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ABSTRACT

THE PHYTOTOXICITY AND MECHANISM OF ACTION OF HERBICIDE AND HERBICIDE-ADJUVANT COMBINATIONS ON QUACKGRASS (AGROPYRON REPENS (L.) BEAUV.)

by Alan R. Putnam

Quackgrass (Agropyron repens (L.) Beauv.) prevails as one of the world's primary noxious weeds. Herbicide practices for quackgrass control are needed which do not injure crops or produce excessive residues in either crops or soils. Herbicide combinations and herbicide-adjuvant combinations have provided enhanced activity over that obtained from individual herbicides, but little is known about the mechanism of action of these combinations.

Adjuvants were evaluated under greenhouse and field conditions as a means of increasing the herbicidal action of simazine, diuron, amitrole-T, and paraquat. An increase in herbicidal action was obtained when adjuvants were added to simazine and diuron applied to cucumber plants in the greenhouse. Adjuvants combined with simazine and diuron did not provide acceptable quackgrass control. The activity of amitrole-T and paraquat was increased by adjuvants in field trials. This improved phytotoxicity was partially due to increased wetting of the plant.

Herbicide combinations provided increases in phytotoxicity which resulted in acceptable season-long quackgrass control. Two types of herbicide combinations displayed synergistic action on quackgrass.

Paraquat at 1/2 lb/A with simazine or diuron at 3-4 lb/A provided long term phytotoxicity greater than that obtained from either herbicide alone. Apparently, this synergism was not due to increases in the absorption or translocation of one herbicide as directly influenced by the other. Paraquat destroyed the aerial portions of quackgrass plants, reduced the regrowth capacity, and increased the plant's susceptibility to simazine absorbed through the roots.

*Paraquat moved both acropetally and basipetally in quackgrass leaves and up to 2.5% of that absorbed was translocated out of the treated leaf. More *paraquat was translocated in the light than under dark conditions. The wettable powder formulation of simazine increased the absorption of *paraquat, but this effect could not be attributed directly to simazine.

The limited *simazine absorbed moved only acropetally. Paraquat did not appreciably increase the absorption or translocation of *simazine.

The second type of synergism observed involved the combination of paraquat and amitrole-T. Pretreatment with amitrole-T 7 days preceding paraquat application provided increased phytotoxicity over that obtained when the 2 herbicides were applied together or singly. In subsequent tests, foliar dessication with paraquat or top removal by cutting following foliar sprays of amitrole decreased regrowth.

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*Designates a ^{14}C-labeled herbicide.

Amitrole or amitrole-T pretreatment increased the basipetal movement of *paraquat in, and translocation out of the treated leaf. The most pronounced enhancement was obtained with amitrole-T.

When amitrole, ammonium thiocyanate (T), or amitrole-T were applied with *paraquat there was a reduction in its absorption and movement. When paraquat was applied with *amitrole, there was also a decrease in the absorption and translocation of the latter herbicide.

These studies indicate that increased herbicidal action was obtained by combining herbicides with adjuvants or other herbicides. Synergisms such as those reported will be valuable in developing herbicide practices for quackgrass and other perennial weed species.

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INTRODUCTION

Quackgrass is one of the most noxious weeds in the Northern United States. Control measures must be established for this weed which are compatible with crop culture. Effective chemical treatments should be non-toxic to the crop and not produce excessive chemical residues in the crop or soil.

A promising new area of herbicide research involves the combining of herbicides with adjuvants or other herbicides to obtain increased herbicidal action. To date, herbicide combinations have been of 2 types; those which controlled a broader spectrum of weed species and those which displayed synergistic action on a single species. The latter type has the most potential for improving perennial weed control.

The objectives of this research were to discover effective herbicide or herbicide-adjuvant combinations for quackgrass control in perennial horticultural crops, and to study the mechanism of the interaction obtained with certain effective mixtures.

REVIEW OF THE LITERATURE

Characteristics of Quackgrass.

Quackgrass (Agropyron repens (L.) Beauv.) is a common perennial grass in the Northern United States, Canada, and Europe. The range in North America has been described as Newfoundland west to Alaska and south to North Carolina, Arkansas, and California (53). Most taxonomists believe it was introduced from Europe but some have reported that it is indigenous to the Atlantic Coast.

Quackgrass is characterized by culms 5-10 dm high arising from long slender rhizomes. The leaves are flat, 5-10 mm wide, with scattered hairs on the upper surface and auricles at the base of the leaf blade. The inflorescence is a terminal solitary spike with numerous spikelets, each of which is 4-8 flowered (53). Since quackgrass is cross pollinated, considerable variation exists among clones (97).

Rhizomes of quackgrass form a dense mat, usually distributed in the upper 3-4 inches of an undisturbed soil (41). Eight tons of rhizomes per acre may exist in a badly infested field (6) and an acre may contain 80 miles of rhizomes (45). Lateral buds are formed at each node along the rhizome and may develop into branch rhizomes or under favorable conditions may form new culms (90). A study conducted in Pennsylvania indicated that one rhizome segment containing 1 lateral bud produced 206 culms and 14 rhizomes measuring 458 feet in length after 1 growing season. The diameter spread of rhizome growth after

this period of time was greater than 10 feet (97).

Life Cycle of Quackgrass.

Quackgrass may be propagated by seed. Flowering generally occurs in late June or early July and the seeds ripen in July (5). Kephart (73) reported that the average seed head contains 25 viable seeds and this may amount to 16 bushels per acre in a heavily infested field. Seeds have been shown to remain viable after 4 years of storage in the soil, however, those near the surface usually germinate within 2 years (36).

The chief means of propagation is by rhizomes. Initiation of rhizomes begins in May and June and is often followed by another period of initiation in the fall (33, 41, 121, 99). Each bud on a rhizome has the potential to produce a new plant and can persist on storage materials in the rhizome. Tillage practices break up rhizomes and disperse them to new areas where they may produce new plants. In undisturbed fields, many rhizome buds remain dormant throughout the life of the rhizome (5).

Several investigators have reported on bud dormancy in quackgrass. Johnson and Buchholtz (70, 71) have proposed 2 types of dormancy associated with lateral buds on the rhizomes. One type, which they call correlation inhibition, occurs in undisturbed rhizomes throughout the growing season. Since these buds initiate growth when cut in sections, or after removing the apex, the type of inhibition is thought to be due to apical dominance. The second type occurs in early summer and apparently is not a result of apical dominance, since rhizomes cut into segments

fail to grow when provided favorable conditions. Other workers have also observed this period of no sprouting (33, 121). This type of dormancy can apparently be overcome by growing plants under high nitrogen nutrition (71).

Meyer and Buchholtz (86, 87) studied several environmental and chemical factors influencing the sprouting of buds. They observed that the optimum temperature for growth was 20^{o}-27^{o} C. Various levels of carbon dioxide and oxygen encountered in their field experiments had no apparent influence on the sprouting of buds. Indoleacetic acid, kinetin, and gibberellic acid had little or no influence on sprouting at the several concentrations tested. Naphthaleneacetic acid at concentrations of 1×10^{-3}M to 1×10^{-5}M caused a decrease in bud growth.

The life expenctancy of rhizomes rarely exceeds 15 months, but since they are produced in such great quantity, quackgrass may reproduce vegetatively for an indefinite period of time (73).

Culm growth is rapid in May and June and declines somewhat during flowering and seed development, however, the production of daughter plants continues throughout the growing season (73). Studies on the level of carbohydrate reserves indicated there is no period during the year when they are extremely low. This phenomenon has not been observed with most other perennial species (7).

Factors Which Effect The Control of Quackgrass.

Since rhizomes have such a high reproductive capacity it is essential that control measures are effective on them. Extensive

cultivation practices have proven effective in controlling quackgrass rhizomes. Tillage practices may be effective because they destroy the culms and expose many rhizomes to dessication. Repeated tillage breaks the dormancy of lateral buds and causes a subsequent depletion of the supply of storage materials (6). Tillage practices are usually more effective than growing several "smother crops" (77).

Nitrogen nutrition influences the growth of rhizomes and the effectiveness of herbicide treatments. McIntyre (79) found that plants grown under high nitrogen levels produced more tillers (on a percentage basis) and those grown under low nitrogen levels produced more rhizomes. However, the net effect was a marked increase in the total number of rhizomes per plant as the nitrogen supply increased. Dexter (32) observed that rhizomes grown with high nitrogen levels were more vigorous, sprouted more readily, and were more sensitive to clipping treatments than those grown under low nitrogen nutrition. Ries (100) reported quackgrass was more effectively controlled with dalapon[1] if nitrogen fertilizer was applied prior to the herbicide application.

Herbicides for Controlling Quackgrass.

Halogenated aliphatic acids:

Salts of TCA have been used at rates of 80-150 lb/A to control perennial grasses and at lower rates have been effective in controlling

[1] Common names of herbicides as approved by the Weed Society of America are employed in the text. Chemical names are shown in Appendix 1.

seedling grasses selectively in crops (29). Several investigations have shown the effectiveness of TCA on quackgrass proportional to the rate used. Rates of 100 lb/A have produced satisfactory top kill and rates of 150 lb/A have completely controlled regrowth (11, 17, 49, 75, 111). At these rates, selectivity in most crops is lost. Barrons et al. (11) reported that root absorption of TCA is more important than foliar absorption in producing phytotoxic effects.

Dalapon is a more effective grass killer by foliar application than TCA and is quite effective on perennial grasses (74). Multiple applications 5-20 days apart of 5-10 lb/A have been more effective than one application at higher rates (74). Dalapon may be absorbed through both the foliage and the roots and apparently moves in both the xylem and phloem (66). The amount translocated is proportional to the rate of application assuming no acute toxicity occurs (28).

Both dalapon and TCA seem to inhibit the growing points of shoots. Anderson et al. (4) observed that dalapon caused degradation of proteins to amino acids. It was also reported that these compounds inhibited pantothenic acid metabolism and when pantothenate was supplied to barley (Hordeum vulgare) plants, they partially overcame the toxic effects (62). Both compounds are known to cause precipitation of proteins at high concentrations of up to 20,000 ppm (98).

Maleic hydrazide:

MH is absorbed slowly by the leaves and inhibits the shoot growth of many plant species. The sodium salt (MH-40) has been used

as a herbicide to control quackgrass (64, 76, 111). Friesen (49) obtained satisfactory control of quackgrass with 16 lb/A but several other workers failed to obtain adequate control unless tillage practices followed the MH application (64). The use of contact herbicides following MH application did not enhance its effectiveness (64).

Sachs and Lang (105) have shown that MH completely prevents cell division in the apical meristem of cocklebur (Xanthium strumarium). Another effect which was observed is a collapse of seive tubes which results in a marked accumulation of carbohydrates in the leaves (78).

Triazines and substituted ureas:

These 2 groups of compounds, differing greatly in chemical structure, show similar distribution patterns and are believed to have a similar mode of action in plants. Their major use has been as preemergence herbicides for controlling germinating annual weeds. They are characterized by low solubility in water. Two triazine herbicides which have been quite effective on quackgrass are simazine and atrazine (18). Atrazine is more effective on established perennial grasses since it is absorbed readily by the foliage and roots, whereas simazine is not absorbed in toxic quantities by the foliage (29). Two substituted ureas, monuron and diuron have been utilized for selective weed control in crops and at higher rates have been effective as soil sterilants (21).

Crafts (30) reported that ^{14}C-atrazine[1] is readily absorbed

[1]Hereafter an asterisk * shall designate a radioactive compound.

by the leaves of both bean (Phaseolus vulgaris) and barley and moves acropetally in the apoplast. When *simazine or *monuron were applied to barley leaves, they moved only in the apoplast and failed to move out of the treated leaf after 16 days.

