKa=5.6
pKa=10.6

is electron-donating, it is likely the pKa_1 value of < 2 is from the phosphonic acid. The pKa_2 of 2.6 is from the carboxyl group of glyphosate. The pKa_2 of methylphosphonic acid is 7.1 (12) where as the pKa_3 of glyphosate is 5.6. It is likely the electron-donating ability of amino group lowered the pKa of the second H^+ on the phosphonic acid group. With glycine, the pKa_2 of the amino group is 9.6 (1) whereas the pKa_4 of glyphosate is 10.6. The pKa_3 and pKa_4 are due to the phosphonic acid and the amino functional groups, respectively. The titration curve of glyphosate from pH 2.4 to 11 was no different from the titration curve of the reverse titration.

Glyphosate was readily degraded in the soil (Table 8). Treatment of the soil with sodium azide completely stopped $^{14}CO_2$ release from Conover sandy loam but did not reduce the rate of degradation as drastically in Toledo clay loam. With the Toledo clay loam, the soil was in clumps and the sodium azide may not have penetrated the soil as well. It is also possible that some chemical degradation took place. The phosphate level of the Conover sandy loam appeared to increase the rate of $^{14}CO_2$ evolution. With the Toledo clay loam, the phosphate level appears to have little effect on the degradation rate. Most of the soils used with the exception of the Toledo clay loam evolved 17.4 to 45.5% of the ^{14}C-glyphosate at $^{14}CO_2$ in 28 days. There are a number of reasons why the Toledo clay loam may degrade glyphosate so slowly. The organisms able to degrade

Table 8.--The effect of soil type, phosphate level, and sodium azide[c] treatment on the soil degradation of ^{14}C-glyphosate to $^{14}CO_2$.

Soil description	Time (days)[a]								
	1	3	5	7	9	11	14	21	28
					(% ^{14}C evolved as $^{14}CO_2$)				
Conover sandy loam, low phosphate, sterilized	0.2 a	0.4 ab	0.4 bc	0.4 bc	0.5 b-d	0.5 b-d	0.5 b-d	0.6 c-d	0.6 d
Conover sandy loam low phosphate[b]	4.2 jk	7.5 r	9.3 st	11.0 v-x	12.1 y-aa	12.9 aabb	14.2 ccdd	16.2 ffgg	17.4 hhii
Conover sandy loam, high phosphate[b]	6.4 o-q	10.6 uv	13.3 bbcc	15.6 eeff	17.2 gghh	18.3 ii	20.0 jj	22.8 ll	24.5 mm
Conover loam	6.0 m-o	13.2 bb	17.7 hhii	21.9 kk	24.7 mm	26.8 nn	29.8 qq	34.7 sstt	37.8 ww
Conover sandy clay loam	14.9 ddee	24.9 mm	29.6 pp	33.3 rr	35.8 ttuu	37.4 vvww	39.7 vv	43.2 yy	45.5zz
Muck	4.2 jk	7.9 r	9.8 tu	11.5 xy	12.7 z-bb	13.7 bbcc	15.4 eeff	18.4 ii	20.9 jj
Spinks sandy loam	17.2 gghh	25.1 mm	28.2 oo	31.0 qq	32.8 rr	34.1 rrss	36.2 uuvv	40.0xx	42.8 yy
Toledo clay loam, low phosphate, sterilized[b]	0.4 b-d	1.1 ef	1.7 g	2.3 h	2.8 i	3.2 i	3.8 j	5.3 l-n	6.6 pq
Toledo clay loam, low phosphate[b]	0.5 b-d	1.4 fg	2.2 h	3.1 i	4.0 j	4.8 l	6.2 o-q	9.4 st	11.9 x-z
Toledo clay loam, high phosphate, sterilized[b]	0.4 a-c	1.0 e	1.5 g	2.2 h	2.8 i	3.2 i	3.8 j	5.2 lm	6.6 q
Toledo clay loam, high phosphate[b]	0.5 b-d	1.4 fg	2.1 h	3.1 i	3.9 j	4.6 kl	5.9 n-p	8.9 s	11.6 xy

[a] Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] The soils used contained the following amounts of phosphate: Conover sandy loam, low phosphate-112 kg/ha; Conover sandy loam, high phosphate-150 kg/ha; Toledo clay loam, low phosphate-9 kg/ha; Toledo clay loam, high phosphate-47 kg/ha.

[c] The sodium azide treatment approximates sterilization and is referred to in the table as sterilized.

glyphosate may not be present in large enough numbers for degradation to occur readily. The glyphosate might have been bound more tightly to the soil and thus was less available to the organisms. The pattern of degradation of glyphosate (Figure 2) suggests that glyphosate is not supporting microbial growth but is cometabolized by the indigenous soil microflora. This pattern is typified by rapid initial degradation followed by a slower, continuous rate of degradation. The degradation curve of Conover sandy clay loam (Figure 2A) and Conover sandy loam (Figure 2B) was typical of most soils and exhibited the type of degradation curve previously described. The second pattern of degradation (Figure 3) shows a slow continuous breakdown of glyphosate with no lag period or rapid initial degradation. Sodium azide treatment (Figure 3B) reduced the rate of degradation (Figure 3A) of Toledo clay loam but did not change the pattern of breakdown. Thus at least part of the degradation was microbial. It is also possible that chemical degradation occurs since sodium azide treatment did not stop $^{14}CO_2$ evolution and the plot of $^{14}CO_2$ evolved versus time was linear.

In summary, glyphosate was readily bound to clay and organic matter. Since Fe^{+++} and Al^{+++} markedly affected the adsorption of glyphosate to both bentonite clay and organic matter, it is likely that the phosphonic acid group is involved in adsorption. Furthermore, the level of phosphate in the soil appeared to be the factor most

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Figure 2. Effect of soil type and sodium azide on the degradation of ^{14}C-methyl-labeled glyphosate to $^{14}CO_2$; A, Conover sandy clay loam; B, Conover sandy loam, low phosphate; C, Conover sandy loam, low phosphate, sodium azide treated.

