

**Proceedings of  
Scotts Turfgrass  
Research Conference**

**Volume 3 – Weed Controls**

**January 1972**





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# Proceedings of Scotts Turfgrass Research Conference

## Volume 3 – Weed Controls

### January 1972

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Proceedings of Scotts Turfgrass Research Conference

Volume 3 — Weed Controls

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Volume 3 — Weed Controls**

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## PREFACE

This volume contains the Proceedings of Scotts Turfgrass Research Conference on Weed Controls. Representatives at the conference included 42 researchers from 38 states and Canada, joined by Scott's research staff. The conference was held at the O. M. Scott & Sons Company, Marysville, Ohio, on July 27-28, 1970.

Ten formal papers were presented on various aspects of weed control - their uses, effects and current recommendations. A question and answer period followed many of the presentations. All of the papers presented at the conference, as well as the transcripts of the discussions, are included in this volume.

This unique endeavor provided rapport between turf weed control specialists, resulting in highly rewarding discussions. Within these proceedings are papers and references that are considered as invaluable aids to researchers, as well as students working with turfgrass herbicides. O. M. Scott & Sons certainly is to be applauded for taking the leadership in sponsoring a genuinely stimulating, educational project as this truly was.

The papers in this Proceedings may be reprinted in whole or in part - subject to accurate quoting with proper credit to the authors and O. M. Scott & Sons.

The editors and Scotts would like to acknowledge the cooperation of the authors and conference participants in preparing this Proceedings.

Richard E. Schmidt  
Chief Editor



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# ECOLOGICAL FORCES AFFECTING WEEDS AND THEIR CONTROL

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## Introduction

A complete discussion of the ecology of weeds would encompass all aspects of plant ecology. There is little that is unique about weeds in this respect, and most of the general concepts and principles of ecology apply to them. Therefore, a review of some of these concepts with specific reference to weeds of turf provides a necessary background for safe and efficient weed control.

The ecological factors related to weed establishment and growth may be divided into the natural factors and the man-determined or man-modified factors--those of turf culture and management. Man, of course, modifies most of the environmental factors to some degree but certain factors are regulated to a much greater extent than others. Outdoor air temperature is a factor that man can modify only slightly, but defoliation (mowing) is a factor that is almost entirely man made.

From the viewpoint of weed control, ecological factors may be considered as they relate directly to the turf and weed plant or as they affect absorption and activity of herbicides. This discussion will be confined largely to the first aspect and to the modification of these factors as a means of weed control.

## Interrelated Ecological Factors

Many of the environment factors of greatest importance to turf culture are those of a micro-environment extending from 2-4 inches above to 2-4 inches below the soil surface. The nature of this micro-environment is largely determined by turf cultural practices and utilization.

Good (1931, 1953) stated that distribution of a species or biotype was controlled primarily by the distribution of climatic factors and, secondarily, by the distribution of edaphic factors. The significance of the concept is demonstrated by weeds such as crabgrass, Digitaris sanguinalis, which may be found wherever temperature, the climatic factor, is satisfactory. However, soil moisture, a factor which can be regulated by man at least to some degree, determines its distribution in any single turf area.

Related to Good's theory of plant distribution are the laws of tolerance proposed by Shelford (1913), Good (1931) and Mason (1936). Plants with wide ranges of tolerance for many factors of the environment will be widely distributed. Tolerances have a genetic base and the range of tolerance of a taxonomic unit is the sum of the ranges of its member biotypes. However, there are times in the life cycle of a plant when it may have a low tolerance to certain specific factors.

Poa annua provides an excellent illustration of these concepts. It is a highly variable species with wide ranges of tolerance for many factors. Because of this, it is one of the most widely distributed of all plants, living and reproducing in many different environments. However, as Hovin (1958b) has shown, moderately high night temperatures during inflorescence development will result in pollen sterility; thus, there is a lower level of tolerance for high temperature at this critical stage of its life cycle.

A third concept, somewhat similar to those just described, is Taylor's (1934) theory of limiting factors. Based on Liebig's "law of the minimum," this theory states that growth and survival of a plant is dependent upon the environmental factor in

least supply, or least favorable at any specific stage in its life cycle. Soil moisture at time of seed germination is a limiting factor for crabgrass and many other plants. Light for seedling development (discussed in more detail later) may often be a limiting factor for Poa annua. Modern weed control practices recognize this principle, using knowledge of critical stages in life cycles for the most advantageous timing of cultural and chemical control methods.

Replaceability of one ecological factor by another (an important ecological principle) is generally illustrated by the classic example of substitution of altitude for latitude. In Riverside, California, with an altitude below 1000 ft., the climate is subtropical and warm season turfgrasses are dominant. Many temperate climate weeds are absent or abundant in winter only. Twenty-five miles away in the Arrowhead region at elevations around 5000 ft. a temperate climate exists, warm season grasses are absent and many weeds found in the more northern regions are common.

Man, through irrigation practices, has made a factor substitution of no less importance. He has substituted water from streams, lakes and wells for the deficient rainfall of the arid southwest. As a result, lush grass and exotic weeds grow in areas which would otherwise support only the hardiest of xerophytic plants.

In most plant communities, competition occurs for the environmental factors in limited supply or availability. Competition may exist among parts of a single plant, among plants of the same species or among plants of different species. Competition among plants is the ultimate concern of weed science. By cultural and chemical methods, we strive to give crops, plants or turfgrasses a competitive advantage over the unwanted species.

Through competition and natural selection of individuals best able to survive and reproduce, modern plants have evolved and have acquired adaptation to specific environmental conditions. Evolution, of course, is a dynamic process today as well as in the past. Turf culture, a relatively recent development,

is exerting new selection pressures on both grasses and weeds. Better adapted turfgrasses and more competitive weeds under specific turf conditions are evolving. Superior turf ecotypes have been recognized in both the grasses used for this purpose and the weeds invading various types of turfs.

Although students of ecology frequently refer to the effects of a single environmental factor on an organism, it is generally recognized that all factors affect a plant more or less simultaneously and interact to modify each other. Cain (1944) referred to this as the holocoenotic environment and stressed the importance of the concept to understanding plant responses. A great simplification of Billings' (1952) diagram illustrating the holocoenotic environment is shown in Fig. 1.

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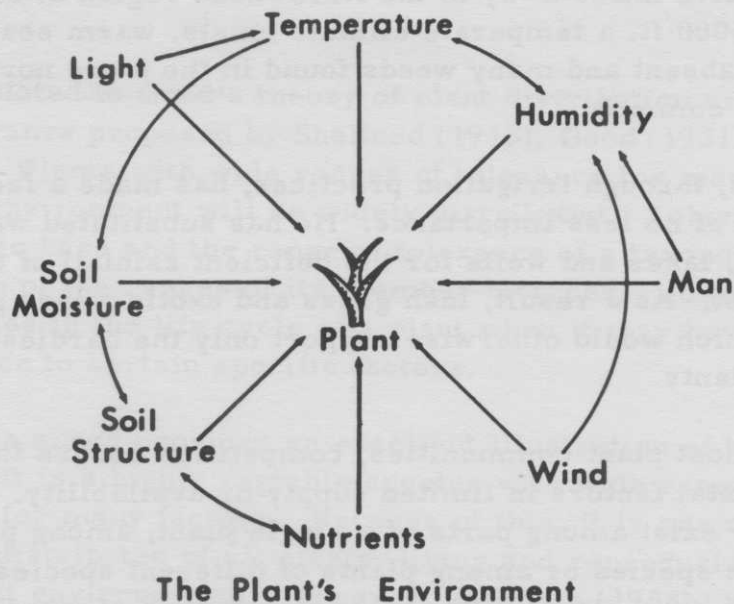


Figure 1. A simplified version of Billings' (1953) illustration of the holocoenotic environment.

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Reference to specific studies and observations will illustrate the aforementioned principles and relate them more directly to turfgrass weed control.