The triazine and urea herbicides are readily absorbed by the roots and move rapidly to the tops of plants. Sheets (109) reported that *simazine was distributed throughout the tops of oat (Avena sativa) plants 3 hours after exposing the roots to the radioactive solution. *Simazine moved to the leaves of cucumber (Cucumis sativus) in less than 30 minutes (31). Crafts (30), using autoradiography, showed that both *monuron and *simazine were absorbed sufficiently in 30 minutes to give strong images of the roots of barley. After 8 hours, both herbicides were distributed throughout the shoots.

Wax and Behrens (119) studied the uptake and distribution of *atrazine by the roots and leaves of quackgrass. The amount of *atrazine accumulated in the leaves after 24 hours from root treatments increased with increasing temperatures. The radioactivity in the leaves decreased as the relative humidity was increased. The uptake of *atrazine by the leaves of quackgrass was not greatly influenced by the temperatures studied. *Atrazine applied to the leaves moved only in an acropetal direction. These results are similar to those obtained by Yamaguchi and Crafts (123) with other plant species, and suggest the triazines move in the transpiration stream.

The triazines and substituted ureas inhibit the photochemical activity of chloroplasts, an effect which may be partially

overcome by the addition of glucose (8, 88). Moreland et al. (88) have shown that simazine interferes with the Hill Reaction. Exer (44) reported a 50% inhibition of oxygen evolution with a concentration of 7×10^{-7}M simazine. All the triazine herbicides tested inhibited oxygen evolution at 10^{-4} to 10^{-7}M. Cooke (27) found that 10^{-6}M monuron completely inhibited the Hill Reaction in spinach (Spinacia oleracea) chloroplasts and calculated that one molecule of monuron prevented the photosynthetic activity of about 125 chlorophyll molecules.

Duysens et al. (37) reported that 2 pigment systems are involved in cytochrome oxidation during photosynthesis. Light of 680 mu oxidized an F or C type cytochrome, whereas light of 560 mu reduced the cytochrome. Diuron at 1.1×10^{-6}M inhibited the reduction at 560 mu, with an oxidation occurring instead. Good (54) suggested that the NH group, which is common to these compounds, may form hydrogen bonds with proteins and hence inactivate an enzyme involved in the oxidation of water.

Corn (Zea mays) has shown excellent tolerance to the triazine herbicides. It metabolized simazine to hydroxy-simazine, a non-phytotoxic compound (55). Eastin et al. (39) studied lines of corn which were susceptible to simazine and atrazine. These lines apparently lacked the ability to detoxify these compounds. By supplying either glucose or sucrose through severed leaf tips they were able to overcome the toxicity produced by these triazine compounds.

Amitrole and amitrole-T:

Amitrole has been very effective as a foliar spray for the control of perennial weeds such as quackgrass, Canada thistle (Cirsium arvense) and poison ivy (Rhus radicans). It is readily absorbed by both the foliage and the roots and is apparently very phloem mobile in the plant (28, 20, 66). Bondarenko and Willard (14) found that *amitrole was absorbed and moved from the leaf to the stem of Canada thistle in 1 hour. After 30 hours, it was distributed throughout Canada thistle and soybean (Glycine Max) plants. Yamaguchi and Crafts (123) reported that the absorption of *amitrole by the lower leaf surface of wandering-Jew (Zebrina pendula) was greater than that of the upper surface which has no stomata. *Amitrole was translocated out of the treated leaf of quackgrass 4 hours after treatment. After 96 hours, the amount of radioactivity moving out of the treated leaf was still increasing (34).

Most studies indicate that *amitrole is readily degraded by plants with little remaining as the parent compound (22, 59, 95). In one experiment it was reported that after 5 days only 7% of the radioactivity could be recovered as *amitrole (95).

*Amitrole and its metabolites accumulate in greatest amounts in meristematic areas such as shoot apices and root tips (3, 14, 95). Very little to none has been shown to accumulate in dormant buds, storage parenchyma, or mature tissues of nutgrass (3). Basipetal movement of *amitrole seems to depend on the movement of carbohydrates. Penot (93) obtained very little basipetal movement in the

dark unless he added sucrose.

*Amitrole is also absorbed by the roots and moves rapidly in the transpiration stream (28). It is translocated through the rhizomes of several perennial weed species including quackgrass (3, 103).

In 1958, it was reported that ammonium thiocyanate, a non-phytotoxic compound, increased the herbicidal activity of amitrole (84). Many workers have shown the combination of amitrole and ammonium thiocyanate (amitrole-T) is much more effective than amitrole on perennial grasses, especially quackgrass (34, 65, 96). This enhancement of activity has not been observed on broadleaved perennials and annual weeds (2, 82). Donnalley and Ries (35) reported that ammonium thiocyanate increased the translocation of *amitrole in quackgrass and postulated that this might account for the increased effectiveness of this combination.

The mode of action of amitrole is not well understood. However, much work has been conducted and many reports of varied effects published. Processes shown to be affected are respiration (58), pigment synthesis (104), porphrin metabolism (104), purine and pyrimidine synthesis (1, 120), ethanol metabolism (89), riboflavin metabolism (113, 114), glycine and serine metabolism (23), catalase activity (94), and histidine metabolism (63).

Histological observations on amitrole induced chlorotic tissue show a lack of chloroplast development rather than a direct effect on chlorophyll. Plastids are often completely lacking in chlorotic tissue (10[illegible]

Amitrole interferes with histidine metabolism in yeast and other organisms (63). Hilton reported that addition of L-histidine to yeast cultures provided protection against amitrole inhibition. This protection has also been observed with corn, oats, wheat (Triticum aestivum) and tomato (Lycopersicon esculentum). More recently, Castelfranco et al. (24) from studies with Scenedesmus postulated that the most likely mode of action at the biochemical level is that amitrole (a) inhibits purine synthesis or (b) is a competitive inhibitor of purine utilization. The former hypothesis is shared by Wolf (122) who conducted similar studies with Chlorella.

Paraquat:

Paraquat is a relatively new herbicide formulated as the dichloride or methyl sulfate salt. It is completely soluble in water and insoluble in most organic solvents (20). Paraquat has been employed as a non-selective herbicide in non-crop areas, in renovation for range seedings, and as a herbicide for aquatic weeds. It also has shown promise for weed control in fruit plantings.

The absorption and translocation of paraquat have not been thoroughly investigated. Baldwin (10) studied the translocation of diquat, a closely related compound. Tomato plants treated with diquat on 1 leaf only, and maintained under normal daylight conditions, exhibited only localized damage. When the plants were maintained in the dark 6 hours after treatment, followed by exposure to the light, they were completely killed. It was hypothesized that

during the dark period, the diquat was distributed throughout the plant and upon exposure to light, phytotoxicity occurred. Subsequent studies with *diquat showed this hypothesis to be false. *Diquat failed to move out of the treated tomato leaf unless the plants were exposed to light. Baldwin has now proposed that during the dark period, because of the lack of acute phytotoxicity, diquat may move into the vascular system. Upon exposure to light, it may then be translocated with other solutes. This hypothesis remains to be proven.

The normal movement of diquat in the presence of light is believed to occur in the xylem. Decreasing the transpiration rate of tomato plants decreased the movement of the herbicide (10). *Diquat and *paraquat were both very immobile when applied either to the leaves or the roots of American pondweed (Potamogeton nodosus) (108).

Kent (72) reported that the light environment prior to, and after treatment is important in determining the response obtained with paraquat. He obtained increased toxicity when the plants were shaded either before or after treatment. However, he could not attribute the response entirely to light differences because the humidity and temperature were altered by his shading technique.

The dipyridylium compounds cause a rapid destruction of plant tissue in the light. This effect has been attributed to the reduction of these compounds to form free radicles by the addition of 1 electron per molecule (15, 19, 83). The toxicity obtained is

believed to result from the formation of hydrogen peroxide which in turn degrades proteins and other macromolecules in the protoplast (83). Oxygen is required for the free radicles to be toxic. When bean, mesquite (Prosopis juliflora), or honeysuckle (Lonicera tartarica) leaves were placed in an illuminated solution containing 10^{-4}M paraquat, the resistance of the solution was rapidly decreased. This indicated a leakage of electrolytes through damaged membranes (85).

The source of electrons for the reduction of paraquat can be either photosynthesis or respiration. Seaman (107) using duckweed (Lemna minor), found the action spectrum for acute paraquat toxicity was similar to that of photosynthesis. The use of diquaternary salts in photosynthesis experiments was first reported by Horowitz (9) who showed that benzyl viologen, a 4,4'-dipyridylium compound was reduced in this process. Since toxicity may also develop slowly in the dark, there is evidence that free radicles are produced slowly by reduction linked to respiratory processes (19). Merkle et al. (85) found the elongation of mesquite seedlings was strongly inhibited by a 10^{-4}M paraquat solution under dark conditions.

Funderburk (50) studied the metabolism of *paraquat in plants and in soil and detected no metabolites in beans or alligator weed (Alternanthera philoxeriodes) 1 week after treatment. However, a metabolite has been detected from the exposure of *paraquat to ultraviolet light and is believed to be similar in structure to one produced by microorganisms (16, 51).

Herbicide Combinations:

Combinations of herbicides have been used frequently in the past to obtain control over a broader spectrum of weed species. Amitrole has been mixed with triazine and substituted urea herbicides to control both established perennial weeds and germinating annual weeds in orchards (102). Amide and carbamate herbicides have been combined to control a broader spectrum of annual species in vegetable crops (101).

Another type of combination utilized very little to date is one displaying synergism or enhancement of activity on a single weed species. The ammonium thiocyanate enhancement of amitrole activity was previously discussed. Colby et al. (26) have shown that the addition of 0.05 lb/A of paraquat to 2-4 lb/A of solan increased the toxicity to crabgrass (Digitaria sanguinalis) and decreased the toxicity on tomatoes. They have also reported that velvetleaf (Abutilon theophrastii) was effectively controlled with a combination of DCPA and sesone but was not injured from applications of either chemical singly. The combination of DNBP and simetone was also reported to be synergistic on tomato plants.

Adjuvants.

Characteristics and responses:

Ebeling (40) has thoroughly reviewed the basic processes involved in the deposition, degradation, persistence, and effectiveness of pesticides. He has defined adjuvants as accessory substances

which while not themselves toxic, are added to a pesticide to improve its physical or chemical characteristics. Surfactants or surface active agents are a common type of adjuvant used for increasing wetting, spreading, penetration, or emulsification. The surfactants used in formulating herbicides have generally been of the anionic or nonionic type. They increase the dispersion properties of wettable powders and act as emulsifying agents for emulsifiable concentrates.

There are many reports in the literature which show that surfactants increase herbicidal action. McWhorter (80) reported that the addition of a polyoxyethylene thioether surfactant to dalapon increased its effectiveness on Johnsongrass (Sorghum halepense). Alkylaryl sulfonates and alkylarylpolyoxyethylenes were shown to increase the absorption of amitrole* in beans (48). Jansen et al. (67) studied the effects of many surfactants on the activity of amitrole, dalapon, 2,4-D, and DNBP on corn and soybeans and found that they may either increase, decrease, or have no apparent effect on herbicide activity. Seventeen of 22 surfactants used with paraquat gave excellent results on downy bromegrass (Bromus tectorum) (43). Surfactants have increased the activity of diuron on established weeds in cotton (Gossypium hirsutum) and are used commercially for this purpose (81).