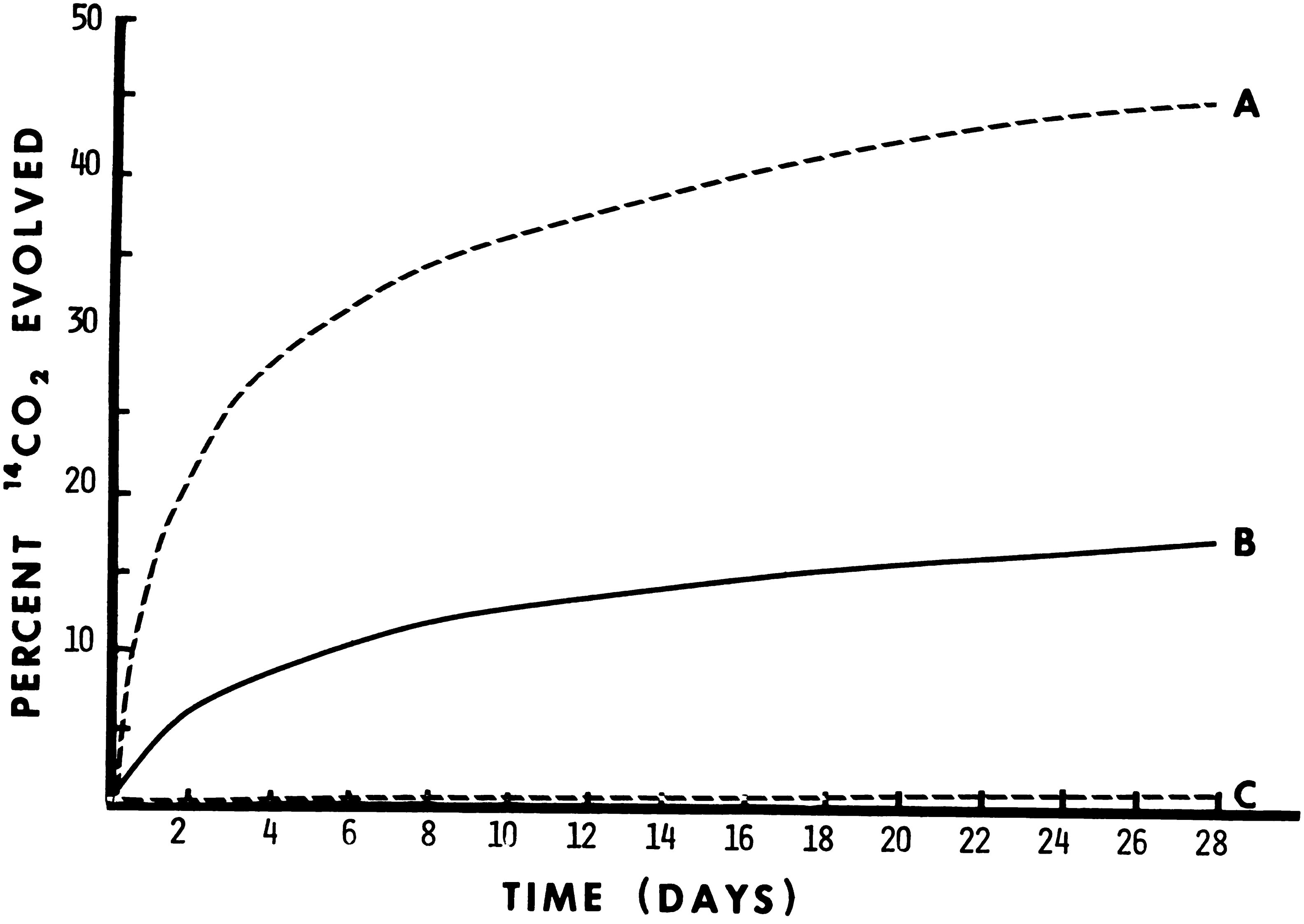

50
40
30
20
10
PERCENT $^{14}CO_2$ EVOLVED
A
B
C
2
4
6
8
10
12
14
16
18
20
22
24
26
28
TIME (DAYS)

Figure 3. Effect of sodium azide on the degradation of ^{14}C-methyl-labeled glyphosate to $^{14}CO_2$ in soil; A, Toledo clay loam, low phosphate; B, Toledo clay loam, low phosphate, sodium azide treated.

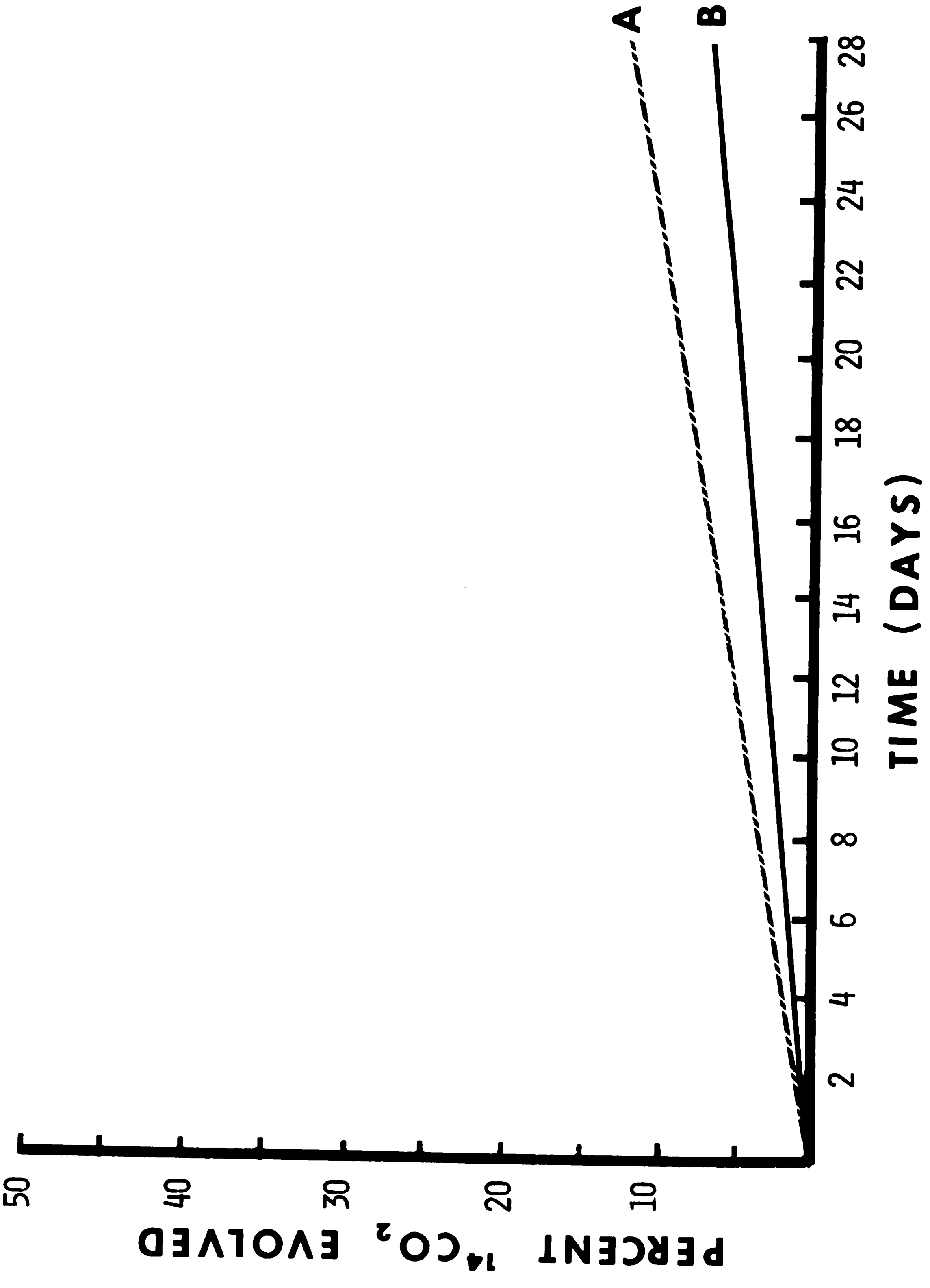
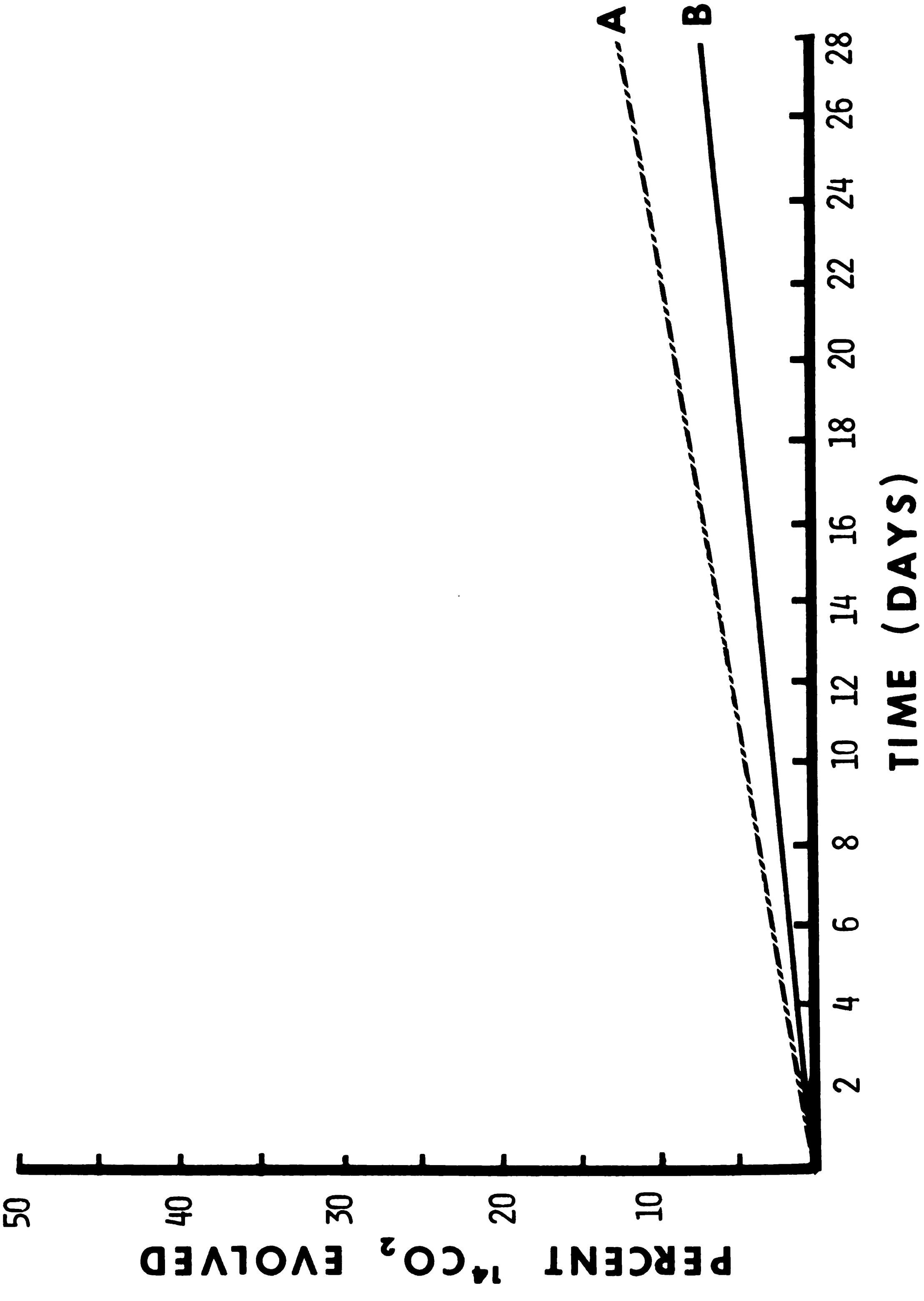