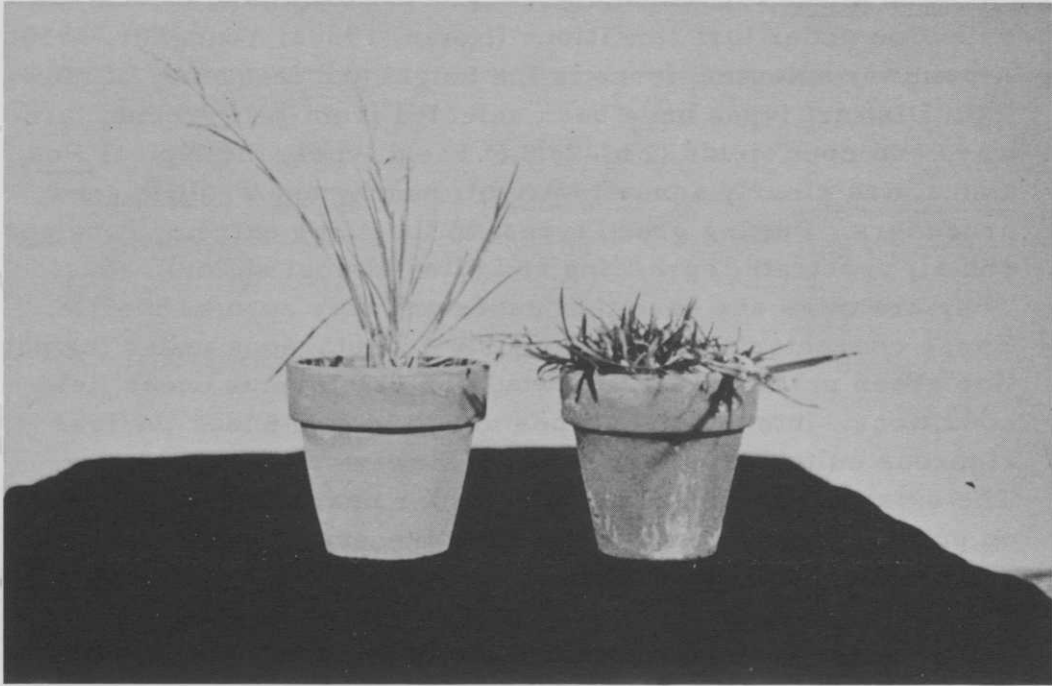


Figure 2. Ecotypes of Poa annua. Comparison of an upright open growing field type (left) with a dwarf compact dark green putting green type (right).

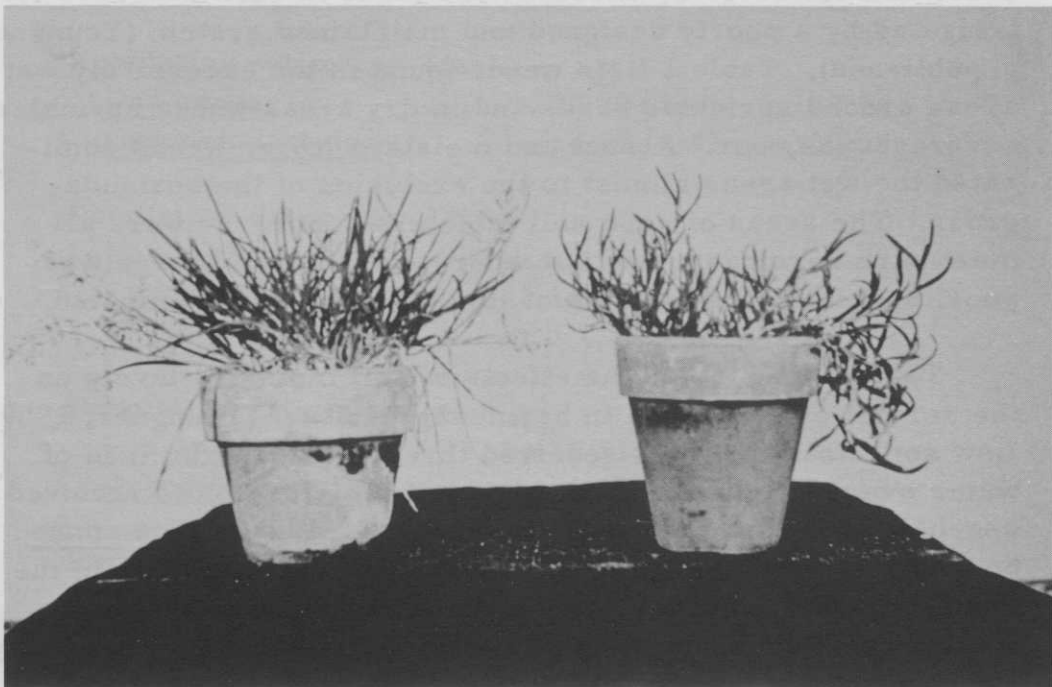


Figure 3. Ecotypes of Poa annua. Comparison of a normal heavy-flowering fairway type (left) with a dwarf creeping non-flowering putting green type (right).

Poa annua furnishes one of the best examples of ecotype selection under turf conditions (Hovin, 1958a; Youngner, 1959). A primary selection force is the height and frequency of mowing. Distinct types have been selected from golf greens, fairways and open fields (Fig. 2, 3). Field types, the typical Poa annua, are clearly annual, upright, bunchy and prolific seed producers. Putting green types, to the other extreme, are perennial, prostrate, spreading and often almost stoloniferous. They are often shy seed producers and may even be sterile. These characteristics are uniquely advantageous under the putting green environment, but would be deleterious under field conditions. Intermediate types may be found under the less vigorous cultural requirement of fairways and general turf. The existence of perennial, sterile, or nearly sterile ecotypes on putting greens reduces the effectiveness of pre-emergence chemical control practices.

#### Moisture Factors

Soil moisture, either excessive or deficient, may favor establishment and competition of weeds with turfgrasses. Weed species in the two moisture conditions will be different, however, as illustrated by observations made in bermudagrass turf irrigated by a poorly designed and maintained system (Youngner, unpublished). Table 1 lists weeds found in the excessively wet areas around sprinkler heads and in dry areas where sprinkler coverage was poor. Annual and moisture loving weeds dominated the wet areas almost to the exclusion of the bermudagrass. The areas of good soil moisture conditions were almost pure bermudagrass, but where sprinkler coverage was poor, species more tolerant of low soil moisture dominated.

Table 2 illustrates the effects of soil moisture levels on the survival of Poa annua in bermudagrass turf (Youngner, 1959). Low soil moisture plots received three-fourths of an inch of water every ten days and the high soil moisture plots received one-half inch of water every three days. Although Poa annua populations were the same in both irrigation treatments in the spring, by mid-summer no Poa annua remained in the dry treatment. Population reduction during the same time was only slight in the wet treatment.

Table 1. Weeds found in wet, moist and dry areas in a bermuda-grass turf.

Excessively wet (Abundant)	Moderate moisture	Dry
Crabgrass	Few or	Bur Clover
Oxalis	no weeds	Black Medic
Spotted Spurge		Drop Seed
Annual Bluegrass		
Bentgrass		

Table 2. Populations of Poa annua and Cynodon dactylon at two levels of soil moisture.

(Low moisture)		
	Mean number of plants per sample	Percent presence
Population estimates-May		
<u>Poa annua</u>	10.20±1.01	100.00
<u>Cynodon dactylon</u>	4.80±0.79	100.00
Population estimates-July		
<u>Poa annua</u>	0.00	--
<u>Cynodon dactylon</u>	14.82±1.05	100.00
(High moisture)		
Population estimates-May		
<u>Poa annua</u>	10.51±0.98	100.00
<u>Cynodon dactylon</u>	4.09±.67	98.36
Population estimates-July		
<u>Poa annua</u>	8.82±0.88	92.10
<u>Cynodon dactylon</u>	6.38±0.51	100.00

## Light Factors

Competition for light occurs within most turfs and other grasslands when fully established. As Donald (1963) pointed out, competition for space rarely exists and that which is often referred to as such is actually competition for light.

More and more of the incident light is intercepted by the leaves as the turf increases in height and density. When leaf density is such that essentially all light is intercepted but all leaves receive adequate light, the optimum leaf area index (the ratio of leaf surface to soil surface) and the maximum growth rate are reached. Eventually, severe competition for light develops among the leaves. As density of the leaf canopy increases, older lower leaves receive insufficient light and eventually die. In time, the death rate of old leaves equals the rate of emergence of new leaves.

A vigorous dense turf is necessary to prevent weed invasion. This can, in part, be achieved by a mowing height and frequency that maintains the leaf area index as near the optimum as other requirements of the turf permit. The resulting high net assimilation rate would permit good tiller and root development. Brougham (1957) has illustrated in Fig. 4 the importance of cutting height to the time required before the optimum leaf area index (95% light interception) is again reached. Of course, it is equally important to maintain a cutting frequency that will prevent lower leaves from yellowing, due to insufficient light.