Mode of Action:

In 1957, Freed (48) postulated that the increase in absorption obtained with *amitrole in sprays containing surfactants was

due to increased wetting and penetration of the plant cuticle. Jansen's experiments showed that surfactants produced varied effects depending on which herbicide was employed (67). One surfactant increased the action of dalapon 7-fold and tripled the activity of amitrole, but did not effect the action of 2,4-D or DNBP. The concentration of surfactant proved critical. Generally at 0.01% there was no increase in herbicide activity, at 0.1% there was a depression in activity, and at 1.0% activity was enhanced. When the surfactants were employed at effective concentrations, there was little additional effect on the sticking, wetting, or spreading properties over that of lower ineffective concentrations. Other workers have confirmed that with all of the surfactants tested, the minimum surface tensions and contact angles occurred at 0.1-0.5%, however, the maximum herbicide activity was obtained at concentrations 10 times as high or greater (13, 46, 47, 80, 115).

McWhorter (80) indicated that the enhancement of herbicide activity could not be correlated with increased solubility, leaf wettability, or other physical indices. Two surfactants which have very similar solution properties differed markedly in their enhancement of herbicide activity. Changes in the alkyl group of an alkylbenzene sulfonate surfactant had a great influence on the effectiveness of the surfactant (69).

Most authors now believe that herbicide-surfactant-plant surface interactions are due to more than increased wetting. Parr and Norman (91) have reviewed several papers which report the effects

of several surfactants on living systems. Several studies with bacteria have shown that low concentrations of surfactant may precipitate and denature proteins (52). Many cationic surfactants cause injury to the membranes of bacterial cells and this property makes them useful as germicides. It seems likely that surfactants may exert biochemical changes at the plant surface or even inside the plant, as well as the physical changes which have been reported. The mode of action of these compounds may vary considerably because they are of such diverse chemical types.

Sodium lauryl *sulfate, an anionic surfactant has been shown to be absorbed by both the roots and leaves of plants (30). When the compound was applied to leaves it was absorbed slowly and moved only acropetally. Several oils are also absorbed by plants. Some researchers have postulated that oils may solubilize the lipids of the cell membrane and that this process may make the semi-permeable membrane more permeable (116). Oils are apparently absorbed through the cuticle, but stomatal entry is believed to be very important. An emulsion of light oil sprayed on plants when the stomates were closed caused no phytotoxicity, but when stomates were open the plants were rapidly killed (116). Oils vary considerably in their phytotoxicity, the aromatics being the most toxic, the olefins intermediate, and the paraffins the least toxic to plants (57).

Summary.

Characteristics of quackgrass such as perennial habit, an extensive rhizome system, and a high potential for regrowth make

it a difficult weed to control. Some manipulations such as increasing the nitrogen level and properly timing the treatments have provided increased effectiveness of herbicide practices.

In general, soil applied herbicides have required rates of chemical at which the tolerance of perennial horticultural crops is jeopardized or lost. Translocated herbicides have also either produced crop injury at effective rates or have encountered registration difficulty because of potential residues in the crop.

The absorption and translocation patterns of most herbicides have been studied quite thoroughly with the aid of radioisotopes. Mode of action studies have shown many isolated cause and effect relationships but the initial site of action at the biochemical level has not been ascertained for any herbicide.

Adjuvants such as surfactants and oils have shown enhancement of herbicide activity on plants chiefly under greenhouse conditions. The mode of action of adjuvants is not yet well understood but apparently consists of both physical effects and more subtle chemical effects. Herbicide combinations show synergism on several plant species. Studies on the mechanism of these herbicide interactions have been limited. The results obtained with herbicide-adjuvant and herbicide combinations have shown enough promise to warrant their evaluation as a means of providing more effective quackgrass control.

GENERAL EXPERIMENTAL PROCEDURES

Field.

Field trials were conducted at East Lansing on established quackgrass sods which had been undisturbed for several years. In both 1964 and 1965, 66 lb/A of nitrogen in the form of ammonium nitrate was applied to the experimental area in April, preceding the application of herbicide treatments.

Logarithmic plots were applied using a carbon dioxide-pressurized sprayer mounted on a sulky. The sprayer components were constructed in a similar manner as that reported by Cialone (25), utilizing a 1/2 pint concentrate bottle and 1 quart diluent bottle. This sprayer delivered 6 half-doses on plots 5 x 60 feet at a volume of 45 gpa. These preliminary screening trials were either not replicated or replicated 2 times.

Randomized field treatments were applied with a carbon dioxide-pressurized small plot sprayer (99) which delivered a volume of 36 gpa. In these tests, the plots were 4 x 25 feet and were placed in a randomized block design with 3 or 4 replications. Commercial formulations of herbicides and adjuvants were employed in all of the field tests. The rate of herbicide used was expressed as lb/A of active ingredient unless otherwise specified. The rate of adjuvant employed was expressed as percent adjuvant volume per total volume.

Visual ratings were obtained on the field plots throughout the growing season. The quackgrass control rating (QCR) system employed

was a scale 1-9, where a rating of 1 indicated no quackgrass control, 6 indicated commercially acceptable control, and 9 indicated complete quackgrass control. Ratings were obtained without knowledge of the treatment to eliminate the possibility of bias. The data were evaluated statistically by analysis of variance. Where other mean comparisons were necessary, either the Least Significant Difference (LSD) test or Duncan's Multiple Range Test were employed.

Greenhouse.

Quackgrass for greenhouse experiments was propagated by harvesting rhizomes in the field, cutting them into sections and planting them in 4 inch pots either in #7 Wausau quartz sand or in a standard soil mix. The soil mix consisted of equal parts of loam, sand, and peat.

The night temperature in the greenhouse was maintained at 18° C but the day temperature could not be satisfactorily controlled and varied from 18° C to 38° C. Natural daylight was supplemented with cool white fluorescent tubes. The light intensity at plant level obtained from these bulbs was about 700 foot candles. A daylength of 16 hours was maintained in all of the studies with supplemental light.

Herbicides were applied in the greenhouse with a system using compressed air as a source of pressure. Plant containers were passed under an 80° flat fan nozzle on a conveyor which moved at a fixed rate of speed. The herbicides and adjuvants were applied in a volume equivalent to 40 gpa. After spraying, the pots were placed in a randomized

block design on the greenhouse benches. All tests were replicated either 3 or 4 times.

Controlled Environment.

Environmental, abosorption, and translocation studies were conducted in growth chambers. Plants for these experiments were grown from single node rhizome sections prepared from rhizomes collected in the field. The segments were planted in #7 Wausau quartz sand in a flat. When the plants were 4-6 inches high, they were transplanted into aerated 1/2 strength Hoagland's solution in beakers. The growth chambers were maintained at a day temperature of 24° C and a night temperature of 18° C. The daylength in all the experiments was 16 hours. Short term absorption and translocation studies were conducted under light conditions at a constant 24° C. The light intensity at the plant surface was approximately 1500 foot candles.

^{14}C-labeled herbicides were utilized for the absorption and translocation experiments. All treatment solutions were buffered at pH 6.9 using a .05M KH_2PO_4-K_2HPO_4 mixture. Ten ul droplets containing a known concentration of herbicide and a known specific activity of isotope were applied to the midrib of the most recently expanded quackgrass leaf with either a 10 ul pipette or Hamilton syringe. Uniform leaves were selected and taped in a horizontal position to assure retention of the droplet (Figure 1). With this method it was not necessary to use a lanolin ring.

Figure 1. Technique used to mount leaves for treatment with ^{14}C-labeled herbicides.

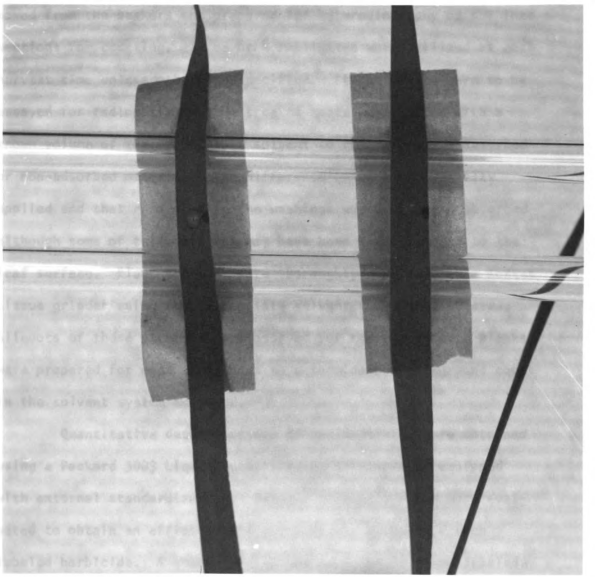

Figure 1.

After the prescribed treatment period, the plants were removed from the beakers and prepared for autoradiography or cut into sections for counting. Three or 4 replicates were utilized at each harvest time unless otherwise specified. If the plants were to be assayed for radioactivity, the treated spots were washed with a known volume of the appropriate solvent to remove the non-absorbed or non-adsorbed material. The difference between the quantity applied and that recovered in the washings was considered absorbed although some of this material may have been tightly bound to the leaf surface. Plant sections were thoroughly macerated in a Kontes tissue grinder using the appropriate solvent for each herbicide. Aliquots of these extracts were assayed for radioactivity. Blanks were prepared for each experiment to determine the background count in the solvent system employed.

Quantitative determinations of radioactivity were obtained using a Packard 3003 Liquid Scintillation Spectrometer equipped with external standardization. Several solvent systems were evaluated to obtain an efficient and reproducible method for each labeled herbicide. A quench series was prepared for each labeled herbicide by adding constant quantities of solvent and 0, X, 2X, 3X, 4X, etc. quantities of quenching material. Ten ul droplets containing a known amount of radioactivity were added and assayed. Quench curves were determined by plotting the percent counting efficiency against the external standard count of the radium source through the sample. From these curves, cpm were converted to dpm (106).

The window setting employed for ^{14}C-labeled materials was 50-1000. The proper gain was determined by inserting a moderately quenched sample and selecting the setting at which the maximum cpm were obtained. External standard counts were made in the blue channel with a window setting of 700-infinity and a gain of 4%.

PROCEDURES AND RESULTS

Preliminary Greenhouse Test with Surfactants.

A preliminary experiment was conducted to determine if surfactants would increase the herbicidal activity of simazine or diuron when applied as a foliar spray. The test plant employed for this experiment was cucumber (Cultivar Spartan Dawn). The plants were seeded on June 10, in 8 ounce styrofoam cups using the standard soil mix. After emergence, the plants were thinned to 1 individual per cup. Herbicide treatments were applied July 2, at the 2-3 true leaf stage. Eight surfactants were employed at concentrations of 0, 0.1, and 1.0%. Information regarding these surfactants is presented in appendix II. The concentrations of simazine and diuron employed were 0, and 1000 ppm suspensions of the 80% wettable powder. Notched cardboard barriers were placed over the pot surface to prevent spray contact with the soil. Injury ratings were obtained 10 days after treatment.

All of the surfactants employed in this experiment at a concentration of 1.0% increased the phytotoxicity of 1000 ppm sprays of both simazine and diuron (Table 1). The initial symptoms observed were interveinal and marginal chlorosis, which in the most effective treatments eventually became necrotic. Typical responses are illustrated in Figures 2 and 3. The enhancement with 0.1% surfactant was more pronounced with diuron than with simazine.

Table 1. Increase in the herbicidal activity of foliar applied simazine and diuron on cucumbers by surfactants.