PERCENT $^{14}CO_2$ EVOLVED
50
40
30
20
10
TIME (DAYS)
2
4
6
8
10
12
14
16
18
20
22
24
26
28
A
B

Figure 3. Effect of sodium azide on the degradation of ^{14}C-methyl-labeled glyphosate to $^{14}CO_2$ in soil; A, Toledo clay loam, low phosphate; B, Toledo clay loam, low phosphate, sodium azide treated.


PERCENT $^{14}CO_2$ EVOLVED
50
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TIME (DAYS)
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B

related to the amount of glyphosate adsorbed. Although glyphosate did not readily move in the soil, mobility on soil thin-layer chromatography plates was influenced by the quantity applied, pH, phosphate level, and soil type. In most cases, 17 to 45% of the ^{14}C-glyphosate was degraded to $^{14}CO_2$ in 28 days. Two patterns of degradation were evident. The herbicide appeared to be cometabolized by the present microbial population of the soil. The second pattern suggested that both cometabolism and chemical degradation occurred. In the soil, the herbicide probably has a net negative charge of -1 or -2.

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CHAPTER 5

ABSORPTION, ACTION, AND TRANSLOCATION OF GLYPHOSATE

Abstract

Radioactive glyphosate [*N*-(phosphonomethyl)glycine] is rapidly absorbed with a large portion of the ^{14}C translocated to the rhizomes and untreated shoots of quackgrass [*Agropyron repens* (L.) Beauv.]. The adjuvant used with glyphosate was important in determining its phytotoxicity to quackgrass. In other perennial weeds and annual species, glyphosate also moved to the areas of highest metabolic activity. In Canada thistle [*Cirsium arvense* (L). Scop.], bentazon (3-isopropyl-1*H*-2,1,3-benzothiadiazin-(4)3*H*-one 2,2-dioxide) at 2.24 kg/ha applied prior to treatment with ^{14}C-glyphosate reduced ^{14}C translocation. Iron or nitrilotriacetic acid (NTA) did not appear to affect glyphosate activity on wheat (*Triticium aestivum* L.). The respiration of quackgrass treated with glyphosate was significantly reduced 9 days after treatment. Glyphosate reduced total photosynthesis more in quackgrass than in wheat.

Introduction

Successful control of perennial weeds with foliar-applied herbicides depends on the rapid absorption and the basipetal translocation of the biologically active compound into the underground storage organs in sufficient quantities to kill the entire plant before metabolism can degrade the compound. A number of factors can affect the absorption and translocation of a herbicide in the plant. The proper adjuvant can increase the rate of absorption and the quantity of herbicide absorbed by the plant. If the herbicide is foliar-applied and phloem-translocated, the compound must be applied at the proper stage of growth to get extensive basipetal translocation into the roots or rhizomes of the plant. For example, dalapon (2,2-dichloropropionic acid) and amitrole (3-amino-*s*-triazole) applied to a 10 to 15 cm quackgrass shoot moved only within the treated shoots and seldom into the attached rhizome whereas if these herbicides were applied to 40 to 50 cm shoots, more radioactivity was found in the rhizome (4). When considering a herbicide in terms of application and action, it is important to know how rapidly the herbicide affects the plant processes.

The objective of this study was to determine some of the factors affecting the rate of action, absorption, and translocation of glyphosate in several plant species.

Materials and Methods

Fifteen-day-old quackgrass plants grown from three-node rhizome sections were sprayed with glyphosate at 0 and 2.24 kg/ha plus MON 0027[1] surfactant at 0.8% (v/v), X-77[2] at 0.2% (v/v), or phytobland oil[3] at 1% (v/v) at 428 L/ha at 2.11 kg/cm^2 pressure. The plants, maintained under greenhouse conditions, were harvested 15 days after treatment and fresh and dry weights measured. The experiment was in a completely randomized design with three replications.

Glyphosate at 2.24 kg/ha and other additives were applied to 17-day-old 'Avon' wheat plants at 935 L/ha and 2.11 kg/cm^2 pressure. The mixture of glyphosate, nitrilotriacetic acid (NTA) at 3.0 x 10^{-2}M, (5.67 L/ha) or ferrous sulfate ($FeSO_4.7H_2O$) at 1.5 x 10^{-2}M (4.12 L/ha) was adjusted to pH 6.6 to 6.9 and MON 0027 surfactant at 0.4% (v/v) was added to the spray solution just prior to

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[1] MON 0027 is a non-ionic surfactant produced by Monsanto Company, St. Louis, Missouri.

[2] X-77 is an non-ionic spreader composed of a mixture of alkylarylpolyoxyethylene glycols, free fatty acids, and isopropanol produced by Chevron Chemical Company, San Francisco, California.

[3] The phytobland oil used was Sun 11E produced by the Sun Oil Company, Philadelphia, Pennsylvania.

application. The plants were harvested 18 days after treatment and fresh and dry weights were measured. The treatments were arranged in a completely randomized design with four replications.

The following procedure was followed to determine the adsorption and rate of translocation of ^{14}C-glyphosate in quackgrass plants. A rhizome piece approximately 23 cm long containing 4 to 6 nodes was placed on quartz sand in a 946-ml cup and covered with 3 cm of sand. The cups were subirrigated with a modified Hoagland's no. 1 solution adjusted to a pH 6.5. The 20-day-old plants, selected for uniformity, were placed in a growth chamber at 25 C and 25.8 klux 2 days prior to treatment. The ^{14}C-methyl-labeled glyphosate (sp. act. = 1.51 mCi/mmole) was converted from the acid to the isopropylamine salt by addition of 4 μl of isopropylamine to 2.20 mg of acid followed by the addition of 0.5 ml of deionized water and 0.8% MON 0818 surfactant.[4] Each of the 3 to 4-leaf quackgrass plants, treated on a middle leaf, received a 5 μl drop containing 0.2 μCi of ^{14}C-glyphosate. The drop of radioactive herbicide was placed in the middle of the leaf between two lanolin bars which were perpendicular to the length of the leaf. After the drop had dried, the plants were moved

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[4] MON 0818 is a non-ionic surfactant produced by Monsanto Company, St. Louis, Missouri.

back to the growth chamber. Harvests were 4, 8, 24, and 48 hr after treatment. The sand was washed from the rhizomes in three successive distilled water baths, the rhizomes were blotted dry, and the plants frozen in dry ice. The plants were freeze-dried and dissected into treated leaf, treated shoot, and rhizomes and attached plants. The area of the spot on the treated leaf which had been previously covered with tape, was discarded since the herbicide in this area was not considered to be translocated. Each plant part was cut into small pieces which then were pulverized with a mortar and pestle. A representation sample was combusted by the Schoeninger combustion method of Wang and Willis (6) to determine the quantity of ^{14}C translocated in each plant part by liquid scintillation radioassay. The treatments were replicated three times in a completely randomized design.

A translocation study was conducted on perennial weeds, crop plants, and annual weeds. The plants were grown in the greenhouse and transferred to a growth chamber 4 days before treatment. All the plants in the growth chamber were grown at 30 C except quackgrass which was grown at 25 C with the light intensity of all the growth chambers at 25.8 klux. Each plant received inside a lanolin ring a 5 μl drop containing 0.2 μCi of ^{14}C-glyphosate on one of its middle leaves. The stages of growth and time of harvest are listed in Table 1. At harvest, the lanolin ring was removed, the area taped,

Table 1.--The species, stage of growth, and time of harvest of the plants used in the translocation study with ^{14}C-methyl-labeled glyphosate.