Clipping height has been shown to lower tillering rates, if leaf tissue only is cut. However, if growing points are removed, tillering will be stimulated by the destruction of apical dominance (Maida and Ehará, 1962; Jamison and Huss, 1959). Thus, in turf, close mowing of stoloniferous grasses where growing points would be removed might encourage turf density, but would have the opposite effect on nonstoloniferous species, such as bluegrass. Clipping increases the flowering of Kikuyugrass as well as increasing its density (Youngner, 1961b).

Another effect of clipping on competition for light may be seen with Poa annua establishment in turf (Youngner, 1959).



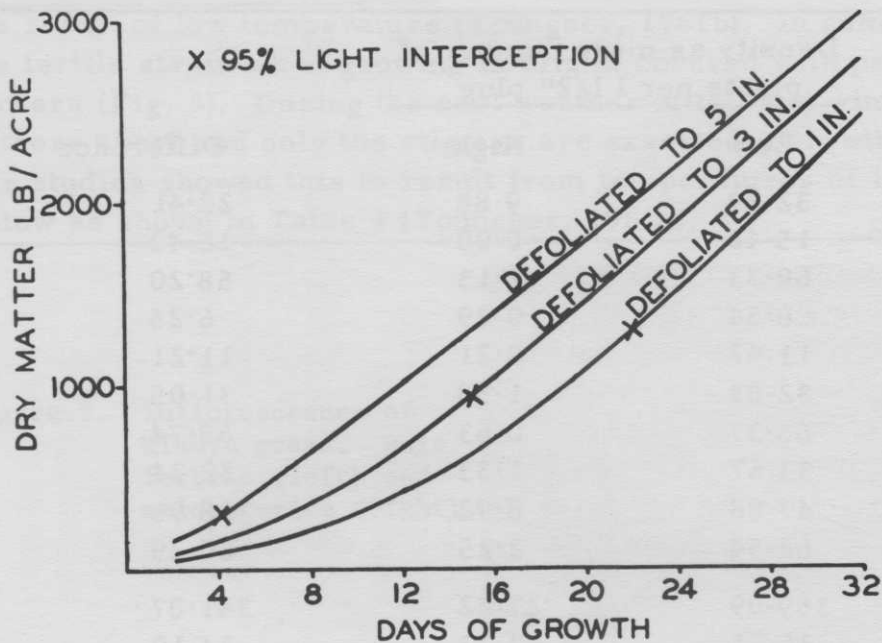


Figure 4. Effects of cutting height of a mixed sward on time required to reach optimum leaf area index (95%) light interception.

Population counts made along each side of a line between the high cut roughs and low cut fairways of ten southern California golf courses showed that lower clipping was favorable to Poa annua establishment (Table 3). Removal of more bermudagrass leaf was thought to permit more light to reach the Poa annua seedlings during the fall germination period. A similar effect was demonstrated for vertical mowing or renovation in the fall (Youngner, 1959, 1968; Youngner and Nudge, 1968a). Poa annua populations were increased by this practice on both bentgrass greens and bermudagrass lawns.

#### Temperature Factors

Temperature also has various effects on plants of great significance to weed control in turf. Flowering of many species is highly temperature sensitive. The previously cited high temperature induced pollen abortion (Hovin, 1958b) of Poa

Table 3. Densities of *Poa annua* populations in low and high-cut turf.

Location	Density as mean number of plants per 1 1/2" plug		
	Low	High	Difference
1	32.29	9.88	22.41
2	15.42	0.00	15.42
3	60.33	2.13	58.20
4	6.54	0.29	6.25
5	11.42	0.21	11.21
6	32.63	1.58	31.05
7	66.37	0.63	65.74
8	33.67	1.33	32.34
9	47.88	8.92	38.96
10	62.54	2.25	60.29
Total	369.09	27.22	341.87
Mean	36.91	2.72	34.19

Calculated t = 5.07

t at 0.01 point, 9 D.F. = 3.25

Difference is significant at 1% level

Table 4. Appearance of florets, after 4 weeks of treatment, in fertile *P. clandestinum*.

Day length (hr)	Stamens	Fertile pollen (%)
Temperature 27°C		
8	Exserted	89 ± 16
16	Exserted	65 ± 11
24	Exserted	71 ± 13
Temperature 10°C		
8	Nonexserted	36 ± 5
16	Nonexserted	21 ± 6
24	Nonexserted	0.4 ± 0.2
Temperature 21°C (day) to 10°C (night)		
8	Exserted	72 ± 13
16	Exserted	82 ± 16

annua is perhaps characteristic of many weeds. In Kikuyu grass, Pennisetum clandestinum, male sterility has been shown to be the result of low temperature (Youngner, 1961b). In summer, the fertile strain when growing in turf is covered with perfect flowers (Fig. 5). During the cool weather of fall and winter, anthers abort and only the stigmas are exerted. Growth chamber studies showed this to result from temperatures of 10°C or below as shown in Table 4 (Youngner, 1961a).

Figure 5. Inflorescences of Kikuyu grass. Male fertile (left) and male sterile (right).

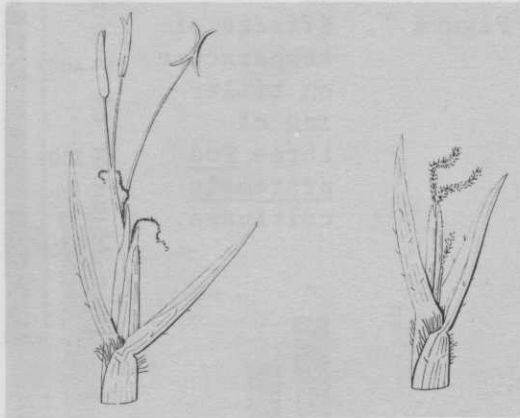
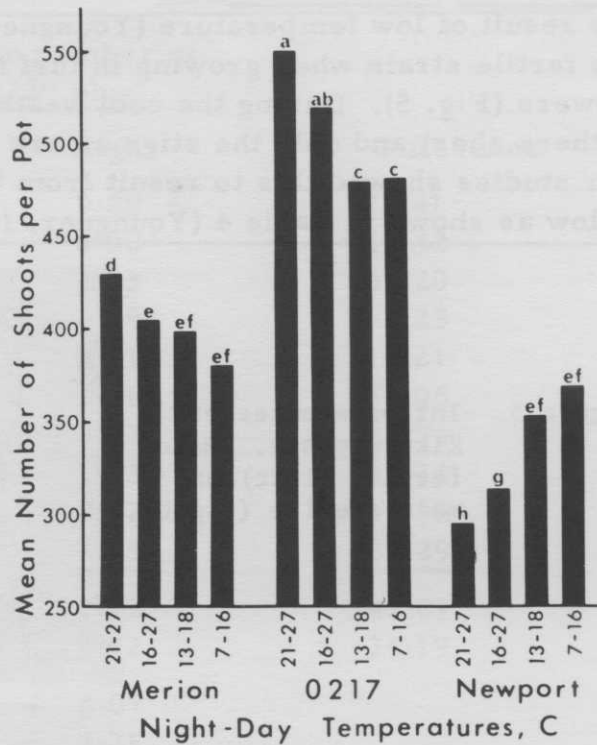


Figure 6. Effects of day length on flowering of Poa annua at low temperature.



Poa annua again provides an interesting example of a temperature-photoperiod interaction. Normally, Poa annua flowering is not responsive to day length. However, some ecotypes flower at cool temperatures (approximately 10°C) only if given long days (16 hours), as shown in Fig. 6. At higher temperatures, flowering occurs at any day length. Long days in this instance seem to substitute for warm temperatures to promote flowering (Youngner and Wilson, unpublished).

Figure 7. Effects of temperature on tillering of three *Poa pratensis* cultivars.



Tillering of Kentucky bluegrass, *Poa pratensis*, is highly temperature sensitive. The optimum temperature for tillering will differ for various cultivars (Youngner and Nudge, 1968b). As shown in Fig. 7, Newport, a selection from the cool Oregon coast, has a distinctly lower optimum than Merion or 0217 Fylking. This observation suggests that variety selection for specific climates may be a step towards maintenance of dense weed free turfs.

Consideration of accumulation of reserve carbohydrates gives further support to this suggestion. Reserve carbohydrates are thought to be highly important to a turfgrass's ability to recover from mowing, injury or disease, and to good root and tiller growth. Figure 8 shows that bluegrasses accumulate more carbohydrates at low temperatures than at high and that the cultivars differ in their ability to store carbohydrates at any temperature. Merion is an especially good accumulator of carbohydrates. Varieties better able to ac-

cumulate carbohydrates may be able to maintain greater vigor and density, especially under adverse conditions. A weak turf is more subject to weed invasion than a vigorous one.