Surfactant	Cucumber injury ratings					
	0.1% surfactant			1.0% surfactant		
	none	simazine	diuron	none	simazine	diuron
BRIJ 30	1.0	3.3	4.0	1.7	4.0	6.7
Triton X-45	1.3	1.0	4.0	1.7	4.0	5.3
Triton B-1956	1.0	2.7	2.7	1.7	2.7	4.0
Surfactant WK	1.7	2.7	5.3	3.7	9.0	8.0
Tween 20	1.0	4.0	6.7	1.3	3.3	6.7
Plyac	1.3	2.7	6.7	1.7	4.3	6.7
Triton GR-7	1.0	1.0	4.7	1.0	3.3	4.7
X-77	1.0	1.0	4.0	1.3	2.7	4.0
None	1.0	1.3	2.0	1.0	1.3	2.0
LSD at 1%	NS	1.7	1.5	1.5	1.9	1.7

Surfactant WK displayed the greates activity and exhibited some phytotoxicity when applied at the 1.0% rate without herbicide. This toxicity was characterized by stunting of the plants and a curling of the leaf margins (Figure 3).

Evaluation of Herbicide-Adjuvant Combinations on Quackgrass.

Adjuvants with simazine or diuron:

This field test was designed to determine if surfactants,

Figure 2. Increase in foliar activity of simazine by addition of Triton X-45. 1- control, 2- 1000 ppm simazine, 3- 100 ppm simazine and 1.0% Triton X-45.

Figure 3. Increase in phytotoxicity of simazine and diuron by addition of Surfactant WK. 1- control, 2- 1000 ppm simazine, 3- 1000 ppm diuron, 4- control, 5- 1000 ppm simazine and 1.0% Surfactant WK, 6- 1000 ppm diuron and 1.0% Surfactant WK.

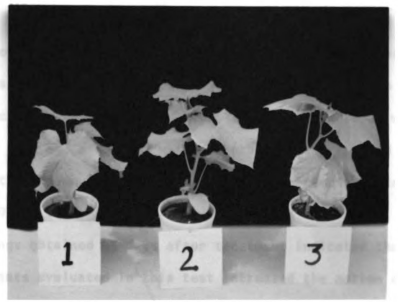

Figure 2.

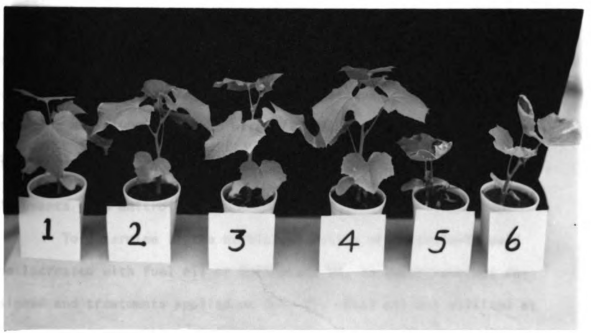

Figure 3.

oils, a systemic insecticide, or low rates of other herbicides would increase the foliar activity of simazine or diuron. On May 2, when the quackgrass was 6-8 inches high, simazine and diuron were applied at 2 lb/A and a control with no herbicide was applied for each adjuvant. The emulsifying agent for the treatments containing oil was 9D-207 at 0.1%.

Ratings obtained 45 days after treatment indicated that none of the adjuvants evaluated in this test increased the action of simazine or diuron to an extent that resulted in acceptable quackgrass control. Paraquat or amitrole-T at 1/2 lb/A combined with simazine or diuron provided effective control until mid-July (Table 2).

Similar tests were conducted in orchards near Benton Harbor and Belding, Michigan. Simazine and diuron were applied at rates up to 4 lb/A with several adjuvants and paraquat. Only 3-4 lb/A of simazine and diuron combined with 1/2 lb/A paraquat produced acceptable season-long quackgrass control.

Adjuvants with amitrole-T:

To determine if the herbicidal action of amitrole-T could be increased with fuel oil or Surfactant WK, an experiment was designed and treatments applied on July 22. Fuel oil was utilized at rates of 1.0% and 10% and Surfactant WK was used at 1.0%. Amitrole-T was applied at 1 lb/A which is not generally a phytotoxic rate. Quackgrass control ratings were obtained on September 17.

During application it was observed that increased wetting

Table 2. Increase in the herbicidal activity of simazine or diuron by the addition of adjuvants or low rates of other herbicides.

Adjuvant or herbicide	Rate (lb/A or %/V)	QCR		
		none	simazine (2 lb/A)	diuron (2 lb/A)
none	-	1.0	2.0	2.0
amitrole-T	1/4	5.3	6.7	7.3
amitrole-T	1/2	6.3	8.0	8.0
paraquat	1/4	2.0	3.7	2.7
paraquat	1/2	3.7	6.3	7.0
X-77	0.1%	1.0	1.7	2.0
dimethoate	0.1%	1.0	2.3	2.3
9D 207	0.1%	1.0	3.3	2.0
L-53	25%	1.0	3.3	2.7
LF 2670	25%	1.0	2.0	2.7
LF 4340	25%	1.0	2.7	1.7
LF 4247	25%	1.0	2.3	3.0
LS 0799	25%	1.0	2.3	3.3
Isooctyl ester of 2,4-D	1/4	1.0	2.7	2.3
Isooctyl ester of 2,4-D	1/2	1.0	2.0	1.7
corn oil	25%	1.0	2.7	2.0
olive oil	25%	1.0	3.3	2.7
LSD at 1%		1.3	1.5	1.3

was obtained with the oil and surfactant treatments. Two months following treatment, both fuel oil and surfactant WK similarly increased the chronic toxicity obtained with amitrole-T. There was no difference obtained between 1% and 10% concentrations of fuel oil (Table 3).

Table 3. Increased chronic toxicity from adjuvants with amitrole-T.

Adjuvant	Rate (%/V)	QCR	
		none	amitrole-T (1 lb/A)
none	-	1.0	5.7
fuel oil	1.0	1.0	7.3
fuel oil	10	1.0	7.3
Surfactant WK	1.0	1.0	7.3
LSD at 1%		NS	1.1

Adjuvants with paraquat:

Eight adjuvant treatments were evaluated for their effects on the herbicidal action of paraquat at 1 lb/A. The compounds tested were Surfactant WK, X-77, PM-4114, Citowet, ML-700, and Plyac at 0.5% and DMSO at 10%. Since it had been established that these compounds were not phytotoxic at this rate, they were not compared independently of paraquat.

In order to determine the effect of the time of day of application, 2 application times were included in this experiment.

The treatments were applied on May 21 at 2 p.m. and at 8 p.m. A split plot design with 3 replications was utilized, with the time of treatment as the main plots and chemical treatments as sub-plots. Visual ratings were obtained 10 and 30 days after treatment.

All of the adjuvant treatments except DMSO increased the phytotoxicity obtained with paraquat. This was shown in early ratings obtained 10 days after treatment and also in ratings obtained 30 days following treatment (Table 4). When paraquat was applied without surfactant, the acute toxicity occurred in localized areas on the leaves. Surfactants combined with paraquat produced more complete and uniform injury to the leaves indicating that increased coverage was influencing the response.

There was a slight increase in phytotoxicity obtained from night application with all treatments except DMSO. Approximately 20 days after treatment, regrowth from rhizome buds was evident and acceptable quackgrass control was not apparent 40 days following treatment.

Evaluation of Herbicide Combinations on Quackgrass.

Several field tests were conducted to determine if herbicide combinations would provide increased quackgrass control. Herbicide combinations were applied in a logarithmic test on May 29, when the quackgrass was 8-10 inches high. Two triazines, simazine and atrazine, and two substituted ureas, diuron and linuron, were combined with either amitrole-T or paraquat (Table 5).

Table 4. A comparison of application time on the phytotoxicity of paraquat with adjuvants after 30 days.

Adjuvant combined with paraquat at 1 lb/A	Rate (%/V)	QCR	
		2 p.m. treatment	8 p.m. treatment[1]
none	-	5.0	5.7
DMSO	10	6.0	6.0
DMSO + Surfactant WK	10 + 0.5	6.0	7.7
Surfactant WK	0.5	5.7	7.3
X-77	0.5	6.7	7.3
PM 4114	0.5	7.0	8.0
Citowet	0.5	7.0	7.7
ML-700	0.5	7.0	7.7
Plyac	0.5	6.7	7.3
LSD at 1%		0.8	0.9

[1] F value for interaction of treatment x time of application significant at the 1% level.

Table 5. Level of herbicide required for commercial control in logarithmic trial with herbicide combinations.

Herbicide Combinations	Initial concentration (lb/A)	Lowest rate for acceptable weed control (lb/A)	
		June 19	Sept. 17
simazine + amitrole-T	10 + 2	2.5 + .5	4.3 + .9
atrazine + amitrole-T	6 + 2	1.5 + .5	3.5 + 1.2
diuron + amitrole-T	10 + 2	2.5 + .5	4.7 + .9
linuron + amitrole-T	6 + 2	3.0 + 1.0	4.8 + 1.6
simazine + paraquat	10 + 2	2.5 + .5	3.1 + .6
atrazine + paraquat	6 + 2	1.5 + .5	4.0 + 1.3
diuron + paraquat	10 + 2	2.5 + .5	2.2 + .4
linuron + paraquat	6 + 2	1.5 + .5	6.0 + 2.0

Three weeks after application, the greatest phytotoxicity from the lowest rate of herbicide was obtained with atrazine and amitrole-T, atrazine and paraquat, or linuron and paraquat. However, about 4 months after treatment the greatest phytotoxicity was obtained with the simazine and paraquat or diuron and paraquat combinations. Paraquat was more effective than amitrole-T when combined with all the triazines and ureas except linuron. These results were similar to those obtained when paraquat was added to simazine and diuron in previously discussed experiments.

Phytototoxicity of Simazine or Paraquat by the Roots or Shoots of Quackgrass.

Phytotoxicity from root treatments:

Twenty-day-old plants which had been grown from rhizome segments in quartz sand were placed in aerated nutrient solutions. The solutions contained either 0, 0.1, 1.0, and 10 ppm paraquat or 0, .01, 0.1, and 1.0 ppm simazine. The plants were maintained in growth chambers and injury ratings obtained after 2 and 14 days. Each treatment was replicated 3 times.

Simazine and paraquat were both phytotoxic when applied in nutrient culture (Table 6). Injury symptoms appeared rapidly on plants receiving 1.0 and 10 ppm paraquat. After 24 hours, severe necrosis of tissue had occurred in bands along the leaves. After 14 days, the shoots of these plants were completely destroyed.

Simazine injury developed more slowly, and was not observed at any concentration after 2 days. However, after 14 days severe injury had occurred to plants receiving 0.1 and 1.0 ppm. This indicated that simazine is phytotoxic to quackgrass if it is transported to the site of action in sufficient concentration.

Phytotoxicity through the foliage:

Five single node rhizome segments were planted in 4 inch pots containing soil, and were grown for 28 days before herbicide application. Paraquat was applied at 0, 1/8, 1/4, 1/2 and 1 lb/A and simazine at 1, 2, 4, and 8 lb/A. Vermiculite was placed over

Table 6. The phytotoxicity of simazine and paraquat from root treatment after 2 and 14 days.

Paraquat rate (ppm)	QCR 2 days	QCR 14 days	Simazine rate (ppm)	QCR 2 days	QCR 14 days
0	1.0	1.0	0	1.0	1.0
0.1	1.7	4.3	.01	1.0	1.3
1.0	5.7	9.0	0.1	1.0	6.7
10	7.7	9.0	1.0	1.0	9.0
LSD at 1%	1.5	1.9		NS	1.8

the soil prior to spraying and removed after spraying to prevent the herbicides from contacting the soil. Injury ratings were obtained after 21 days.