Species	Stage of growth or height of plant	Time of harvest
		(days after tmt)
Quackgrass [*Agropyron repens* L. Beauv.]	young: 1 to 2-leaf old: 3 to 4-leaf	4 4
Nutsedge (*Cyperus esculentus* L.)	10 leaves	7
Field bindweed (*Convolvulus arvensis* L.)	10 to 12 leaves	4
Canada thistle [*Cirsium arvense* (L.) Scop.]	young: 10 to 15 cm old: bud-to-flowering stage	7 7
Corn (*Zea mays* L. 'Michigan 400')	4 to 5-leaf	4
Soybeans [*Glycine max* (L.) Merr. 'Anoka']	2nd trifoliate leaf	4
Redroot pigweed [*Amaranthus retroflexus* (L.)]	10 leaves	4

and the roots washed. The plants were quickly frozen with dry ice, freeze-dried, rehydrated, mounted, and radioautographed. The treatments were replicated three times in a completely randomized design.

Photosynthesis and respiration measurements were made at 0, 3, 24, 72, and 216 hr after treatment with glyphosate at 2.24 kg/ha plus MON 0027 surfactant at 0.8% (v/v) on 12-day-old wheat plants and 24-day-old quackgrass plants grown from rhizomes. The cup containing the plant was placed in a sealed clear plastic test chamber located in a growth chamber and attached to a Beckman Model 215 CO_2 infrared gas analyzer. Air from a compressed air tank at 330 ppm of CO_2 was passed through the chamber at the rate of 500 cc/min and measured at the analyzer outlet for change in CO_2 content. The foliage was then removed and taped to a piece of paper. Leaf area was determined and the foliage was oven dried and weighed. All data presented are the means of two experiments with three or four replications each.

Results and Discussion

At the proposed use rate of 2.24 kg/ha, glyphosate must be applied with an adjuvant to obtain herbicidal activity (Table 2). After 15 days, glyphosate at 2.24 kg/ha alone caused no loss in moisture content while the same herbicide rate with MON 0027 or X-77 caused a significant loss in moisture indicating extensive phytotoxicity.

Table 2.--The effect of adjuvants, metal, and chelating agent on the absorption and action of glyphosate on quackgrass or wheat plants.

Species	Glyphosate[b] rate	Adjuvant	Rate[g]	Moisture content[a]
	(kg/ha)		(L/ha or kg/ha)	
Quackgrass	0	. .	0	80.0 a
	2.24	. .	0	80.8 a
	0	MON 0027[c]	5.61	72.3 ab
	2.24	MON 0027	5.61	51.6 c
	0	X-77[d]	1.87	80.8 a
	2.24	X-77	1.87	59.5 bc
	0	Sun 11E[e]	9.35	82.2 a
	2.24	Sun 11E	9.35	76.2 a
Wheat	0	MON 0027	3.74	83.4 a
	2.24	MON 0027 [f]	3.74	69.2 b
	0	MON 0027+NTA	3.74+5.67	82.6 a
	0	MON 0027+$FeSO_4$	3.74+4.12	83.2 a
	2.24	MON 0027+$FeSO_4$	3.74+4.12	72.5 b
	0	MON 0027+NTA+$FeSO_4$	3.74+5.67+4.12	83.3 a
	2.24	MON 0027+NTA+$FeSO_4$	3.74+5.67+4.12	72.1 b

[a] Means within the first part or the second part of the column are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] Mono(dimethylamine) salt of glyphosate used.

[c] MON 0027 is a non-ionic surfactant produced by Monsanto Company, St. Louis, Missouri.

[d] X-77 is a non-ionic surfactant produced by Chevron Chemical Company, San Francisco, California.

[e] Sun 11E is a phytobland oil produced by Sun Oil Company, Philadelphia, Pennsylvania.

[f] Nitriolotriacetic acid.

[g] The surfactant rates are in L/ha, the chemical rates are in kg/ha.

Glyphosate with the phytobland oil appeared to contribute significantly less activity than glyphosate with the surfactants.

With wheat, the $FeSO_4 \cdot 7H_2O$ or NTA did not cause any reduction in plant moisture content of the control (Table 2). The addition of $FeSO_4 \cdot 7H_2O$ plus NTA to glyphosate did not appear to significantly affect the phytotoxicity when compared to glyphosate at 2.24 kg/ha alone. Although monophosphonic acids may be weak chelating agents (3), glyphosate did not appear to form any stable complex with Fe or Fe plus NTA as determined by the loss in moisture content of the wheat plants.

Glyphosate was rapidly absorbed and translocated in quackgrass plants. When a surfactant was added, glyphosate absorption occurred most rapidly within 4 hr after treatment and continued to increase but absorption was not significantly greater than the 4 hr reading until 48 hr after treatment (Table 3). This appears consistent with the field information on glyphosate absorption. Rainfall usually washes foliar-applied herbicides off the leaves and thus prevents absorption. If rain fell within 0 to 8 hours after treatment, a decrease in glyphosate activity was usually observed.[5] Translocation also occurs rapidly.

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[5] Upchurch, R. P., D. D. Baird, and G. F. Begeman. 1972. Influence of temperature and diluent properties of MON 0468 performance. Weed Sci. Soc. Amer. Abstr. No. 156.

Table 3.--Foliar absorption of ^{14}C-glyphosate by 3 to 4-leaf quackgrass.

Time	Absorption of ^{14}C-glyphosate applied[a]
(hr)	(%)
4	34.2 a
8	39.6 a
24	44.7 ab
48	53.2 b

[a] Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

After 8 hr, the quantity of ^{14}C in the treated leaf did not significantly decrease (Table 4). The treated shoot maintained a rather constant level of ^{14}C over time while the quantity of ^{14}C increased significantly over each time period with 66.7% of the ^{14}C absorbed present in the rhizome and untreated shoots. Field research with foliar application of glyphosate to quackgrass has shown similar results. Plowing at various time intervals after glyphosate application would destroy the rhizome system thus interrupting further translocation after plowing. If a sufficient quantity of glyphosate was not translocated into the rhizomes by the time of plowing, a reduction in quackgrass control would result. Plowing 15 days after glyphosate application may increase quackgrass control 5 or 10% over glyphosate application without plowing. Brockman

Table 4.--The effect of time on the translocation of ^{14}C-glyphosate in 3 to 4-leaf quackgrass.

Time	Treated leaf	Treated shoot	Rhizomes and untreated shoots
(hr)	(% of total ^{14}C translocated)[a]		
4	85.1 c	5.8 a	9.1 a
8	63.5 b	10.5 ab	26.0 b
24	25.1 a	26.0 b	48.9 c
48	15.8 a	17.5 ab	66.7 d

[a] Means within a column followed by similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

et al.[6] found that plowing 1 day after glyphosate application provided significantly better quackgrass control than plowing the day of herbicide application. Little increase in quackgrass control was observed with longer periods of time between glyphosate application and plowing.

Glyphosate appears to be translocated in all of the crop and weed species studied. In quackgrass, ^{14}C moved to the leaf tip as well as to the rapidly growing rhizomes, roots, and untreated shoots (Figure 1A and B). Thus the movement of the ^{14}C from the treated spot appeared

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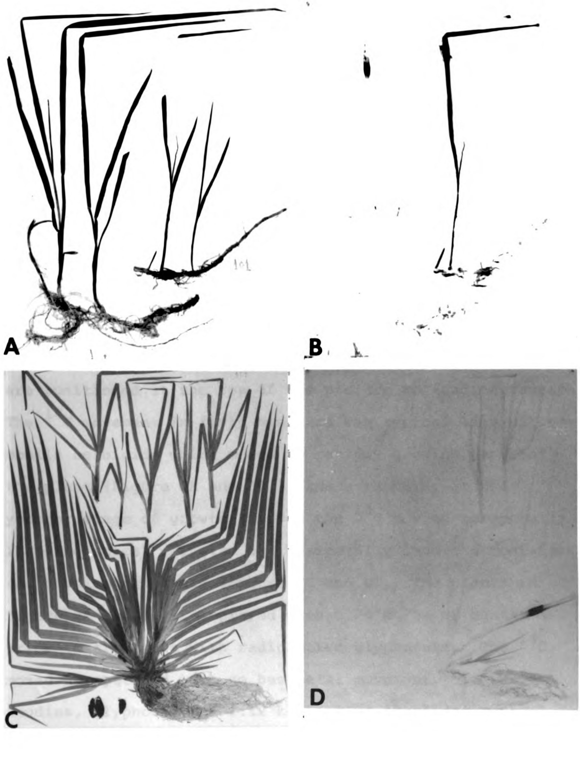
[6] Brockman, F. E., W. B. Duke, and J. F. Hunt. 1973. Agronomic factors affecting use of glyphosate for quackgrass control. Weed Sci. Soc. Amer. Abstr. No. 27.