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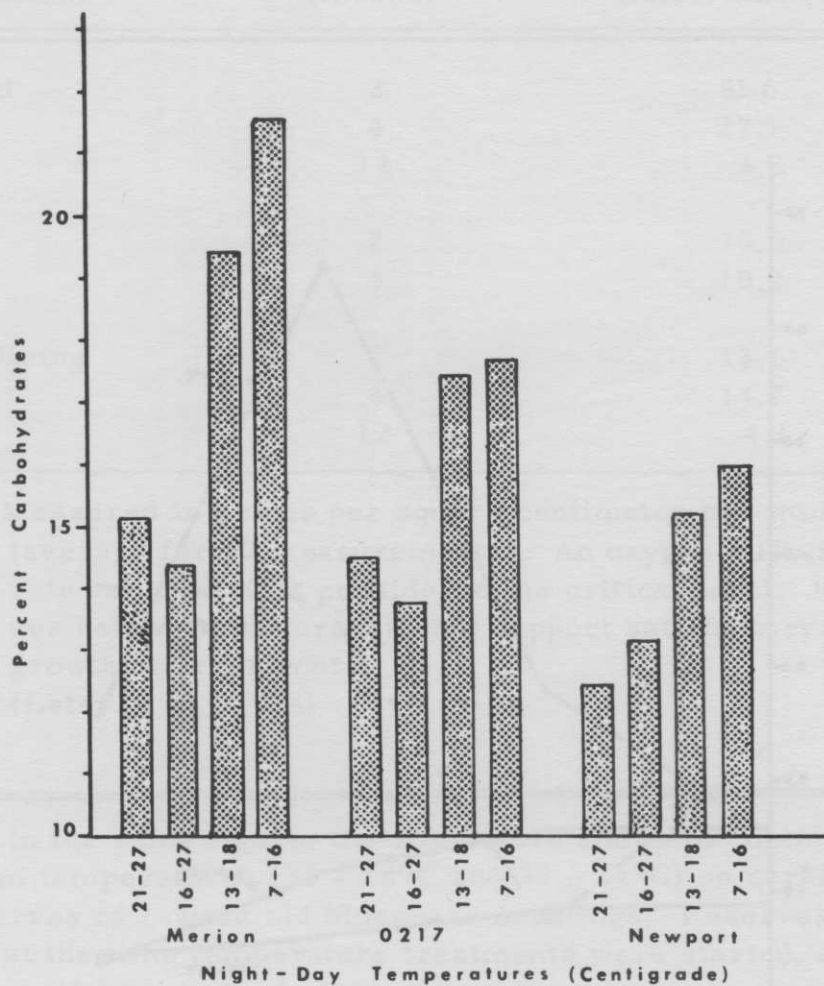


Figure 8. Effects of temperature on carbohydrate accumulation in three cultivars of Poa pratensis.

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Some grasses subject to periods of extreme temperature may lose reserve carbohydrates quickly, as shown in Fig. 9. Night temperature in the 13 - 7°C growth chambers was over 35°C for three consecutive nights during the twelfth week,

resulting in severe loss of carbohydrates (McKell et al., 1969). Thus, turfgrasses, such as Kentucky bluegrass, may be subject to permanent injury following periods of high temperature. Herbicides applied at such time could be harmful to the turf as well as the weed.

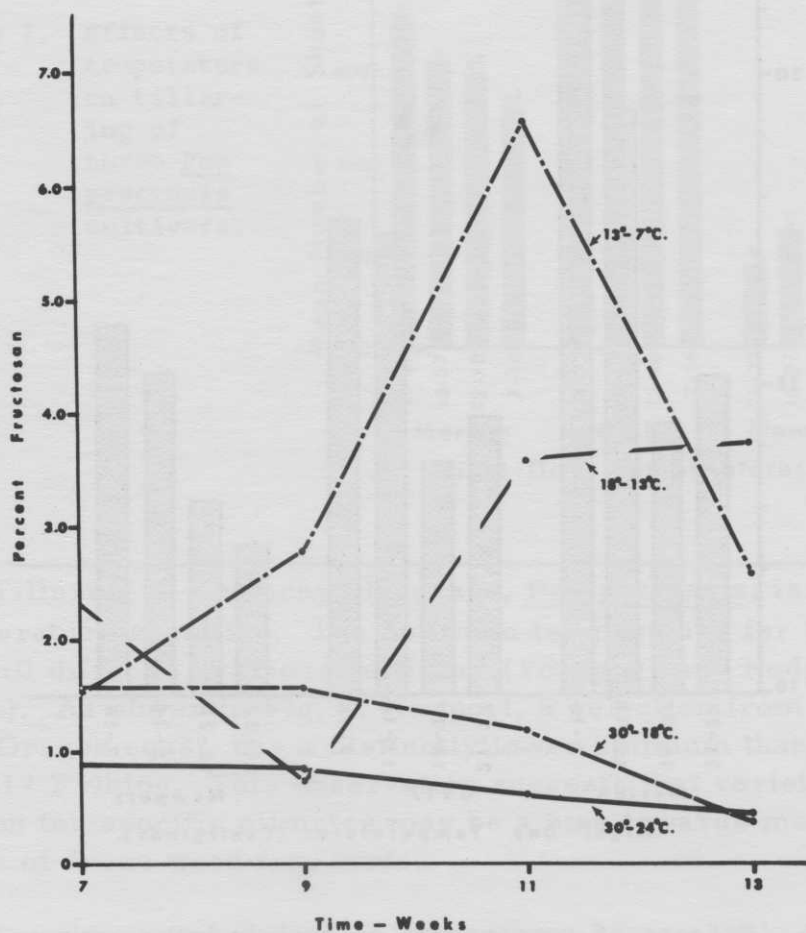


Figure 9. Effects of temperature on the rate of carbohydrate accumulation in Newport Kentucky bluegrass, *Poa pratensis*, seedlings. Night temperatures in the 13 - 7°C growth chambers were over 35°C for three nights during the twelfth week.

Table 5. A correlation of putting green condition with oxygen diffusion rates at different soil depths.

Putting Green Condition	Depth of Measurement (inches)	Oxygen Diffusion Rate Value (1)
Good	2	51.6
	4	27.1
	12	3.8
Bad	2	10.0
	4	10.2
Declining	2	13.6
	4	14.7
	12	4.1

(1) Measured in grams per square centimeter per minute (average for 20 measurements). An oxygen diffusion rate value of 20 is considered the critical level. Values below this figure will not support satisfactory growth of grass roots.  
(Letey et al., 1964)

In the same figure, the effects are shown of continuous warm temperatures (30 - 18°C and 30 - 24°C) on carbohydrate reserves of 7-week old bluegrass seedlings. Reserves were low at the time temperature treatments were started, and there was a slight but steady loss of reserves during the six weeks of the experiment. This indicates that summer planted bluegrass turfs may be less able to resist injury and the resulting weed invasion than turfs started in the fall or early spring when temperatures are conducive to carbohydrate accumulation (McKell et al., 1969).

#### Other Environmental Factors

In a similar manner, other environmental factors affect turf growth, density and vigor and, consequently, the turf's ability to resist weed invasion. Leguminous weeds are espec-

ially common invaders of nitrogen deficient turf, but many other species may invade also. Similarly, high soil salinity, a common problem of the southwest, weakens many turf grasses and subjects them to ready invasion by salt tolerant weeds. Diseases, nematodes and insects may also open the way for invasion by weeds. A common observation in southern California is extensive kill of dichondra turf from a combination of several fungous pathogens and root-knot nematode. This is usually followed by an invasion of common bermudagrass.

Soil compaction and soil layering restrict oxygen movement into the soil, often resulting in poor turf. The turf is readily invaded by weeds, such as Poa annua, that are able to survive under low soil oxygen levels. Letey et al. (1964) showed that the oxygen diffusion rate on a poor quality putting green was only half of the rate considered to be critical for growth of grass roots (Table 5). The grass on this green was almost entirely Poa annua. Another green considered to be good quality with much bentgrass had oxygen diffusion rates above the critical level at the 4-inch depth but not at 12 inches.

Aerification is a standard remedy for turf soil composition. Letey et al. (1964) showed that aerification did increase the oxygen diffusion rate (Table 6). The deeper and more extensive the aerification, the greater the improvement in the oxygen diffusion rate.

Soil organic matter is important to good plant growth. Many soils used for turf are naturally low in organic matter, so various organic soil amendments are often added prior to planting. However, established turf builds its own organic matter through the death and decay of roots and other plant parts in the mineral soil. Although this improves the water and nutrient relationships, it may also affect the use of some soil applied herbicides through increased adsorption. Sandy soils might be especially affected over a period of years with increased adsorption necessitating increased herbicide application rates.