The phytotoxicity of paraquat increased with rates up to 1/2 lb/A (Table 7.) All shoot growth including the apical meristem was destroyed with 1/2 and 1 lb/A paraquat. There was no apparent regrowth from these rhizomes at 21 days. The phytotoxicity obtained from foliar treatment with simazine was only slight at the highest rate of 8 lb/A, indicating that very little simazine was absorbed through the foliage.

Table 7. The phytotoxicity of foliar applications of simazine and paraquat after 21 days.

Paraquat rate (lb/A)	QCR	Simazine rate (lb/A)	QCR
0	1.0	0	1.0
1/8	3.0	1	1.0
1/4	5.0	2	1.3
1/2	8.7	4	1.3
1	8.7	8	2.3
LSD at 1%	1.9		0.8

The Nature of the Paraquat Interaction With Other Herbicides.

Field:

Two field experiments were conducted to determine if the response obtained with paraquat and other herbicides was due to increased action through the foliage. In one experiment, the 80% wettable powder formulation and the 4% granular formulation of simazine and diuron were compared. These chemicals were applied May 21 at 4 lb/A with and without paraquat at 1/2 lb/A.

In the second experiment, a split application procedure was employed. Simazine, diuron, and amitrole-T were applied at 4, 4, and 1 lb/A respectively with and without 1/2 lb/A paraquat. The

paraquat was applied either 7 days before, at the same time, or 7 days after the other herbicides. Treatment dates were May 6, 13, and 20.

The combinations of simazine and paraquat or diuron and paraquat produced better weed control after 10 days or 90 days than either chemical alone. After 10 days, the wettable powder treatments appeared slightly superior. However, after 90 days there was no difference in the response between the granular or wettable powder formulation of simazine or diuron (Table 8). This indicated that an increase in foliar absorption or translocation was not a major factor in the enhanced control with these combinations.

Table 8. The effect of paraquat on the activity of granular and wettable powder formulations of simazine and diuron.

Herbicide	Rate (lb/A)	QCR (90 Days) Form of simazine or diuron[1]	
		Granular	Wettable powder
simazine	4	1.0	1.3
diuron	4	3.3	4.0
simazine + paraquat	4 + 1/2	5.0	6.0
diuron + paraquat	4 + 1/2	7.3	6.7
LSD at 1%		1.7	1.5

[1]F value for formulation not significant.

The results of the second experiment in which split applications were utilized are shown in Table 9. The combinations of simazine and paraquat or diuron and paraquat produced the same degree of quackgrass control after 90 days. The time of application of paraquat did not influence the control obtained with simazine or diuron. However, with paraquat and amitrole-T combinations, the time of application of paraquat did influence the response obtained. A high increase in activity was observed when paraquat treatment followed amitrole-T treatment by 7 days.

Table 9. Split applications of paraquat with other herbicides for quackgrass control.

May 13 herbicide Treatment	Rate (lb/A)	QCR (90 days) Time of paraquat application[1]		
		May 6	May 13	May 20
simazine	4	7.3	6.0	7.0
diuron	4	7.3	6.0	6.0
amitrole-T	1	7.0	5.3	9.0
none	-	1.7	2.0	2.3

[1]F value for the interaction of amitrole-T vs. other herbicides x time of paraquat application significant at the 1% level.

Greenhouse:

A greenhouse experiment was designed to determine how

different foliar treatments would influence the phytotoxicity of simazine applied to the soil. Five single-node rhizome segments were planted in 4 inch pots in soil on September 10 and grown 7 weeks to develop an extensive rhizome system. On November 2, treatments were applied to the foliage and the soil. The shoots were either left intact, cut off mechanically, or sprayed with 1/2 lb/A paraquat. Superimposed on these shoot treatments was either 0, 1, or 2 lb/A simazine. Shoot counts were made on the regrowth after 30 days.

Greater phytotoxicity occurred with the foliar paraquat treatment compared to cutting regardless of the rate of simazine (Table 10). The amount of regrowth which occurred decreased with increasing rates of simazine. The new shoots which emerged were very chlorotic, especially at the 2 lb/A rate. The regrowth obtained after treatment with 1/2 lb/A paraquat was much greater in this experiment in which plants had been allowed to develop an extensive rhizome system. In previous experiments, using young plants still attached to single node rhizome segments, very little regrowth occurred. When the foliage was removed by cutting, there was rapid regrowth both from the intercalary and apical meristem. When paraquat was employed, all regrowth occurred from buds on the rhizomes.

A similar test was initiated to determine the nature of the phytotoxicity obtained when amitrole treatment preceded paraquat treatment. Plants were grown as in the previous experiment. The foliage was sprayed with either 0, or 1 lb/A amitrole. After 72 hours, the

shoots were either left intact, cut off mechanically, or sprayed with 1/2 lb/A paraquat. Ratings were obtained after 28 days (Table 11). These same treatments were applied to quackgrass plants grown from single rhizome sections. These plants were placed in half strength Hoaglands solution in flasks. This method of culture made it possible to remove the plants periodically and observe the phytotoxicity on new growth.

Table 10. Quackgrass regrowth following several foliar and root treatments.

Herbicide applied to roots	Rate (lb/A)	New shoots initiated/pot Top treatment		
		none	cutting	paraquat
none		9.3	8.7	7.3
simazine	1	8.3	9.3	4.3
simazine	2	8.7	7.7	3.0*
mean[1]		8.8	8.6	4.9

[1] F value for paraquat vs other top treatments significant at the 1% level.

*Plants displayed severe chlorosis.

The greatest phytotoxicity was obtained when amitrole treatment preceded top removal or foliar dessication by treatment with paraquat (Figure 4). The new tillers initiated from plants treated in this manner exhibited typical amitrole injury. Paraquat applied alone caused inhibition of new tillers. The tillers that were initiated

showed some injury, indicating that paraquat had moved into them from the shoot.

Table 11. The effect of amitrole pretreatment and subsequent shoot treatments on quackgrass regrowth.

Pretreatment 1 lb/A	Treatment after 72 hours	QCR	New tillers initiated
none	none	1.0	5.0
none	cutting	1.0	4.3
none	paraquat	4.0	2.3
amitrole	none	5.7	6.3
amitrole	cutting	8.0	2.7
amitrole	paraquat	8.7	2.7
LSD at 1%		1.9	2.1

Controlled environment:

An experiment was conducted in growth chambers to determine if the light regime after treatment, or moisture level at the time of treatment, influenced the action of paraquat or paraquat-simazine mixtures. The plants were subjected to either 10 hours of light or 10 hours of darkness after treatment. Another variable included in this experiment was moisture level. One group of plants received normal watering and the other group received no water two days prior to spraying in order to produce a moisture stress. In the latter group, water was applied again one day after treatment when the plants had started to wilt. In this

Figure 4. Phytotoxicity obtained with amitrole treatments.

A-N - amitrole followed by no treatment

A-C - amitrole followed by top removal after 72 hours

A-P - amitrole followed by paraquat treatment after 72 hours.

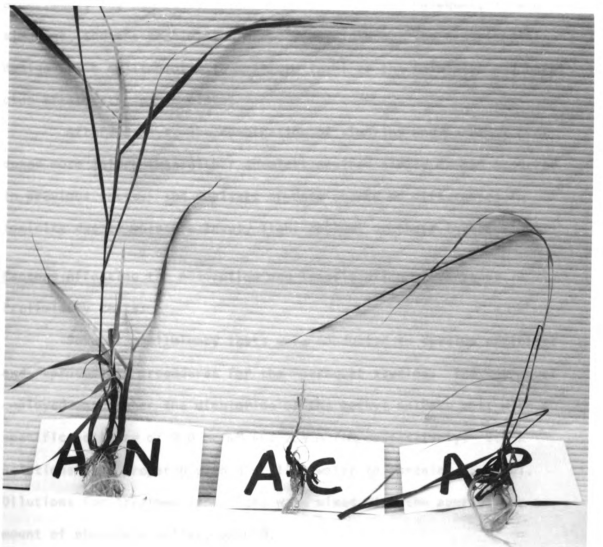

Figure 4.

experiment, the herbicide treatments were 1/4 lb/A paraquat, 1 lb/A simazine, and the combination of both herbicides. The experimental design was a split plot with moisture level as the main plot and herbicide treatments as sub plots.

After 30 days, the combination of simazine and paraquat produced more injury than either chemical applied singly as had occurred in previous tests. The analysis of data showed no differences in toxicity due to moisture level, light regime, or their interaction.

Factors Affecting the Absorption and Translocation of *Paraquat.

Preliminary tests:

Several preliminary tests were conducted to develop efficient and reproducible procedures for the *paraquat studies. The *paraquat employed was either the dichloride or the methyl sulfate salt with a specific activity of 2.0 mc/mM and 2.4 mc/mM, respectively. Stock solutions were prepared with distilled water to contain .05 uc/ul. Dilutions for treatment solutions were mixed with the appropriate amount of phosphate buffer, pH 6.9.

German millet (Setaria italica (L.) Beauv.) seedlings were utilized in the preliminary tests to develop washing, extracting, and counting procedures. After treatment with *paraquat, a 1.0 cm section containing the treated spot was removed from the treated leaf. Ethyl alcohol, methyl alcohol, and distilled water were evaluated as solvents to remove the unabsorbed material from the treated area. These solvents were also tested for efficiency in extracting the *paraquat from the

macerated tissue. Distilled water proved to be the most efficient solvent for both purposes.

Several systems were evaluated to determine an efficient counting solution. The scintillation fluid consisted of 4.0 g BBOT per liter toluene. Since both paraquat and water are insoluble in toluene, a cosolvent was necessary. Absolute ethanol, absolute methanol, and several different volumes of Triton X-100 were tested as suspending agents for the aqueous extracts. Triton X-100 had been reported as a useful compound in counting aqueous extracts in toluene (92) and proved to be the most efficient compound evaluated for counting *paraquat.

A quenched series of samples was prepared as follows: Six German millet plants were macerated in a tissue grinder in 2.0 ml of distilled water. From this extract, 1.0 ml was removed and diluted 1:1, 1:2, 1:4, 1:8, etc. One ml of each solution was placed in a counting vial and spiked with a 10 ul droplet containing 0.05 uc of *paraquat. Ten ml of toluene-BBOT and 4.0 ml of Triton X-100 were added and the mixture was shaken to form a stable transparent emulsion. The samples were counted for 10 minutes and from the data obtained, quench curves were drawn. The same procedure was repeated using quackgrass tissue and similar results were obtained. Maximum counts with this system were obtained with a gain setting of 15%. This counting system proved to be both efficient and reproducible and was utilized in all subsequent test.

*Paraquat absorption and translocation:

Ten ul droplets containing 0.025 uc *paraquat were applied to quackgrass leaves under light conditions in the growth chamber. Three replicates were harvested after 2, 4, 8, and 16 hours. The unabsorbed material was removed with distilled water washes and 1.0 ml aliquots were counted. Plants with the treated leaves removed were assayed for radioactivity.

The absorption of *paraquat was very rapid, reaching a maximum at 4 hours, after which there was no increase (Figure 5). After 4 hours, severe tissue injury was evident in the area of application. Translocation of *paraquat was rapid in the first 2 hours and continued to increase slowly up to 16 hours. The maximum amount of translocation was probably not reached in the experiment. After 16 hours, the amount of *paraquat moved out of the treated leaf was only 0.5% of that absorbed.

In a similar test, 0.1 uc of *paraquat was applied and after 48 hours, the treated leaves were removed and the remaining portion divided into shoot, root, and rhizome. Each of these 3 portions was assayed for radioactivity.