Figure 1. Translocation of ^{14}C-glyphosate in quackgrass and nutsedge. The treated plants (A) and corresponding radioautograph (B) show quackgrass in the 3 to 4-leaf stage (left) compared to the 1 to 2-leaf stage (right) which was harvested 4 days after foliar application. The treated plant (C) and corresponding radioautograph (D) show nutsedge in the 10-leaf stage harvested 7 days after foliar application.


A
B
C
D

to be primarily in the phloem with the photoassimilates following the established source to sink relationships. It appears that the plants in the 1 to 2-leaf stage may have translocated more ^{14}C into the rhizomes than plants in the 3 to 4-leaf stage. This phenomena was not consistent with field data on the effect of stage of growth on quackgrass control with glyphosate. Glyphosate was more effective when applied at the 4-leaf stage of growth than at the 1 1/2 to 2-leaf stage of growth (1). In yellow nutsedge, the ^{14}C moved acropetally in the treated shoot and basipetally into the untreated shoots and developing tillers (Figure 1C and D). Some of the developing tillers are positioned at the top of the picture and radioautograph. The ^{14}C movement in field bindweed was typical of a phloem-mobile herbicide which moves to rapidly growing parts of the plant (Figure 2A and B). Canada thistle, at the younger stage of growth, showed the ^{14}C moving acropetally into the apical meristem and basipetally into the rootstock and developing plants (Figure 3C and D). The plants in Figure 3A and B were sprayed with 2.24 kg/ha of bentazon prior to treatment with radioactive glyphosate. The ^{14}C moved acropetally with no basipetal movement. In field studies, glyphosate at 1.12 kg/ha gave excellent control of Canada thistle while glyphosate plus bentazon, 1.12 plus 1.12 kg/ha gave rapid initial kill but did not provide long term control. Thus, if glyphosate is used in combination with a herbicide with a high level of foliar

Figure 2. Translocation of ^{14}C-glyphosate in field bindweed in the 10 to 12-leaf stage harvested 4 days after foliar application. The treated plants (A) and the corresponding radioautograph (B) are shown.

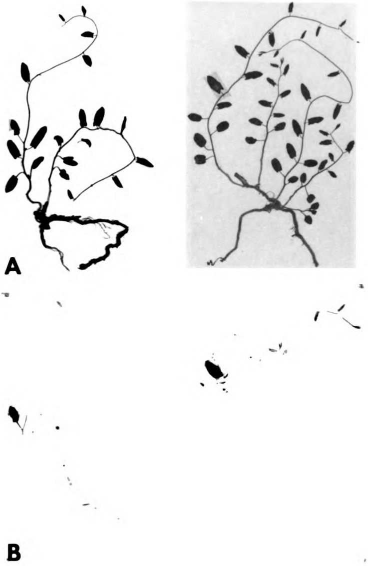
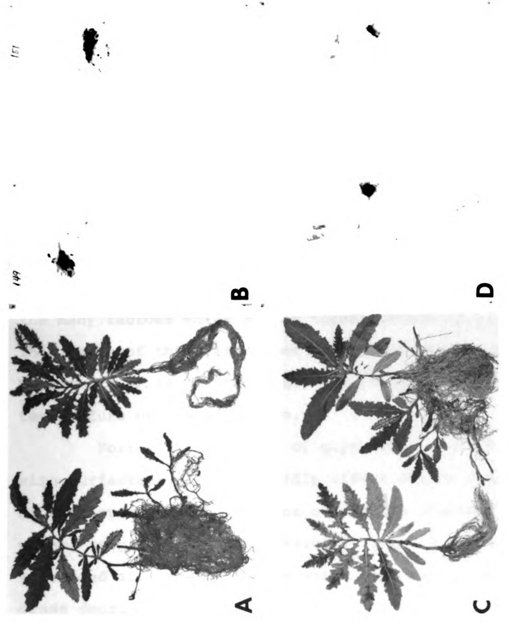

A
B

Figure 3. Translocation of ^{14}C-glyphosate in 10 to 15 cm tall Canada thistle harvested 7 days after foliar application. The treated plants (A) and the corresponding radioautograph (B) show Canada thistle plants pretreated with foliar application of 2.24 kg/ha of bentazon prior to ^{14}C-glyphosate application. The treated plants (C) and corresponding radioautograph (D) show Canada thistle plants treated with ^{14}C-glyphosate only.


A
B
C
D
149
151

activity, translocation may be inhibited. In Canada thistle in the bud stage, compared to the younger stage of growth, less ^{14}C was translocated from the point of application to the other plant parts (Figure 4A and B). In corn, soybeans, and pigweed, which are very susceptible to glyphosate, glyphosate was translocated throughout the plant (Figure 4C and D, Figure 5A and B, and Figure 5C and D, respectively). It is readily apparent that anything which affects the source to sink relationship will also affect the translocation of glyphosate in plants. In field studies, researchers have reported the effects of stage of growth (1), physiological activity (5), and temperature (2) on the control of quackgrass with glyphosate. These are a few of the many factors which affect translocation of glyphosate. Thus, some of the differences in control may be explained by effects of stage of growth, physiological activity, and temperature on translocation.

Foliar applications of glyphosate at 2.24 kg/ha with surfactant did not rapidly affect either respiration or photosynthesis in wheat or quackgrass (Table 5). In wheat, respiration dropped slightly after 3 hr but then increased slightly with time while respiration in quackgrass decreased slowly with time. The rate of respiration of quackgrass after 216 hr was significantly different from the control. Photosynthesis was more rapidly affected than respiration. The photosynthetic rates of the treated plants began to drop significantly 72 hr after treatment

Figure 4. Translocation of ^{14}C-glyphosate in Canada thistle and corn. The treated plant (A) and corresponding radioautograph (B) show Canada thistle in the bud-to-flowering stage which was harvested 7 days after foliar application. The treated plants (A) and corresponding radioautograph (B) show corn in the 4 to 5-leaf stage which was harvested 4 days after foliar application.


A
B
C
D

Figure 5. Translocation of ^{14}C-glyphosate in soybeans and redroot pigweed. The treated plant (A) and corresponding radioautograph (B) show soybeans in the 2nd-trifoliate-leaf stage which was harvested 4 days after foliar application. The treated plant (C) and corresponding radioautograph (D) show redroot pigweed in the 10-leaf stage which was harvested 4 days after foliar application.

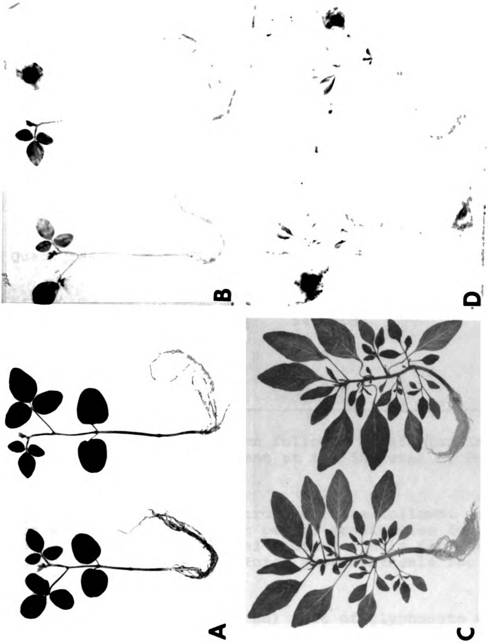

A
B
C
D

Table 5.--The effect of the foliar application of 2.24 kg/ha glyphosate[c] over time on the respiration and photosynthesis of wheat and quackgrass plants.

Species	Time	Respiration[a]	Total photosynthesis
	(hr)	(% of control)	
Wheat	0[b]	100 bcd	100 d
	3	89 abc	100 d
	24	109 bcd	101 d
	72	116 d	68 c
	216	114 cd	23 b
Quackgrass	0	100 bcd	100 d
	3	103 bcd	95 d
	24	94 abcd	88 d
	72	82 ab	28 b
	216	68 a	1 a

[a] Means in a column followed by similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] Average for controls were as follows: respiration for wheat, 246 µg CO_2/min per g; respiration for quackgrass, 99 µg CO_2/min per g; total photosynthesis for wheat, 0.395 µg CO_2/min per cm^2; and total photosynthesis for quackgrass, 0.904 µg/min per cm^2.

[c] Mono(dimethylamine) salt of glyphosate was used. 0.8% (v/v) MON 0027 surfactant was added.

with quackgrass affected more rapidly than wheat. Thus, respiration of quackgrass and photosynthesis of wheat and quackgrass were not affected until 72 hr or more after treatment. This indicates that either photosynthesis is not the primary mode of action or the herbicide acts slowly on the photosynthetic processes. It is also possible that the herbicide affects other plant processes before photosynthesis is affected.