Table 6. The effect of three different aeration treatments on the oxygen diffusion rate at different soil depths under putting green conditions.

Aeration Treatment	Depth of Measurement (inches)	Oxygen Diffusion Rate Value (1)
Regular	2	86.3
1. Mechanical Procedure (check)	4	43.7
	10	4.4
2" Holes	2	101.7
2. 10" Deep Backfilled with loamite	4	69.2
	10	22.7
1" Hole	2	95.0
3. 10" Deep Left Open	4	72.4
	10	28.3

(1) Measured in grams per square centimeter per minute, (average for 20 measurements). An oxygen diffusion rate value of 20 is considered the critical level. Values below this figure will not support satisfactory growth of grass roots. (Letey et al., 1964)

### Summary

It is apparent that all environmental factors as they play upon each other, the turf grasses and the weed plants, affect weed control. As these factors change, cultural practices, herbicides, application methods, application rates and timing of applications, all must be adjusted in order to achieve the best possible weed control. Proper turf cultural practices can in themselves reduce weed populations; nevertheless, herbicides are an essential part of most weed control programs. However, herbicides must be viewed as factors of the total environment, and

their constant interaction with all other factors must be recognized. By using them in this context, safe and effective weed control can be achieved without unnecessary and undesirable contamination of our environment. Our failure to properly recognize herbicides as critical environmental factors, is at least in part responsible for the adverse publicity and criticism given them today.

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## Discussion Period

Dr. Hemphill: In reference to the accumulation of organic matter below the thatch, how significant is this? How much accumulation of organic matter do we get? Are we really increasing the organic matter down at the 4 to 6 inch level?

Dr. Youngner: It seems to me that we are, but I was raising this as a question myself. I don't know that we have a lot of good experimental evidence of this, but the casual observations that I have made, in respect to other studies and experiments, seems to indicate that we were accumulating moderate amounts of organic material through repeated decomposition of the root system. I don't know how long a time interval may be required for this to occur. This is why our best agricultural soils have developed over the ages under grass conditions. Possibly the same thing will be occurring in turf. It is certainly evident where we are growing tall fescues, which have an extremely aggressive wide-ranging root system. Decomposition of the root system seems to bring about a definite improvement of soil structure over a period of time through organic matter accumulation.

Dr. Ledebøer: Under the fine grasses, though, we find that most of the root system, once a thatch layer has developed, will remain in that thatch layer. Consequently, the amount of accumulation of organic matter in the soil itself, which becomes quite compact, is rather limited. The problem is in the thatch layer on top.

Dr. Youngner: I'm quite sure that is almost universally true. It is not unusual to see turf growing where the entire root system is essentially in that accumulation of thatch. You can roll the turf off the soil like a blanket. There is very little contact with the soil below. I would like to raise the question, how would growing the root system in pure organic matter affect the use of herbicides?

Dr. Ledebøer: The picture is entirely different with tall fescue, since it really does not form thatch.

Dr. Kaufman: I don't know of a lot of work that has been done to answer your question, only what we know about adsorption of herbicides to soil organic matter. In cases where the herbicide is adsorbed by this soil organic matter, I would think this eventually could become a problem. Many of the common herbicides, like the phenoxy compounds, move readily in soil and are not influenced much by organic matter. They probably wouldn't be affected over a long term. Other compounds which do not move, simply because they are adsorbed on organic matter, would be affected. And these are also some of the more persistent. I'm not sure if the increased persistence would be counteracted or offset by the increased adsorption.

Dr. Youngner: This is a concern only where we are dealing with herbicides that are adsorbed on clay or organic matter in the soil, and not those different types.

Mr. Holyoke: Would it be possible to use this organic content differential to explain the effectiveness of one herbicide between different regions, even within a climatic region? We find comments that this one works for me or this one gives terrific damage in our area and, perhaps, it is the organic matter differentials that cause the effectiveness or damage, or lack of damage. You get a differential under a particular condition that might be due to the age of your plots or the location of the plots. So this is one of the things that sometimes makes it difficult for some of us who have a limited turf program to use results from other states. We get into problems and perhaps it's because of these differences we just aren't duplicating.

Dr. Ahrens: We have to be careful about what kind of organic matter we're talking about. Most thatch is like peat. It's not finely divided and it's probably not as active in adsorbing herbicides as finely divided organic matter. Judging from the work we've done on containers in peat-sand mixtures, I expect that there might be a factor of maybe 20% more herbicide required, but it's not going to be any big factor.

Organic matter in soil generally reaches an equilibrium for a given climatic situation. We are not going to get continual

build-up of organic matter. It will reach a peak and level off for the temperature and soil moisture condition. You can put 10 tons of manure on a corn field every year and never get the organic matter level above a certain point. I think it will happen in turf, too.

Dr. Youngner: This is very true. However, in southern California, where many of our soils are naturally almost devoid of organic matter, we can increase the amount of organic matter by applying an organic amendment, or possibly through the growth of vegetation over a period of time.

Dr. Seely: We've got an offsetting factor here that should be considered. Where we have a relatively high organic matter content and irrigate as we do, we have a much higher biological activity which tends to decompose the herbicides applied, as well as adsorption. Also, we tend to liberate those which are adsorbed.

Dr. Youngner: That's a good point.

Dr. Horn: We found that it takes five pounds of the triazines on our organic muck soils in Florida to do the same job that two pounds will do on a mineral soil--as far as a weed control is concerned.

Dr. Hemphill: I've had some plots growing for 13 years where annual applications were made with the same herbicide. I don't see any increased demand to control crabgrass, and we overseed these each time. Admittedly, we did get some thatch. It is difficult for seed to germinate in this situation, but I haven't seen any decreased level of control with a given rate of Dacthal, for example. This is one of the herbicides we have been using the longest. The arsenates (lead and calcium arsenate) have been used for an equal length of time, but I haven't seen this need for an increased level of treatment.

Dr. Youngner: You may have achieved the point of equilibrium mentioned earlier, where there was no further increase in organic matter in that soil, no matter what was taking place. If this is the case, you would continue to have the same conditions and results with your herbicides.

Dr. Schmidt: I'm sure that many of you are familiar with research at the Sports Turf Institute in Bingley, England, where the effect of arsenicals actually increased organic matter. Evidently, the pesticide had some effect or microbial activity within the soil, so you can have another interaction here as far as the herbicide is concerned.

I would like you to verify another point. I was wondering if there are any data to support the fact that lower leaves are parasitic when shaded by leaves of other species, or with leaves of the plant per se. As a matter of information, one of our colleagues at the Virginia Polytechnic Institute has data indicating that the lower leaves are not parasitic, but in fact, the carbohydrates of these dying leaves could be utilized by the plant. Consequently, I question the statement about the lower leaves being parasitic.

Dr. Youngner: As the leaf area index builds up to the point where it is over the optimum (creating a shading effect on the lower leaves) and then you decrease the mowing height, you would supposedly remove most of the good active leaves. The remaining leaves would be senescent due to the lack of light. These senescent leaves must be used by the plant to recuperate until it develops new leaves. I think this is the point we must consider.

Dr. Bingham: I would like to return to the subject of peat and charcoal for a moment. Some herbicides, bensulide, for example, respond readily to activated charcoal. Yet, when charcoal was applied a few months before this herbicide, we obtained drastically reduced effects of the charcoal. It seemed that once the charcoal becomes neutralized in the soil, it will not inactivate the herbicide. Are there any soil people here who might be able to clarify this?

Dr. Ahrens: A lot of other organic compounds are adsorbed on charcoal and peat. Once these sites are filled (by physical adsorption--largely on micro-pores and macro-pores in charcoal), herbicide adsorption is reduced. Charcoal and peat also are effective in adsorbing herbicides only when the



physical placement is such that the charcoal or peat is in contact with the herbicide. This physical placement is difficult to achieve, for you may dilute the adsorbent at greater depths in the soil. The herbicides, especially bensulide, should be on the surface. This may explain why the effective could be lessened when the charcoal is applied before the herbicide.

Dr. Daniel: One of the current seeding practices on bluegrass in the Northwest is rows about 18 inches apart. The rows are covered with a two-inch strip of charcoal, and then a pre-emergence herbicide is applied that stops growth everywhere else. As long as the charcoal isn't washed off, they can get a perfect stand.