After 48 hours, *paraquat was translocated throughout the plant, with the greatest quantity located in the shoot, however, this also represented the largest amount of tissue. Considering the 3 plant sections as a whole, 2.5% of the paraquat absorbed was translocated out of the treated leaf. At the time of harvest, the treated leaves displayed severe paraquat phytotoxicity both acropetally and

basipetally to the treated area. No phytotoxicity was observed in other sections of the plants.

Table 12. Translocation of *paraquat from the treated leaves of quackgrass after 48 hours.

Section	Translocation	
	DPM	% of that absorbed
shoot	755	1.53
root	315	.64
rhizome	163	.33

The effect of light on the translocation of *paraquat:

In the initial test, quackgrass leaves were treated with 10 ul droplets of *paraquat containing 0.08 uc. After treatment, the plants were placed either under light conditions or under dark conditions for 6 hours. The plants were harvested and sections 2.0 cm in length were removed from the treated leaves both 2.0 cm acropetal and 2.0 cm basipetal to the site of treatment. These sections were macerated and assayed for radioactivity.

In the second experiment, 4 light regimes were used. The plants received either 6 hours of light before or after treatment, or 6 hours of darkness before or after treatment. Washings were obtained to determine the quantity of material absorbed. After removing the treated leaves, the remainder of the plant was assayed to determine the degree of translocation.

Figure 5. Rate of absorption and translocation of ^{14}C-paraquat by quackgrass leaves.

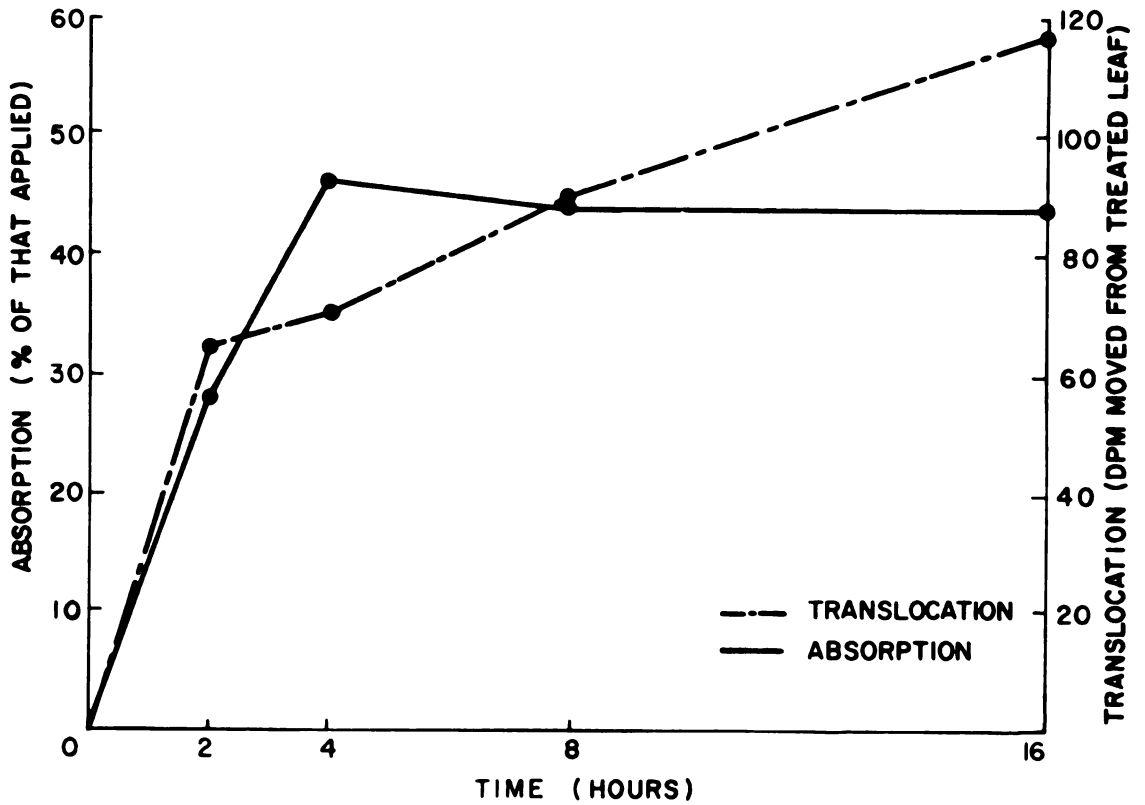
ABSORPTION (% OF THAT APPLIED)
TRANSLOCATION (DPM MOVED FROM TREATED LEAF)
TIME (HOURS)
TRANSLOCATION
ABSORPTION
0
2
4
8
16
10
20
30
40
50
60
20
40
60
80
100
120

Figure 5.

Table 13. Movement of *paraquat in the treated leaf as influenced by light.

Light regime after treatment	DPM/2.0 cm section of leaf	
	acropetal	basipetal
light	2802	1150
dark	1713	717
mean[1]	2258	933

[1]F value for comparison of basipetal vs acropetal significant at the 5% level.

The absorption of *paraquat was not influenced by the light regimes studied in this experiment. However, the light regime had a great influence on the translocation of *paraquat. When plants received light after treatment, the translocation out of the treated leaf was much greater than that which occurred under dark conditions. More *paraquat was moved in plants that received light before treatment and darkness after treatment than in those that received only dark treatment. There was no phytotoxicity observed on the treated leaves in those plants receiving dark periods after treatment, with the exception of a slight discoloration of tissues at the site of treatment. Plants receiving light after treatment showed severe toxicity both acropetal and basipetal to the treated area.

The effect of simazine on the absorption and translocation of *paraquat:

*Paraquat (0.1 uc) was applied at a concentration of 1500 ppm

Table 14. Absorption and translocation of *paraquat as influenced by light.

Light Regime			
before treatment	after treatment	Absorption (% of that applied)	Translocation (DPM)
dark	dark	36.5 a	161 a[1]
light	dark	43.9 a	638 b
dark	light	41.2 a	2314 c
light	light	42.7 a	1899 c

[1] Means with uncommon letters are significantly different at the 1% level.

both alone and in aqueous suspensions containing 5000 ppm simazine (wettable powder). The plants were harvested after 6 hours and the treated areas removed. Washings were assayed for radioactivity to determine absorption, and 2.0 cm sections of the treated leaf were assayed to determine differences in movement.

When simazine was applied with *paraquat there was an increase in both the absorption and the quantity of material moved in the treated leaf (Table 15). Acropetal movement of *paraquat was again greater than basipetal movement. It was observed that droplets of the herbicide mixture had lower contact angles than those droplets containing only *paraquat. Upon drying, the area covered by the treatment spot was also greater with the combination than with *paraquat alone.

Table 15. The effect of simazine on the absorption and movement of *paraquat.

Treatment with 1500 ppm *paraquat	Absorption (% of that applied)[1]	DPM/2.0 cm of leaf		
		acropetal	basipetal	mean[1]
none	24	1459	815	1137
5000 ppm simazine	34	2141	1035	1588
	mean[1]	1800	925	

[1] F value for these comparisons significant at 5% level.

The effect of amitrole on the absorption and translocation of *paraquat:

Since increased action was obtained with combinations of amitrole-T and paraquat in the field, studies were conducted to determine how amitrole influenced the absorption and translocation of *paraquat. An experiment was designed to determine the influence of amitrole when applied either with, or 72 hours preceding *paraquat. Amitrole was employed at a concentration of 4500 ppm and *paraquat was employed at 1250 ppm (.05 uc). Amitrole treatment prior to *paraquat was applied as a foliar spray with a small pressurized hand sprayer. There were 6 replications of each treatment. In the initial test, only 2.0 cm sections basipetal to the treated spot were assayed. This was accomplished 7 hours after treatment.

In this test there was no difference in the basipetal movement obtained when comparing *paraquat alone and *paraquat-amitrole applied

together (Table 16). However, when amitrole treatment preceded *paraquat treatment by 72 hours, there was a significant increase in the basipetal movement of *paraquat in the treated leaf.

Table 16. The effect of amitrole on the absorption and movement of *paraquat.

Treatment with 1250 ppm *paraquat	Time of *Paraquat application	Absorption (% of that applied)	Basipetal movement (DPM)
none	---	30 a[1]	4178 a[1]
4500 ppm amitrole	same	24 a	3692 a
4500 ppm amitrole	72 hours before	24 a	7409 b

[1]Means with uncommon letters are significantly different at the 5% level.

A second experiment was conducted in which amitrole, ammonium thiocyanate, and the combination were applied either with *paraquat or 72 hours prior to *paraquat. In this experiment, washings were assayed to determine absorption, and the plant parts other than the treated leaf were assayed to determine the degree of translocation.

The data from this experiment (Table 17) indicated that when *paraquat was applied with amitrole, ammonium thiocyanate, and amitrole-T antagonism in absorption and translocation resulted. The antagonism was greatest with amitrole-T and least with ammonium thiocyanate.

Table 17. Antagonism and synergism of amitrole and amitrole-T on the absorption and translocation of *paraquat.

Treatment with 1500 ppm *paraquat	Conc. (ppm)	Time of application	Absorption (% of that applied)	Translocation (DPM)
none	---	same	32.4 c[1]	1456 c[1]
amitrole	4500	same	24.5 b	542 a
NH_4SCN	4500	same	31.3 bc	928 b
amitrole-NH_4SCN	4500+4500	same	18.7 a	620 a
amitrole	4500	72 hours before	33.6 c	2059 d
NH_4SCN	4500	72 hours before	29.5 bc	1026 b
amitrole-NH_4SCN	4500+4500	72 hours before	35.6 c	3133 e

[1]Means with uncommon letters are significantly different at the 5% level.

When these treatments preceded *paraquat treatment by 72 hours, there was no difference obtained in absorption over that of *paraquat alone. However, there was a significant effect of amitrole and amitrole-T on the quantity of *paraquat translocated from the treated leaf The greatest increase in movement was obtained when amitrole-T preceded *paraquat treatment by 72 hours.

The Absorption and Translocation of *Simazine by Quackgrass Leaves.

Application and counting techniques:

Since simazine has a low water solubility (5.0 ppm at 20°C), it was necessary to devise a means of obtaining uniform aqueous suspensions to apply this material to the leaves. To accomplish this, 1.0 mg of ring labeled *simazine (6.7 uc/mg) was mixed with 5.0 mg of simazine wettable powder. A stock suspension was prepared containing 10,000 ppm *simazine with a specific activity of 0.013 uc/ul. Other treatment solutions were prepared from the stock solutions. By agitating these solutions before removing the 10 ul droplets, uniformity in the radioactivity of the droplets was obtained.

Since *simazine did not count efficiently when placed directly into toluene, several different volumes of acetone and chloroform were evaluated as co-solvents. Both compounds were severe quenching agents when used at quantities greater than 0.2 ml/15 ml toluene. The most efficient system evaluated was the counting of 0.1 ml aliquots of chloroform extracts. Chloroform also proved to be effective in washing the unabsorbed *simazine from the leaves and in extracting the simazine from macerated leaf tissue. The maximum efficiency using 15 ml of toluene-BBOT and 0.1 ml chloroform was obtained with a gain setting of 11%.

The influence of paraquat on the absorption and translocation of *simazine:

In a preliminary test, 10 ul droplets of 5000 ppm *simazine 0.07 uc) were applied alone and with 250 ppm paraquat. Three replicate

of plants were harvested after 96 hours, oven dried, and mounted on blotting paper for autoradiography. Medical X-ray film was exposed to these mounts in a dark chamber for a period of 3 weeks, after which the film was developed.