The results of this study indicate that glyphosate, with the use of the proper surfactant, is rapidly absorbed and the ^{14}C readily translocated in quackgrass. Since the herbicide is probably phloem-translocated and nonselective, extensive translocation occurs in many annual and perennial species. Respiration and photosynthesis of quackgrass and wheat were not affected until at least 3 days after treatment with glyphosate. This indicates that the glyphosate either slowly inhibits the vital plant processes as respiration and photosynthesis or that these processes are not the primary mode of action of the herbicide and are affected after some other plant process has been inhibited.

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CHAPTER 6

SEPARATION OF GLYPHOSATE AND SEVERAL POSSIBLE METABOLITIES BY THIN-LAYER CHROMATOGRAPHY

Abstract

Glyphosate [*N*-(phosphonomethyl)glycine] was separated from aminomethylphosphonic acid (AMP), glycine, and sarcosine by using 500 mu-thick cellulose plates developed in ethanol:water:concentrated NH_4OH:trichloroacetic acid:acetic acid (55:35:2.5:3.5g:2,v/v/v/w/v).

Body

Glyphosate, a postemergence herbicide which appears exceptionally promising for perennial weed control, is rapidly inactivated in the soil. Determination of the metabolism of glyphosate in plants and soil required identification of the metabolites. This requires the development of a simple separation procedure for glyphosate from its likely metabolites of sarcosine, glycine, and AMP. Our objective was to use thin-layer chromatography to separate glyphosate from its metabolites.

Preliminary work indicated that cellulose gave greater resolution between these compounds than silica gel G or silica gel H. Thus, 500-um thick cellulose plates were used throughout all of the subsequent work. Technical grade glyphosate (98.5% pure) and glycine, sarcosine, and AMP of reagent grade were utilized. Twenty microliters of a 1 mg/ml solution of each of the four compounds was spotted on the plate at 1.5 cm from the bottom of the plate as a standard while 20 μl of each compound was applied to a single spot to test for separation. The lower 5 mm of the plate was submerged in the solvent and developed for 15 cm. After the plates were removed and dried, a 0.5% ninhydrin in butanol solution was uniformly sprayed on the plate. The plates were placed in an oven at 100 C for 5 minutes to develop the plate. The spots, usually pink or purple, faded within 48 to 72 hr after the initial development. The Rf values were defined as the distance from the origin to the middle of the spot divided by the distance from the origin to the solvent front.

Many of the initial methods tried for separation of these compounds did not provide resolution. In the preliminary work, only glyphosate, glycine, and sarcosine were used. Many of the solvents normally used for amino acid separation were used with the cellulose plates but most of these failed to satisfactorily separate glycine from glyphosate. For example, phenol:water (3:1, v/v) provided good separation of sarcosine and glycine but did not separate glycine from glyphosate. Thin-layer plates of mixtures of cellulose and silica gel G used with the solvents phenol:water (3:1, v/v) and methanol:water (2:1, v/v) did not increase resolution but increased smearing of the compound. Another method used was buffering the pH of the solvent system but this too did not increase the resolution. The most successful solvent for the separation of these three compounds was methanol:water:conc. NH_4OH: trichloroacetic acid (TCA):conc. acetic acid (55:35:5: 3.5g:2, v/v/v/w/v). This gave good resolution of the three compounds and developed in 2 1/2 to 3 hr. The Rf values of glyphosate, glycine and sarcosine were 0.30, 0.62, and 0.74, respectively. All of the constituents of the solvent system were necessary for separation. However, if 5 ml of concentrated acetic acid were substituted for 3.5 g of TCA and 2 ml of acetic acid, resolution was equally as good.

Later when the separation of AMP from the other compounds was attempted, Solvent E did not separate glyphosate from AMP. Changing the concentration of concentrated NH_4OH from 1, 2.5, 5, and 7.5 ml in the above system did not provide good separation. Solvent B and other solvents used in Table 1 did not provide good separation of all four compounds. Nonpolar solvent systems reduced the Rf values of these compounds. Of those solvents in Table 1, solvent E provided the best separation but still did not give separation of glyphosate and AMP. Solvents F through K all consisted of the same components but in different

Table 1.--Separation of glyphosate and its possible metabolites with five different solvent systems.

Compounds	Rf value in solvent[a]				
	A	B	C	D	E
Glyphosate	0.62	0.42	0.92	0.05	0.34
Aminomethylphosphonic acid	0.49	0.32	0.85	0.05	0.26
Glycine	0.48	0.36	0.80	0.43	0.55
Sarcosine	0.65	0.47	0.86	0.60	0.66
All four	0.48	0.32	0.81	0.05	0.32
			0.88	0.44	0.58
	0.61		0.94	0.61	0.68

[a] A = Methanol-water (67 + 33, v/v)

B = Ethanol-water (67 + 33, v/v)

C = Pyridine-methanol-water (4 + 20 + 80, v/v/v)

D = Chloroform-methanol-17% NH_4OH (40 + 45 + 20, v/v/v)

E = Methanol-water-conc. NH_4OH-TCA-acetic acid (55 + 35 + 5 + 3.5 g + 2, v/v/v/w/v).

proportions (Table 2). Only solvents F and I gave separation of all the compounds. If solvents H through K are compared, as the concentration of NH_4OH increased the Rf values decreased. Good separation was achieved with solvent I especially if the plate was developed for 17 to 18 cm. This solvent system was tested six times with the same results. Solvent F may also offer good possibilities for separation of these compounds. This simple one dimensional thin-layer chromatography system offers a means of separating glyphosate and its various metabolites from plant and soil extracts.

Table 2.--Separation of glyphosate and various possible metabolites with variations of single solvent system.

Compounds	Rf value in solvent[a]					
	F	G	H	I	J	K
Glyphosate	.11	.36	.50	.24	.20	.20
Aminomethylphosphonic acid	.20	.35	.53	.36	.26	.24
Glycine	.35	.61	.74	.49	.53	.50
Sarcosine	.53	.72	.73	.59	.64	.63
All 4	.10 .20 .35 .50	.36 .60 .72	.51 .71	.26 .36 .49 .59	.23 .54 .67	.23 .52 .66

[a] F = Ethanol-water-conc. NH_4OH-TCA-acetic acid (65 + 35 + 2.5 + 3.5 + 2, v/v/v/w/v)

G = Ethanol-water-conc. NH_4OH-TCA-acetic acid (45 + 45 + 5.0 + 3.5 + 2, v/v/v/w/v)

H = Ethanol-water conc. NH_4OH-TCA-acetic acid (55 + 35 + 1.0 + 3.5 + 2, v/v/v/w/v)

I = Ethanol-water-conc. NH_4OH-TCA-acetic acid (55 + 35+ 2.5 + 3.5 + 2, v/v/v/w/v)

J = Ethanol-water-conc. NH_4OH-TCA-acetic acid (55 + 35 + 5.0 + 3.5 + 2, v/v/v/w/v)

K = Ethanol-water-conc. NH_4OH-TCA-acetic acid (55 + 35 + 7.5 + 3.5 + 2, v/v/v/w/v).

CHAPTER 7

SUMMARY AND CONCLUSIONS

Field, greenhouse and laboratory studies were initiated to determine the factors affecting the use of glyphosate for quackgrass control in agronomic crop production, to understand the nature of the inactivation of glyphosate in the soil, and to determine the factors affecting its absorption, action, and translocation in the plant.

In the field, foliar applications of glyphosate at 1.12 to 2.24 kg/ha in the fall or the spring gave effective quackgrass control. Glyphosate more effectively controlled 25 to 30 cm tall (3 to 4-leaf) quackgrass than 15 to 20 cm tall (2 to 3-leaf) quackgrass. For example, late spring applications of glyphosate at 1.12 or 2.24 kg/ha provided season long control of quackgrass in soybeans and navy beans. If the quackgrass was treated when it was taller than 30 to 36 cm, at least 2.24 kg/ha was required for effective control. Fall tillage followed by early spring application gave poor control while tillage 7 or more days after treatment aided quackgrass control. No injury to corn, soybeans, or dry beans was observed after preplant applications of glyphosate.