# THE NATURE OF BIOCHEMICAL MECHANISM OF HERBICIDE SELECTIVITY

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## Introduction

Physiologist and biochemist have made considerable progress in the understanding of biochemical aspects of herbicide-plant responses. Especially important aspects are studies on the fate of the herbicidal chemical inside the plant, understanding of photosynthesis as a result of important herbicide reactions, rapid responses in RNA-DNA-Protein yielding broad effects on many different metabolites, and physical actions of chemicals on membranes.

The basis for selectivity varies greatly from herbicide to herbicide, and the interpretation of the different biochemical responses for a chemical in resistant versus susceptible plants must also take into account the internal concentrations of the herbicide. Certainly, the intensity of the response varies with the concentration present. A differential biochemical response between resistant and susceptible plants may be a reflection of the internal concentrations of the herbicide. When different species receive similar internal concentrations, the biochemical responses may well be similar.

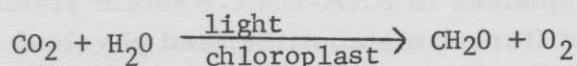
Plants also vary in their metabolic pathways and at times may shift in response to various inhibitors. It is presently thought that selectivity is related to (1) differential penetration, (2) differential translocation, (3) differential detoxification or herbicide metabolism and (4) variation in plant metabolic pathways. The duration of the toxic action is related to the ability of the compound to reach the site(s) of action and rate at which it is metabolized. The biochemical transformations which her-

bicides undergo include: oxidation (hydroxylation, dealkylation, carboxylation), dehydrogenation, reduction, conjugation (glucoside, metal complex) and hydrolytic reactions.

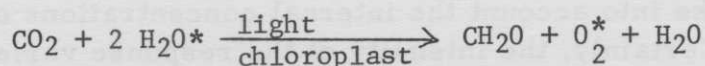
### Photosynthesis and Herbicides

Many of our best herbicides act via photosynthesis, seemingly as the major response in plants. The chloroplasts are organelles on which is centered the photosynthetic activity of the cell. They are easily seen with the light microscope but their fine structure requires higher magnification. Disc-shaped objects in the cytoplasm have a lamellar system with a stack of nearly identical membranes at various points called granum. The proteinaceous matrix is called the stroma and contains the enzymes involved in fixation of carbon. The chlorophylls and carotenoids are in close association in the membranes of the grana, allowing for efficient transfer of light energy.

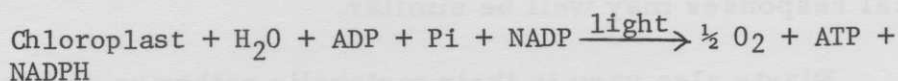
In early work, the overall reaction of photosynthesis was demonstrated:



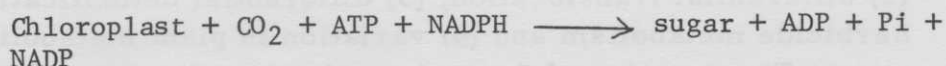
A further important discovery provided convincing evidence that the oxygen released in plants was from water, not carbon dioxide:



Summary reactions of photosynthesis are now divided into two general groups of reactions, one known as the light reactions:

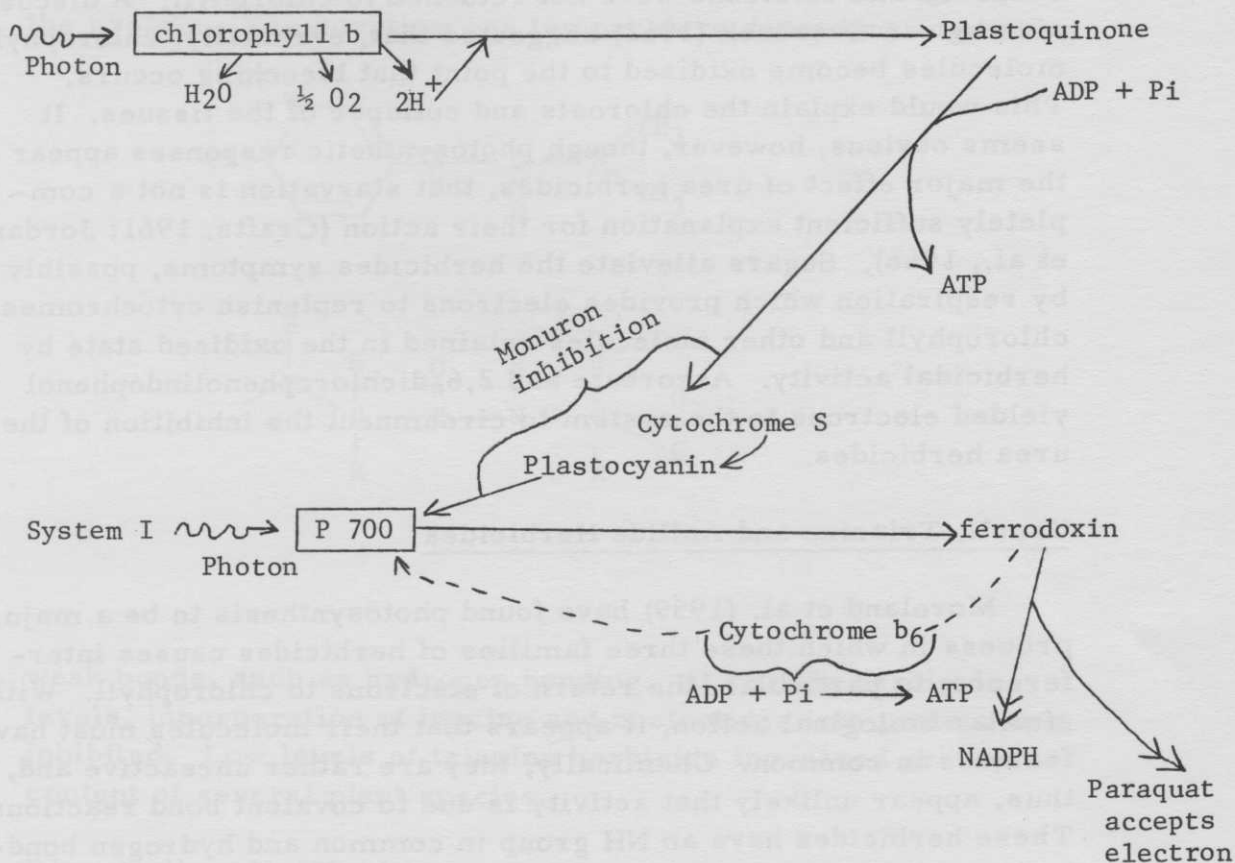


The second as dark reactions:



Other essential compounds have been identified in chloroplast, providing the ability for alternate oxidation and reduction and participate in electron transport. These include cytochrome f, possibly cytochrome b<sub>6</sub>, plastoquinones, plastocyanin, ferredoxin and there are others yet unidentified (Salisbury and Ross, 1969). Then, a model for the light reactions of photosynthesis may be shown:

### System II



In System I, light energy may be converted to chemical energy of ATP through electron flow back to chlorophyll (P700). The process is called photosynthetic phosphorylation. In another pattern of electron flow, they are captured by NADP, forming the reduced pyridine nucleotide. NADPH and ATP are products storing the energy of light and assimilatory power for the dark reactions. Chlorophyll b appears to be associated with the splitting of water and functioning of non-cyclic phosphorylation in System II.

## Urea Herbicides

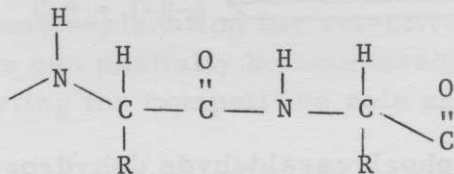
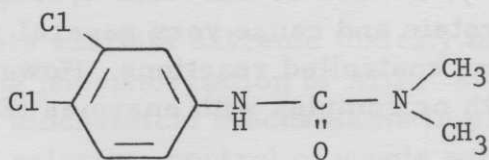
Cooke (1956) and Wessels and Van der Veen (1956) concluded that urea herbicides interfere with the oxidation of water. Monuron was observed to interfere with the electron flow system that provide low energy electrons to fill the holes in the chlorophyll a, or P700 (Jagendorf and Margulies, 1960). All evidence supports the conclusion that interference occurred in the non-cyclic portion of the electron flow systems. Accumulation of oxidized cytochrome occurred and electrons were not returned to chlorophyll. A discussion by van Overbeek (1962) suggested that, eventually, chlorophyll molecules become oxidized to the point that bleaching occurs. This would explain the chlorosis and collapse of the tissues. It seems obvious, however, though photosynthetic responses appear the major effect of urea herbicides, that starvation is not a completely sufficient explanation for their action (Crafts, 1961; Jordan et al., 1966). Sugars alleviate the herbicides symptoms, possibly by respiration which provides electrons to replenish cytochromes, chlorophyll and other molecules retained in the oxidized state by herbicidal activity. Ascorbate and 2,6-dichlorophenolindophenol yielded electrons to the system to circumvent the inhibition of the urea herbicides.