The autoradiographs obtained in this experiment are shown in Figures 6 and 7. It appeared that paraquat might slightly increase the absorption of *simazine by quackgrass leaves.

To test this hypothesis, a quantitative test was conducted. Ten ul droplets of 5000 ppm *simazine were applied either alone or as a mixture with either 100 or 1000 ppm paraquat. After 72 hours, 4 replicates were harvested. The treated area was removed and washed to remove the unabsorbed *simazine. Two cm sections were removed from the treated leaf both acropetal and basipetal to the treated area and assayed for radioactivity.

Although there appeared to be an increase in the percentage of *simazine absorbed when paraquat was added, this was not the case in the analysis of data (Table 18). More *simazine was moved in an acropetal direction when paraquat was added at either 1000 or 100 ppm. There was no movement in a basipetal direction with any treatment that could be detected as significantly above the counts received in the blank vials.

The Effect of Paraquat on the Absorption and Translocation of *Amitrole.

An experiment was conducted to determine if paraquat, when applied with *amitrole, would influence its absorption and translocation.

Figure 6. Autoradiograph and treated plant showing the movement of *simazine 96 hours after treatment with 5000 ppm aqueous suspension.

Figure 7. Autoradiograph and treated plant showing the movement of *simazine 96 hours after treatment with 5000 ppm simazine and 1000 ppm paraquat.

Figure 6.

Figure 7.

Table 18. The effect of paraquat on the absorption and translocation of *simazine.

Treatment with 5000 ppm *simazine	Concentration (ppm)	Absorption (% of that applied)	Acropetal movement DPM/2 cm Section of leaf
none	-	6.6 a[1]	6.0 a[1]
paraquat	1000	9.7 ba	15.8 b
paraquat	100	11.6 a	18.5 b

[1]Means with uncommon letters are significantly different at the 5% level.

The *amitrole employed was labeled at carbon 5 and had a specific activity of 0.95 mc/mM. Aqueous solutions were prepared containing 1800 ppm *amitrole (.025 uc/ul). Ten ul (20 uc) droplets of both *amitrole and *amitrole with paraquat at 1000 ppm were applied. Harvests of 3 replicates were made at 6, 12, and 24 hours after treatment. Since ethanol had been shown to be an effective extracting solvent, (34) it was utilized in this study. The unabsorbed material was washed with 25 ml of ethanol of which 1.0 ml aliquots were removed for counting. The plants were divided into root and shoot and macerated in 5.0 ml of ethanol. One ml aliquots of these extracts were counted. All *amitrole samples were counted in 15 ml toluene-BBOT with a gain setting of 10%.

The absorption of *amitrole increased with time through the

24 hour period (Figure 8). With the addition of paraquat, the absorption curve was similar up to 12 hours after which there was no increase in absorption. The translocation of *amitrole was most rapid during the period 6-12 hours after application, after which it continued to increase at a slower rate. With the addition of paraquat, the rate of translocation decreased after 6 hours and the quantity of *amitrole moved reached a maximum at 12 hours. An apparent decrease was observed after 24 hours.

Figure 8. *Amitrole absorption and translocation as influenced by the addition of paraquat.

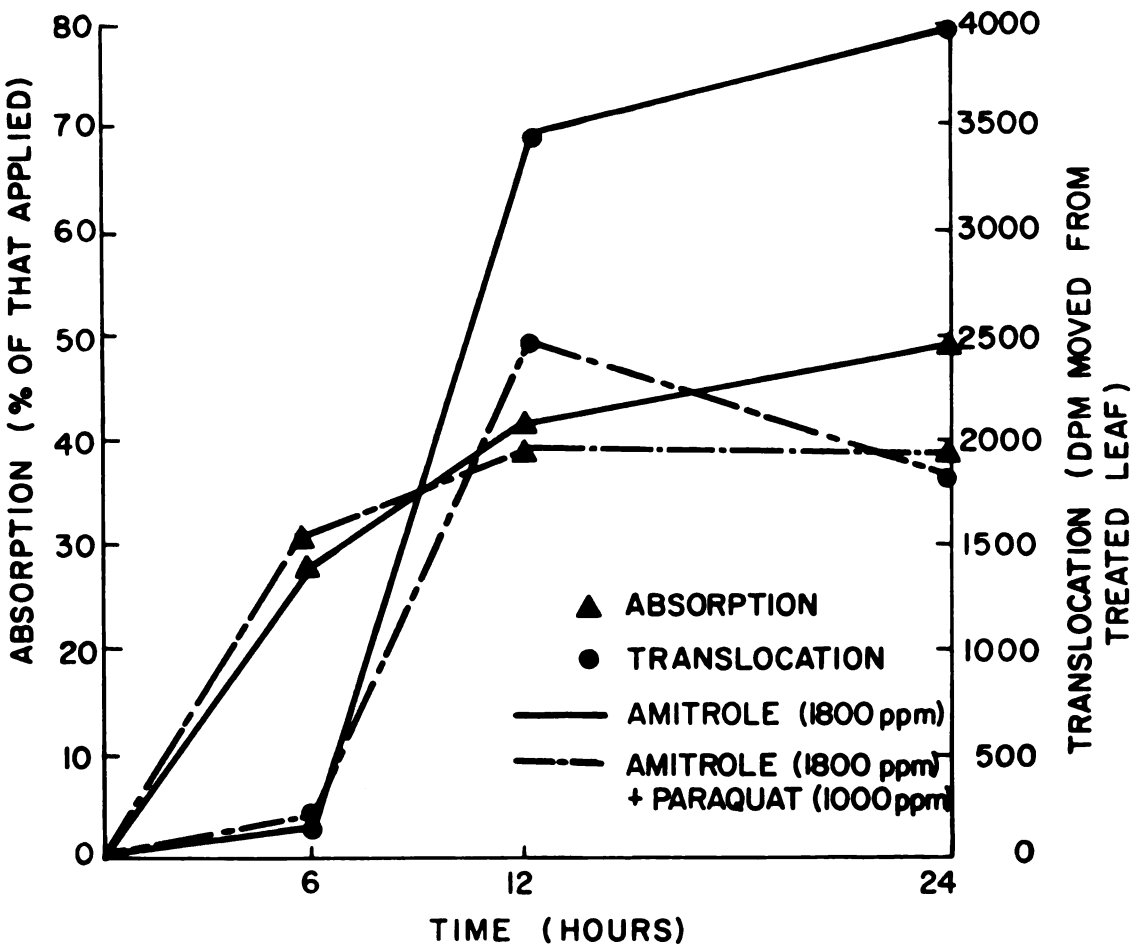
ABSORPTION (% OF THAT APPLIED)
TRANSLOCATION (DPM MOVED FROM TREATED LEAF)
TIME (HOURS)
0
10
20
30
40
50
60
70
80
0
500
1000
1500
2000
2500
3000
3500
4000
6
12
24
ABSORPTION
TRANSLOCATION
AMITROLE (1800 ppm)
AMITROLE (1800 ppm) + PARAQUAT (1000 ppm)

Figure 8.

DISCUSSION AND SUMMARY

The Effects of Adjuvants on the Foliar Activity of Herbicides.

Simazine has generally shown very little phytotoxic action when applied to the foliage of established plants. Diuron, which is generally considered to have more foliar activity than simazine has been effective when surfactants were added under field conditions (81).

In preliminary tests, cucumbers were utilized as the test plant. Cucumbers have a relatively thin cuticle and are not difficult to wet compared to other plant species, particularly grasses. They are also susceptible to injury from low rates of the herbicides used.

Under greenhouse conditions, surfactants were effective in increasing the activity of both simazine and diuron through foliar applications to cucumbers. The increase was most pronounced at higher rates of surfactant. This agrees with the results of several other workers with several plant species (13, 47, 67, 81). Surfactant WK, the most effective surfactant employed in these tests, displayed some toxicity at the 1.0% concentration. Rates of surfactant which are on the threshold of being phytotoxic themselves, may in some instances prove to be the optimum rates to use.

These results, supported by other research, indicate that herbicidal action can be enhanced with surfactant concentrations that provide increased wetting or spreading of the spray solution. However, with higher rates of surfactant there appears to be some other factor responsible for this increase, rather than changes in

the physical properties of the solution. It has been suggested by Behrens (13) that the ability of surfactants to maintain the herbicide in a liquid state rather than a high viscosity liquid of a crystal may account for a portion of their mode of action. Other mechanisms which have been proposed include a promotion of the hydration of the cuticle under adverse humidity conditions, a disruption of the integrity of the cuticle by partial solubilization of its components, and solubilization of the membranes of underlying cells (68).

With quackgrass under field conditions, significant increases were obtained with adjuvants only when combined with herbicides that are normally absorbed readily by the foliage, i.e. amitrole-T and paraquat. No increases were observed with adjuvants when they were mixed with simazine or diuron. From these field tests it could not be concluded with certainty whether these two herbicides were not being absorbed or whether quackgrass was very tolerant to them.

Increased wetting may have been an important factor in the response obtained with paraquat and amitrole-T. Quackgrass leaves have a thick cuticle and the habit of growth of the plant makes it difficult to wet. In the field experiments employing paraquat, increased wetting was observed. Since paraquat produced rapid phytotoxicity on the leaves, the degree of contact was easily observed. Paraquat sprays without surfactant produced initially, a blotchy pattern of injury on the leaves where the droplets of the spray solution had dried. Sprays which included surfactant produced a more uniform toxicity over all the leaves.

Application of paraquat in the evening was slightly more effective than application made at mid-day. Several factors may have been responsible for this effect. Increased humidity may have resulted in an increase in the absorption of paraquat. The lack of rapid toxicity which occurs in the light may have allowed more of the herbicide to be translocated.

When amitrole-T was applied it was observed that the spray solution was retained on the leaves as scattered droplets. Sprays which contained surfactant or fuel oil produced more uniform coverage of the foliage.

From these studies it cannot be concluded that increased wetting was the only factor contributing to the action of adjuvants. However, from the observations which were made and from the nature of the plant under study, it seems likely that this was an important factor.

Increased Action with Herbicide Combinations on Quackgrass.

Simazine and diuron have not been effective on quackgrass at rates which are either economical to use or which provide an adequate safety margin for crops. In initial phases of this research the combination of paraquat at rates not exceeding 1/2 lb/A and either simazine or diuron at rates of 3-4 lb/A produced excellent quackgrass control throughout the growing season. In the studies that followed the objective was to determine why these combinations are effective.

Initial greenhouse studies with applications of either simazine or paraquat to the roots or shoots of quackgrass indicated the degree of phytotoxicity which could be expected from either chemical applied singly. Both chemicals were phytotoxic when applied in nutrient culture. This indicated they were readily absorbed by the roots and moved to the shoots via the transpiration stream. Other workers have reported this type of movement for both herbicides in other plant species (10, 30, 50, 66). This experiment indicated that simazine was very phytotoxic to quackgrass when provided in sufficient quantity at the site of absorption. Failure to provide these conditions in the soil has probably been a major factor for the poor results obtained on quackgrass in the field. The fact that 8 lb/A simazine applied to quackgrass foliage did not produce appreciable injury indicated that foliar absorption was limited.

Since the paraquat cation is rapidly adsorbed to binding sites in the soil (16), it seems improbable that this route of entry is important under field conditions. Paraquat was phytotoxic when applied to the foliage of quackgrass. About 1/4 lb/A was the minimum rate which produced destruction of a high percentage of the foliage. It destroyed the intercalary meristems as well as the apical meristems of the shoots.