Glyphosate appeared to be inactivated in the soil since only small quantities of ^{14}C were found in corn and soybean plants grown in ^{14}C-glyphosate-treated soil. To investigate the phenomena, wheat, a sensitive bioassay plant, was used. At 1.2×10^{-4} M, the moisture content of wheat plants grown in nutrient solution was affected. However, wheat plants grown in clay loam or muck soil treated preplant with 56.0 kg/ha of glyphosate did not show injury. Since soil autoclaving prior to herbicide application did not affect the phytotoxicity of glyphosate to wheat plants grown in the soil, microbial degradation was eliminated as the means of initial rapid inactivation in the soil. Thus, it is likely that adsorption is responsible for the rapid inactivation since increases in pH and soil phosphate level increased the phytotoxicity of soil applications of large quantities of glyphosate.

Examination of the soil components for herbicide adsorption showed that ethyl cellulose did not bind the herbicide as effectively as charcoal or muck soil. If cations were added to the muck or the clay, adsorption was affected. Iron and aluminum-saturated bentonite clay or muck adsorbed larger quantities of glyphosate than calcium or sodium-saturated bentonite or muck. Illite and kaolinite bound large quantities of ^{14}C-glyphosate. In the soil, glyphosate was rapidly adsorbed with soils low in phosphate binding the most glyphosate. Glyphosate was relatively immobile in the soil and was degraded to CO_2 by microbes. The sequence of glyphosate inactivation in the soil is its rapid adsorption followed by the microbial degradation. Glyphosate has a net charge of -1 or -2 at pH 4 to 9 since its pKa values are < 2, 2.6, 5.6, and 10.6.

With the observed effectiveness of glyphosate in the field, it was desirable to find out more about its action, absorption, and translocation. The type of adjuvant used with glyphosate had a significant effect on its initial activity. Iron or iron-NTA treatments did not appear to affect the activity of glyphosate on wheat. In quackgrass, absorption is rapid and a large portion of the ^{14}C was translocated into the rhizome and untreated shoots. In the four perennial weeds, two crop plants, and the annual weed tested, the ^{14}C acted as a phloem-mobile compound moving to the areas of highest metabolic activity such as shoot or root apices.

Since glyphosate was shown to be metabolized in the soil and possibly in the plant, a separation procedure was necessary. A thin-layer chromatography procedure capable of separating glyphosate from several of its possible metabolites was developed.

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APPENDICES

APPENDIX A

Modified No. 1 Hoagland's Solution

1.	1 M KH_2PO_4	2 ml/L
2.	1 M KNO_3	2 ml/L
3.	1 M $Ca(NO_3)_2 \cdot 4H_2O$	3 ml/L
4.	1 M $MgSO_4 \cdot 7H_2O$	2 ml/L
5.	1.5 g/L $MnCl_3 \cdot 4H_2O$ 2.5 g/L H_3BO_4 0.1 g/L $ZnCl_2$ 0.05 g/L $CuCl_2 \cdot 2H_2O$ 0.05 g/L MoO_3	1 ml/L
6.	26.3 g/L Sequestrene^R	1 ml/L
	pH 6.5 to 6.8 with 1 M NaOH	

APPENDIX B

Method of recorder chart paper conversion to $\mu g/CO_2/min$

Compressed air flow rate	500 cc/min
CO_2 content of compress air	330 ppm or 0.033%
Molecular weight of CO_2	44
Standard volume	22.4 L/mole

22.4 L contains 1 mole of gas

0.5 L/min contains 0.0223 M (g/L) of gas/min.

1 mole of gas contains 0.033 percent CO_2

Therefore 0.0223 M/min contains 7.359×10^{-6} M CO_2/min

or $7.359 \times 10^{-6} \times 44 = 3.23 \times 10^{-3}$ g CO_2/min

or 3.23 mg CO_2/min = 323 μg CO_2/min

therefore on Beckman #101283 recorder paper, 1 unit change = 6.46 μg CO_2/min.

APPENDIX C

Table C-1.--The effect of glyphosate (MON 0468) in sand culture on the growth of 16-day-old 'Anoka' soybeans.

Glyphosate	Germination	Emergence	Plant height	Fresh weight	Dry weight
(kg/ha)	(%)	(%)	(cm/plant)	(g/plant)	(g/plant)
0	100[a] a	93 c	13.4 d	1.40 c	0.110 d
0.56[b]	96 a	97 d	4.2 c	0.60 b	0.033 c
1.12[b]	93 a	57 c	2.4 b	0.44 a	0.020 b
2.24[b]	98 a	42 b	1.1 ab	0.39 a	0.011 ab
4.48[b]	98 a	23 a	0.3 a	0.39 a	0.006 a
0.8% MON 0027	97 a	90 e	12.7 d	1.25 c	0.095 d

[a] Values are the means of two experiments with four replications per experiment. Means in a column followed by similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] 0.8% (v/v) MON 0027 surfactant added, product of Monsanto Company, St. Louis, Missouri.

APPENDIX D

Table D-1.--The effect of glyphosate (MON 0468) applied in sand culture on the growth of 16-day-old 'B-5128' flax.

Glyphosate	Germination	Emergence	Plant height	Fresh weight	Dry weight
(kg/ha)	(%)	(%)	(cm/plant)	(g/plant)	(g/plant)
0	92[a] a	88 c	8.6 c	0.14 b	0.016 b
0.56[b]	88 a	40 b	1.4 b	0.03 a	0.004 a
1.12[b]	88 a	15 a	0.5 a	0.03 a	0.003 a
2.24[b]	81 a	18 a	0.7 a	0.03 a	0.003 a
4.48[b]	83 a	10 a	0.1 a	0.03 a	0.003 a
0.8% MON 0027	92 a	93 a	8.9 c	0.02 b	0.021 b

[a] Values are the means of two experiments with four replications per experiment. Means in column followed by similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] 0.8% (v/v) MON 0027 surfactant added, product of Monsanto Company, St. Louis, Missouri.

APPENDIX E

Table E-1.--The effect of glyphosate (MON 0468) applied in sand culture on the growth of 16-day-old 'Wisconsin SMR 15' cucumber.

Glyphosate	Germination	Emergence	Plant height	Fresh weight	Dry weight
(kg/ha)	(%)	(%)	(cm/plant)	(g/plant)	(g/plant)
0	100[a] a	95 a	4.9 d	0.62 d	0.046 d
0.56[b]	96 a	92 a	3.3 c	0.39 c	0.035 c
1.12[b]	93 a	82 a	2.6 b	0.32 b	0.030 b
2.24[b]	98 a	87 a	2.3 ab	0.24 a	0.025 a
4.48[b]	98 a	77 a	1.9 a	0.21 a	0.021 a
0.8% MON 0027	100 a	100 a	4.4 d	0.56 d	0.040 d

[a] Values are the means of two experiments with four replications per experiment. Means in a column followed by similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] 0.8% (v/v) MON 0027 surfactant added, product of Monsanto Company, St. Louis, Missouri.

APPENDIX F

Table F-1.--The effect of glyphosate (MON 0468) applied in sand culture on the growth of 16-day-old 'Michigan 400' corn.

Glyphosate	Germination	Emergence	Plant height	Fresh weight	Dry weight
(kg/ha)	(%)	(%)	(cm/plant)	(g/plant)	(g/plant)
0	95[a] a	95 e	25.3 d	1.11 c	0.125 d
0.56 b	100 a	75 d	8.1 c	0.48 b	0.047 c
1.12[b]	100 a	55 c	2.8 b	0.15 a	0.019 b
2.24[b]	98 a	42 b	2.0 ab	0.12 a	0.017 b
4.48[b]	98 a	13 a	0.3 a	0.02 a	0.004 a
0.8% MON 0027	93 a	94 e	23.7 d	0.94 c	0.102 d

[a] Values are the means of two experiments with four replications per experiment. Means in a column followed by similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] 0.8% (v/v) MON 0027 surfactant added, product of Monsanto Company, St. Louis, Missouri.

APPENDIX G

Table G-1.--The effect of glyphosate (MON 0468) applied in sand culture on the growth of 16-day-old 'Larker' barley.

Glyphosate	Germination	Emergence	Plant height	Fresh weight	Dry weight
(kg/ha)	(%)	(%)	(cm/plant)	(g/plant)	(g/plant)
0	90[a] a	88 c	14.7 d	0.21 e	0.025 d
0.56[b]	92 a	78 c	9.3 c	0.12 c	0.016 c
1.12[b]	90 a	48 b	3.9 b	0.04 b	0.006 b
2.24[b]	92 a	35 b	2.6 b	0.02 ab	0.003 ab
4.48[b]	87 a	17 a	1.1 a	0.01 a	0.002 a
0.8% MON 0027	94 a	88 c	13.7 d	0.18 d	0.023 d

[a] Values are the means of two experiments with four replications per experiment. Means in a column followed by similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] 0.8% (v/v) MON 0027 surfactant added, product of Monsanto Company, St. Louis, Missouri.