## Uracil, Triazine and Anilide Herbicides

Moreland et al. (1959) have found photosynthesis to be a major process in which these three families of herbicides causes interference; in particular, the return of electrons to chlorophyll. With similar biological action, it appears that their molecules must have features in common. Chemically, they are rather unreactive and, thus, appear unlikely that activity is due to covalent bond reactions. These herbicides have an NH group in common and hydrogen bonding is well known with such groups. There is also C O or -C N- groups next to the NH group in every case and they may give similar hydrogen bonds. Thus, the high biological activity seems to be related to a capacity to form hydrogen bonds with the protein of enzymes as well. Further support of hydrogen bonding aspects were demonstrated by replacing the hydrogen on the NH group with an ethyl group and observing much reduced activity on the photosynthetic process.

Siduron, another urea herbicide, does not appear to interfere with the photosynthetic process as monuron does (Splittstoesser and Hopen, 1968). It has the two functional groups, but steric hindrance may be a possibility.

Diuron and several N-phenyl carbamates were found to absorb to bovine serum albumin (animal protein - BSA). Substitution of chlorine in the 3 and 3,4-positions of the phenyl ring was correlated with increased absorption to BSA (Camper and Moreland, 1966). This appeared to alter the electron density so that the amide hydrogen became more acidic. The sorption of diuron and propanil to plant protein was several fold greater than to BSA (Camper and Moreland, 1967). Sorption appeared to be between the amide group of the herbicide and amino groups of the protein. The sorption was temperature dependant suggesting



weak bonds, such as hydrogen bonding. At certain herbicide levels, incorporation of leucine and nucleotides into protein was inhibited. Low levels of triazine herbicide increased protein content of several plant species.

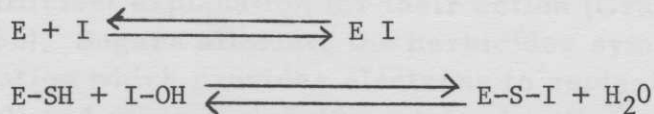
### Bipyridylum Herbicides

The bipyridyl herbicides do not have the hydrogen bonding characteristic of the other photosynthetic inhibitors and appear to pick up an electron destined to reduce NADP (Funderburk and Lawrence, 1964; Mees, 1960). The herbicidal activity might be related to the formation of free radicals by the uptake of one electron. System II, as described previously, is inhibited by urea, triazine, uracil and amilides, while System I may remain functional. System I is affected by the bipyridyl herbicides.

## Respiration and Herbicides

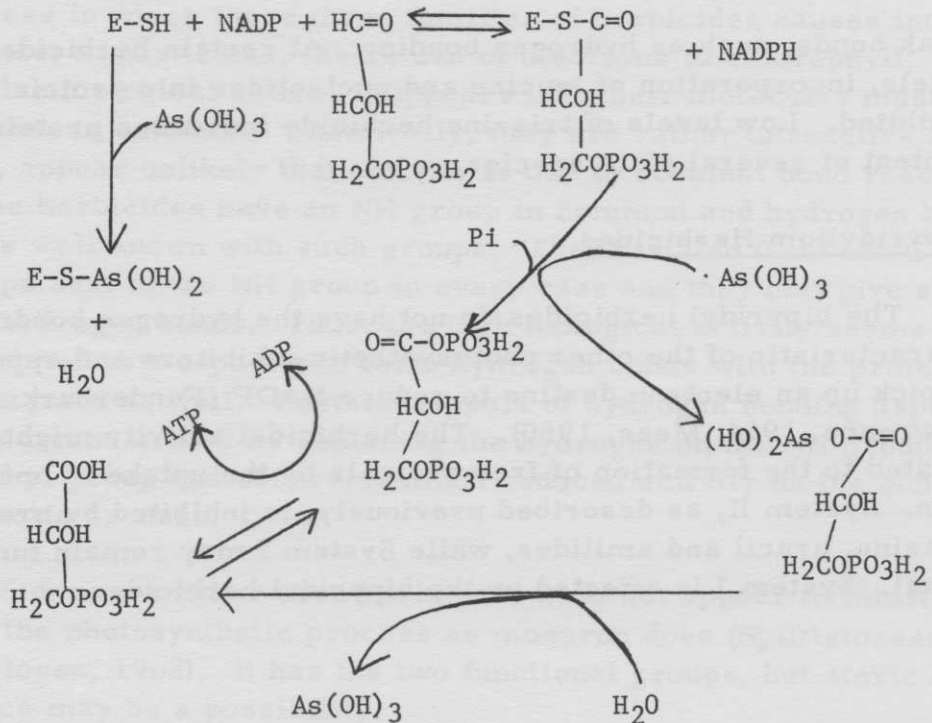
Respiration is usually described in three or more phases, including glycolysis, Krebs cycle and electron transport system. Glycolysis is the process by which starch is broken down into pyruvic acid. The Krebs cycle further breaks down pyruvic acid to CO<sub>2</sub> and, eventually, through the electron transport system, H<sub>2</sub>O.

Many herbicides show various effects on these processes. As described previously, chemicals can form hydrogen bonds or become absorbed to protein and cause very general responses among the many enzyme controlled reactions. However, some chemicals (I) react with or complex with enzymes (E) as:



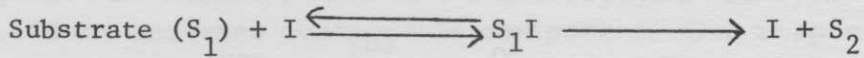
### Arsenical Herbicides

The enzyme, phosphoglyceraldehyde dehydrogenase, contains sulfhydryl groups that are essential to the oxidation of glyceraldehyde 3-phosphate to diphosphoglyceric acid 1,3-diphosphate:





Here the enzyme reacts with the substrate resulting in an acylthioester of the enzyme and a nucleophilic agent, Pi, forming the diphosphate (Salisbury and Ross, 1969). The first reaction of the arsenate herbicide is to tie up the functional group of the enzyme, rendering it inactive. A second type inhibition may be described as:

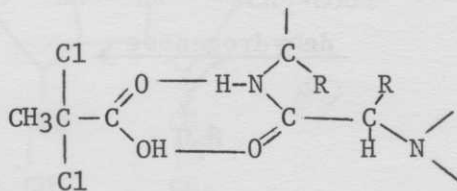


Arsenate exhibits extreme toxicity in this manner reducing or bypassing phosphorylation of ADP. Many arsenate herbicides show these biochemical mechanisms in plants. This does not explain the selective control of weeds with arsenate; but among many other factors, relative penetration of these herbicides into different tissues and conversion of the various forms to arsenic acid, offer some explanation for selective control. The response from arsenate can partially be counteracted with phosphate fertilizer supporting the competitive role shown above.

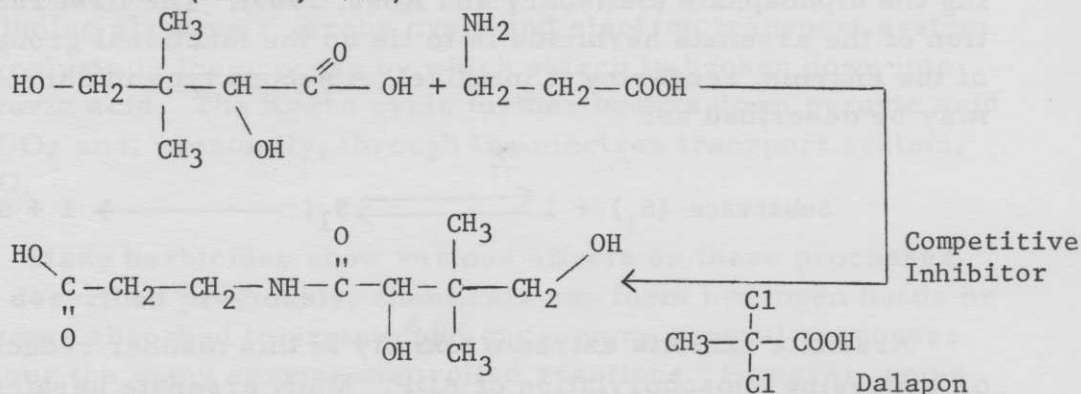
Arsenate reacts with sulfhydryl groups of many enzymes and, upon penetration of the symplast, causes protein to precipitate, becoming less available for plant processes.