The first hypothesis formulated for explaining the synergism of simazine and paraquat or diuron and paraquat was that low rates of paraquat might increase the foliar absorption or the translocation of

these herbicides. The results of two field experiments indicated that this could not be a major factor in determining the response. In one test, where granular formulations of simazine or diuron were employed, the degree of toxicity obtained was similar to that obtained from foliar applications of the wettable powder formulation. In another test, where split applications were employed, similar results were obtained whether simazine or diuron were applied seven days before, with, or seven days after paraquat application. When these herbicides were applied seven days after paraquat application, the foliage had already been completely destroyed which eliminated this route of entry. Although the foliar route may be eliminated as the major source of the increased action due to these combinations, some relationships were found to exist in later studies with radioactive herbicides.

Another hypothesis formulated for the synergism obtained with the simazine and paraquat combination was that foliage toxicity with paraquat made quackgrass more susceptible to simazine action through the soil. Tests were conducted in the greenhouse where the shoots were either left intact, cut off mechanically or destroyed with paraquat. When the tops were cut off, there was rapid regrowth from the same shoots after 10 days. However, with paraquat treatment, all regrowth occurred from buds on the rhizomes and these shoots were not evident until 20-25 days following treatment. When these new shoots emerged, they rapidly became chlorotic displaying typical simazine injury symptoms. The time elapsed before the emergence of new shoots

may be very important in allowing the simazine to move through the soil to the site of absorption. Another important factor may be the reduced shoot growth available for the simazine to move into as compared to the greater amount present on those plants receiving no top treatment with paraquat or cutting.

When amitrole-T, a translocated herbicide, was applied in combination with paraquat, a different type of relationship was observed. A large increase in activity was obtained when amitrole-T treatment preceded paraquat treatment by seven days in the field. No significant increase was observed when the two herbicides were applied together.

To determine the nature of this response, greenhouse tests were conducted in which amitrole treatment was followed by either no treatment, top removal by cutting, or 1/2 lb/A paraquat. This experiment indicated that top removal was an important factor in determining the response. The new shoots which were initiated after plants had received pretreatment with amitrole, followed by either cutting or paraquat, showed severe amitrole injury and were subsequently killed. When paraquat treatment followed amitrole treatment, the number of new shoots was also reduced.

Amitrole has been reported to be translocated rapidly in high concentrations to meristematic areas (3, 103). It is possible that after top removal, these actively growing areas which are preloaded with amitrole cannot dissipate or detoxify it. Since there is no further production of food reserves, the plants die. This experiment

indicated that most of the chronic toxicity was due to amitrole, since cutting after amitrole treatment produced complete kill. However, some phytotoxicity occurred on the new shoots following treatment with paraquat only. There was also a decrease in the number of new shoots initiated after treatment with paraquat only.

Quackgrass growing in the field has a more extensive rhizome system, more stored reserves, and hence more capacity for regrowth than the plants utilized in these greenhouse studies. These greenhouse results only serve as an indication of what may happen in the field.

The Absorption and Translocation of ^{14}C Labeled Herbicides.

There are no quantitative results reported in the literature on the absorption and translocation of paraquat. Studies conducted with *paraquat and *diquat utilizing autoradiographic techniques have shown that they move both acropetally and basipetally in tomato (10) and snap bean (50). The greatest movement occurs in an acropetal direction. Most authors have postulated that paraquat moves principally in the xylem and have failed to explain the basipetal movement in the treated leaves and translocation out of the treated leaf.

Since no metabolites of *paraquat have been detected in plants, all of the radioactive material detected in these studies was assumed to be in the form of *paraquat. Studies conducted with *paraquat indicated that it was absorbed very rapidly by quackgrass leaves, reaching a maximum after about four hours. The degree of absorption ranged

from 20-45% depending on the quantity applied. *Paraquat moved both acropetally and basipetally in the treated leaf, with more moving acropetally. A significant amount of that absorbed moved out of the treated leaf in several experiments. The greatest translocation occurred under light conditions and was associated with phytotoxicity to the foliage which is similar to the findings of Baldwin (10) on the movement of *diquat in tomato.

These results might indicate several possibilities concerning the mechanism of paraquat movement. They perhaps indicate apoplastic movement with the aqueous media as the leaves are injured and drying out. Increased translocation in the light might also indicate that paraquat is actively translocated with carbohydrates moving out of the treated leaf and/or that free radicle formation is necessary for movement to occur. The movement of this herbicide differs from that of 2,4-D in that the greatest translocation is obtained in the presence of acute phytotoxicity.

These experiments did not provide the answer to the exact mechanism of paraquat movement in a basipetal direction. However, the fact that paraquat did move in significant quantity in the dark, when applied immediately following a light treatment, and in the absence of phytotoxicity, suggests that a portion of the movement occurs in the symplast.

When the wettable powder of simazine was added to *paraquat there was an increase in the absorption and translocation obtained over that of *paraquat applied alone. At the time of application,

it was observed that the droplets containing simazine had a lower surface tension and covered more of the leaf surface. This was probably due to the compounds in the wettable powder formulation. The amount of absorption is a function of the area covered and since only one droplet was applied to the leaf, this area was very critical. A direct effect of simazine cannot be entirely discounted but does seem unlikely. The increased action incurred on the foliage in early ratings made with this combination in the field may be explained by this increase in paraquat absorption.

Amitrole and amitrole-T were antagonistic and decreased the absorption and translocation of *paraquat which may indicate that they were competing at similar sites for absorption or that amitrole was being preferentially absorbed. The antagonism present in the isotope experiments was not manifested by decreased paraquat toxicity when these two herbicides were applied together in the field.

When amitrole or amitrole-T were applied 72 hours prior to *paraquat, there was an increase in the quantity of *paraquat translocated out of the treated leaf. This increase was most marked with amitrole-T. If amitrole in some manner reduced the source of energy for the formation of free radicles and thus reduced the rate of acute paraquat toxicity, then perhaps more paraquat could be translocated. However, no decrease in the initiation of toxicity occurred, in fact, there was an apparent increase. This observation might support the hypothesis that paraquat moves with the aqueous media as the toxicity

progresses down the leaf. At the present time, the mechanism of this paraquat movement is not known. It may be responsible for the increased phytotoxicity obtained with these combinations of herbicides under field conditions. Previously discussed data indicated an inhibitory effect of paraquat on the regrowth capacity of quackgrass. The greater amount of this herbicide that is moved into the rhizome, the greater the amount of chronic toxicity that would be expected.

*Simazine was not absorbed and translocated to a great extent by quackgrass leaves. Paraquat at 100 and 1000 ppm slightly increased the absorption and acropetal movement of simazine. The lower non-phytotoxic rate appeared to be the most effective. This response may have been due to a rapid alteration of the leaf surface allowing more simazine to penetrate. The increase with the higher rate of paraquat had to have occurred rapidly before tissue destruction occurred. It has been reported that paraquat injures the membranes of leaf tissue allowing the cell contents to leaf out (85). No basipetal movement of simazine could be detected in any of the treatments.

*Amitrole was readily absorbed by quackgrass leaves and distributed throughout the plant. There was no increase in the absorption of *amitrole as a result of paraquat treatment. An apparent decrease resulted after 6-12 hours. Amitrole is a translocated herbicide and is normally absorbed quite steadily over a

long period of time. Translocation in quackgrass has been shown to continue to increase after 96 hours (34). It seems very probable that the injury produced by the paraquat inhibited the further absorption and movement of *amitrole.

Future Research Needs in This Area.

In view of the results obtained in this research, several areas should receive more extensive investigation. Experiments should be designed to separate and evaluate the various mechanisms of action of surfactants on perennial weeds. This information would allow more intelligent and effective use of these compounds.

Other herbicide combinations should be evaluated for possible synergisms. The results obtained with paraquat in combination with triazine and urea herbicides warrant further testing of contact herbicides in combination with those of long residual life. The synergism obtained with pretreatment of amitrole followed by paraquat opens a new area of investigation with herbicide combinations applied as split applications.

The movement of the bipyridylium herbicides in plants appears to be somewhat unique from other compounds studied. More investigations into the mechanism of translocation and the importance of symplastic movement of these herbicides is needed.

APPENDICES

Appendix I. Description of herbicides discussed in text.

Common name	Chemical name	Group
amitrole	3-amino-1,2,4-triazole	heterocyclic
amitrole-T	above + ammonium thiocyanate	
atrazine	2-chloro-4-ethylamino-6-isopropylamino-s-triazine	triazine
2,4-D	2,4-dichlorophenoxyacetic acid	phenoxy acid
dalapon	2,2-dichloropropionic acid	aliphatic acid
DCPA	dimethyl-2,3,5,6-tetrachloroterephthalate	
diquat	6,7-dihydrodipyrido(1,2-a:2',1'-c)-pyrazidiinium salt	dipyridylium
diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea	substituted urea
DNBP	4,6-dinitro-o-sec-butylphenol	substituted phenol
linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	substituted urea
MH	1,2-dihydropyridazine-3,6-dione	heterocyclic
monuron	3-(p-chlorophenyl)-1,1-dimethyl urea	substituted urea
paraquat	1,1'-dimethyl-4,4'-bipyridylium salt	dipyridylium
sesone	sodium 2,4-dichlorophenoxyethyl sulfate	phenoxy
simazine	2-chloro-4,6-bis(ethylamino)-s-triazine	triazine
simetone	2-methoxy-4,6-bis(ethylamino)-s-triazine	triazine

Appendix 1. Continued.

Common name	Chemical name	Group
solan	3'-chloro-2-methyl-p-valero-toluidide	
TCA	trichloroacetic acid	aliphatic acid

Appendix II. Compounds evaluated as adjuvants for foliar applied herbicides.

Common or trade name	Chemical	Source
BRIJ 30	lauryl alcohol	Atlas Chemical Ind.
Citowet	alkylarylpolyglycol ether	Badische Anilin Soda Fabrik Company
corn oil	vegetable oils	several
9 D-207	undisclosed	American Oil Company
Dimethoate	0,0-dimethyl-s-(n-methyl-carbamyl-methyl) phosphoro-dithioate	American Cyanamid Company
DMSO	dimethyl sulfoxide	several
fuel oil	blended hydrocarbons	several
glycerine	glycerol	several
Glyodin	2-heptadecylglyoxa-lidone acetate	Union Carbide Company
L 53	blended hydrocarbons	American Oil Company
LF 2670	blended hydrocarbons	American Oil Company
LF 4247	blended hydrocarbons	American Oil Company
LF 4340	blended hydrocarbons	American Oil Company
LS 0799	blended hydrocarbons	American Oil Company
ML 700	undisclosed	Chevron Chemical Company
olive oil	vegetable oils	several
Plyac	emulsifiable polyethyl-ene fatty acid amine condensates alkylaryl sulfonates	Allied Chemical Company

Appendix II. Continued.

Common or trade name	Chemical	Source
PM 4114	tergitol-NP-27 (80%) isopropanol (20%)	Union Carbide Company
stoddard solvent	mixed hydrocarbons	several
Surfactant WK	dodecyl ether of polyethylene	E. I. duPont Company
Triton B-1956	phthalic glycerol alkyd resin in ethylene dichloride	Rohm and Haas Company
Triton GR-7	sodium salt of a sulfonated alkyl ester	Rohm and Haas Company
Triton X-45	octylphenoxypolyethoxyethanol	Rohm and Haas Company
Tween 20	sorbitan monolaurate	Atlas Chemicals Ind.
X-77	alkylarylpolyoxyethylene glycol, free fatty acids, isopropanol	Colloidal Products Co.

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