APPENDIX H

Table H-1.--The effect of glyphosate (MON 0468) applied in sand culture on the growth of 16-day-old 'Clintland 66' oats.

Glyphosate	Germination	Emergence	Plant height	Fresh weight	Dry weight
(kg/ha)	(%)	(%)	(cm/plant)	(g/plant)	(g/plant)
0	100[a] b	100 b	18.2 e	0.19 e	0.025 e
0.56[b]	98 b	98 b	14.7 d	0.20 e	0.022 d
1.12[b]	100 b	98 b	11.1 c	0.14 c	0.017 c
2.24[b]	97 ab	92 b	8.6 b	0.10 b	0.014 b
4.48[b]	90 a	80 a	6.4 a	0.06 a	0.008 a
0.8% MON 0027	99 b	97 b	18.1 e	0.17 d	0.024 e

[a] Values are the means of two experiments with four replications per experiment. Means in a column followed by similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] 0.8% (v/v) MON 0027 surfactant added, product of Monsanto Company, St. Louis, Missouri.

APPENDIX I

Table I-1.--The effect of glyphosate (MON 0468) applied in sand culture on the growth of 16-day-old 'Avon' wheat.

Glyphosate	Germination	Emergence	Plant height	Fresh weight	Dry weight
(kg/ha)	(%)	(%)	(cm/plant)	(g/plant)	(g/plant)
0	93[a] a	87 c	21.2 d	0.23 e	0.033 e
0.56[b]	98 a	78 c	10.6 c	0.11 c	0.015 c
1.12[b]	93 a	43 b	6.1 b	0.07 b	0.009 bc
2.24[b]	95 a	30 ab	3.1 a	0.03 a	0.005 ab
4.48[b]	93 a	22 a	1.6 a	0.02 a	0.002 a
0.8% MON 0027	93 a	88 c	20.4 d	0.20 d	0.028 d

[a] Values are the means of two experiments with four replications per experiment. Means in a column followed by similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] 0.8% (v/v) MON 0027 surfactant added, product of Monsanto Company, St. Louis, Missouri.

APPENDIX J

Table J-1.--The effect of temperature on glyphosate (MON 0468) activity on quackgrass.[c]

Pretreatment temp. (C)	Posttreatment temp. (C)	Glyphosate (kg/ha)[b] 0	2.24
		(% H_2O)[a]	
20	20	77.9 b	64.0 ab
	25	77.6 b	56.0 ab
	30	75.0 b	56.3 ab
25	20	74.8 b	61.5 ab
	25	72.8 b	52.8 ab
	30	73.1 b	58.8 ab
30	20	75.2 b	57.7 ab
	25	73.5 b	46.3 a
	30	41.1 a	59.0 ab

[a] Values are the means of two experiments with four replications each. Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] 0.8% (v/v) MON 0027 surfactant added, product of Monsanto Company, St. Louis, Missouri.

[c] The plants were treated 20 days after planting and harvested 18 days after treatment.

APPENDIX K

Table K-1.--The effect of foliar application of glyphosate (MON 0468) on the moisture content of 15-day-old quackgrass plants.

Treatment	Rate	Days after treatment		
		9 days	15 days	21 days
	(kg/ha)			
Control	0	82.41[a] f	79.98 ef	77.73 ef
Glyphosate[b]	0.56	79.03 ef	77.91 ef	77.02 ef
Glyphosate[b]	1.12	78.72 ef	73.07 ef	64.82 de
Glyphosate[b]	2.24	77.09 ef	50.05 bc	38.63 ab
Glyphosate[b]	4.48	56.37 ed	37.53 ab	29.75 a

[a] Values are the means of two experiments with three replications each. Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] 0.8% (v/v) MON 0027 surfactant added, product of Monsanto Company, St. Louis, Missouri.

APPENDIX L

Table L-1.--The effect of diluent volume on the herbicidal activity of glyphosate (MON 0468) as measured by moisture content on 14-day-old quackgrass.[c]

Glyphosate	L/ha 206	L/ha 421	L/ha 823
(kg/ha)		(%)	
0	81.1[a] f	80.7 f	81.3 f
0.56[b]	71.0 ef	74.9 ef	68.5 ef
1.12[b]	42.3 bc	55.1 cd	62.4 de
2.24[b]	40.0 ab	39.1 ab	46.7 bc
4.48[b]	39.0 ab	27.2 a	39.8 ab

[a] Values are the means of two experiments with four replications per experiment. Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] 0.8% (v/v) MON 0027 surfactant added, product of Monsanto Company, St. Louis, Missouri.

[c] The plants were harvested 12 days after treatment.

APPENDIX M

Table M-1.--The effect of herbicide rate and surfactant rate of glyphosate (MON 0468) on the moisture content of 15-day-old quackgrass seedlings.[c]

Glyphosate	MON 0027 (%)[b]					
	0	0.08	0.2	0.4	0.6	0.8
(kg/ha)			(%)			
0	79.9[a] e	81.2 e	80.7 e	81.2 e	72.3 de	80.3 e
0.56	80.0 e	79.2 e	78.4 e	80.2 e	77.4 e	79.6 e
1.12	78.5 e	76.8 e	76.5 e	75.0 d	72.8 de	77.2 e
2.24	80.8 e	67.2 de	66.9 de	61.9 ed	51.6 bc	60.8 cd
4.48	78.5 e	50.4 bc	39.4 ab	34.4 a	31.6 a	33.5 a

[a] Values are the means of two experiments with three replications per experiment. Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] MON 0027 is a surfactant produced by Monsanto Company, St. Louis, Missouri.

[c] The plants were harvested 15 days after treatment.

APPENDIX N

Table N-1.--The effect of rate, surfactant and stage of maturity on the desiccation of quackgrass following a postemergence application of glyphosate (MON 0468).[e]

Adjuvant	Rate, %	Chemical	Rate, kg/ha	Plant age 15 days	 22 days	 29 days
					(% H_2O)	
Control		Glyphosate	0	81.6[a] g	80.7 g	74.6 fg
MON 0027,[b]	0.8%	Glyphosate	0	81.8 g	80.3 g	76.9 fg
MON 0027,	0.8%	Glyphosate	0.56	77.6 fg	72.5 d-g	70.5 d-g
MON 0027,	0.8%	Glyphosate	1.12	74.3 fg	66.5 c-f	68.3 c-g
MON 0027,	0.8%	Glyphosate	2.24	47.3 a-e	52.7 a-f	52.8 a-f
MON 0027,	0.8%	Glyphosate	4.48	34.0 a	36.1 a	47.3 a-e
MON 0027,	0.8%	Glyphosate + trazine	2.24 + 2.24	74.2 fg	64.4 c-g	70.4 d-g
X-77,[c]	0.2%	Glyphosate	0.56	80.8 g	79.4 fg	74.5 fg
X-77,	0.2%	Glyphosate	1.12	79.9 fg	73.6 e-g	70.1 d-g
X-77,	0.2%	Glyphosate	2.24	59.5 a-g	59.9 a-g	62.8 b-g
X-77,	0.2%	Glyphosate	4.48	46.7 a-d	35.7 a	43.6 abc
Sun 11E,[d]	1.0%	Glyphosate	0.56	82.2 h	79.4 fg	76.4 fg
SUN 11E,	1.0%	Glyphosate	1.12	80.3 g	79.3 fg	73.0 d-g
SUN 11E,	1.0%	Glyphosate	2.24	76.2 fg	70.0 d-g	70.0 d-g

Adjuvant	Rate, %	Chemical	Rate, kg/ha	Plant age 15 days	 22 days	 29 days
					(% H_2O)	
Sun 11E,	1.0%	Glyphosate	4.48	54.5 a-g	38.2 ab	65.2 e-g
Sun 11E,	1.0%	Atrazine	2.24	78.0 fg	74.6 fg	74.0 fg
---------		Atrazine	2.24	75.7 fg	74.7 fg	78.9 fg

[a] Values are the means of two experiments with three replications per experiment. Means with similar letters are not significantly different at the 5% level by Duncan's Multiple Range Test.

[b] MON 0027 is a surfactant produced by Monsanto Company, St. Louis, Missouri.

[c] X-77 is a non-ionic surfactant produced by Chevron Chemical Company, San Francisco, California.

[d] Sun 11E is a phytobland oil produced by the Sun Oil Company, Philadelphia, Pennsylvania.

[e] The plants were harvested 15 days after treatment.