### Chlorinated Aliphatic Herbicides

Dalapon and TCA precipitate protein and cause many types of responses in plants. Dalapon was found to bind with protein to change configuration of an enzyme, resulting in inactivation (Kemp et al., 1969). Hydrogen bonding is proposed scheme as:



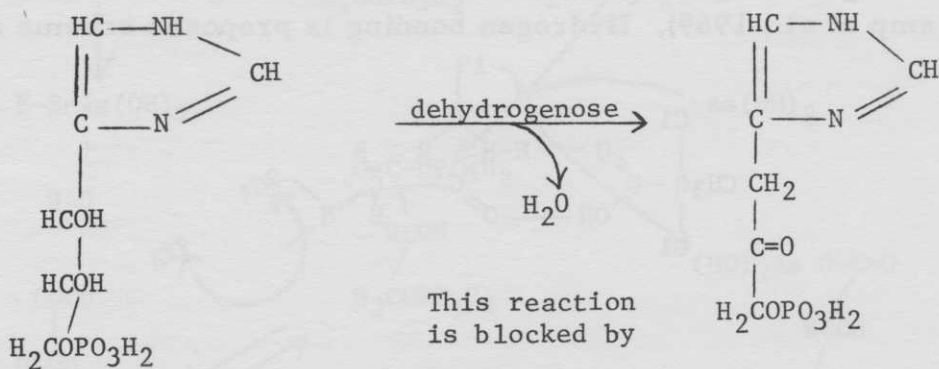
Dalapon provided competitive inhibition of pantothenate biosynthesis as the chemical structure resembles somewhat both substrates (Hilton, 1966):



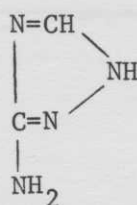
Pantothenate is essential for coenzyme A production. Perhaps dalapon acts as an antimetabolite for pyruvic acid as their chemical structures resemble each other. Although the chlorinated aliphatics interfere with such reactions, at high concentrations they are very effective protein denaturants and may be acting simply as enzyme denaturants.

### Amitrole

The immediate response of plants to amitrole is a striking color change resulting in bleached white tissue. The chlorosis may be independent of the growth-inhibiting actions responsible for herbicidal actions. Amitrole inhibits biosynthesis of histidine, riboflavin and, possibly, nucleic acid and purine metabolism. The step in histidine biosynthesis blocked by amitrole (Hilton and Kearney, 1965):



Imidazole  
glycerol  
phosphate

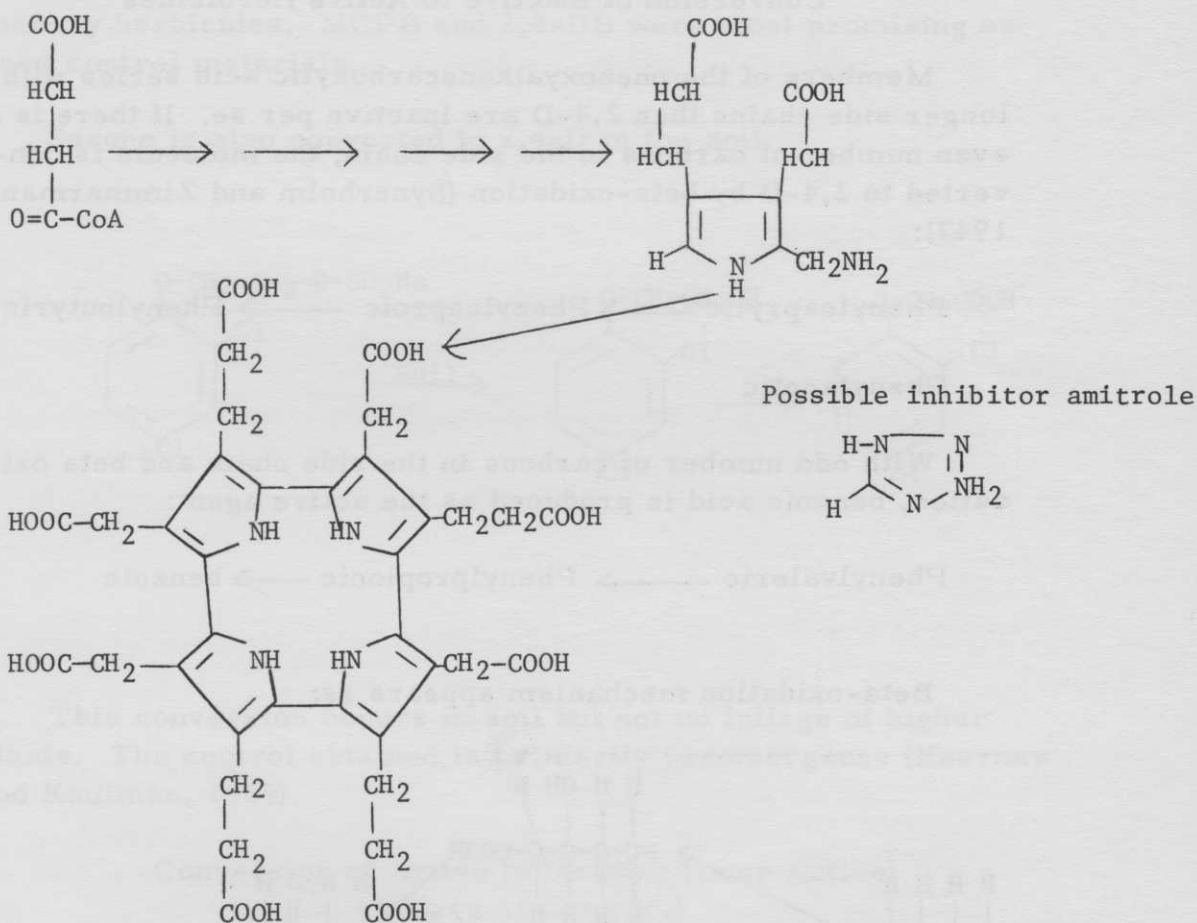


Amitrole

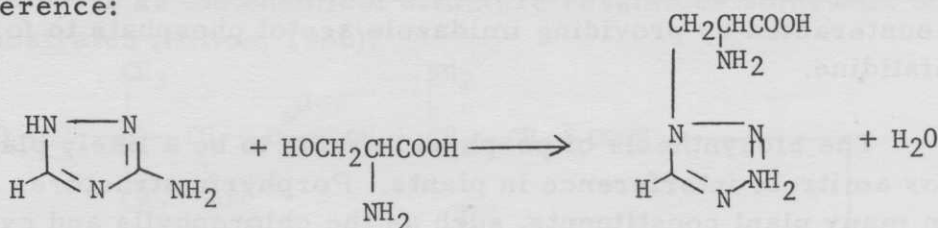
Imidazole  
acetyl  
phosphate

Some of the previous substrates accumulate following amitrole treatment. However, the competitive inhibition can be counteracted by providing imidazole acetol phosphate to form histidine.

The biosynthesis of porphyrin seems to be a likely place for amitrole interference in plants. Porphyrin structures appear in many plant constituents, such as the chlorophylls and cytochromes. Many enzymes contain this component. One response of plants to amitrole is the loss of chlorophyll and prevention of new molecules. The synthesis of porphyrin has several steps from succinyl-CoA to uroporphyrin, and the amitrole structure is quite similar to a couple precursors as:



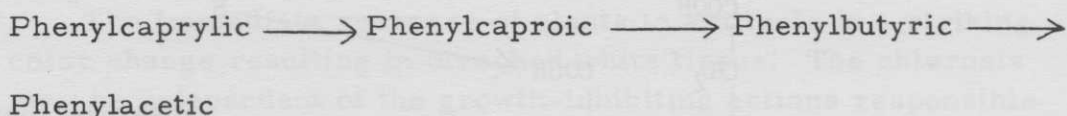
A conjugate of amitrole and serine may also play a role in interference:



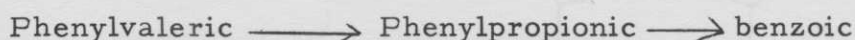
Chlorophyll content declines after herbicidal applications of amitrole, and this led to speculation of this type interference. The abundance of this conjugate in chlorotic tissue may be associated with the inhibition of chlorophyll synthesis and plastid production.

### Conversion of Inactive to Active Herbicides

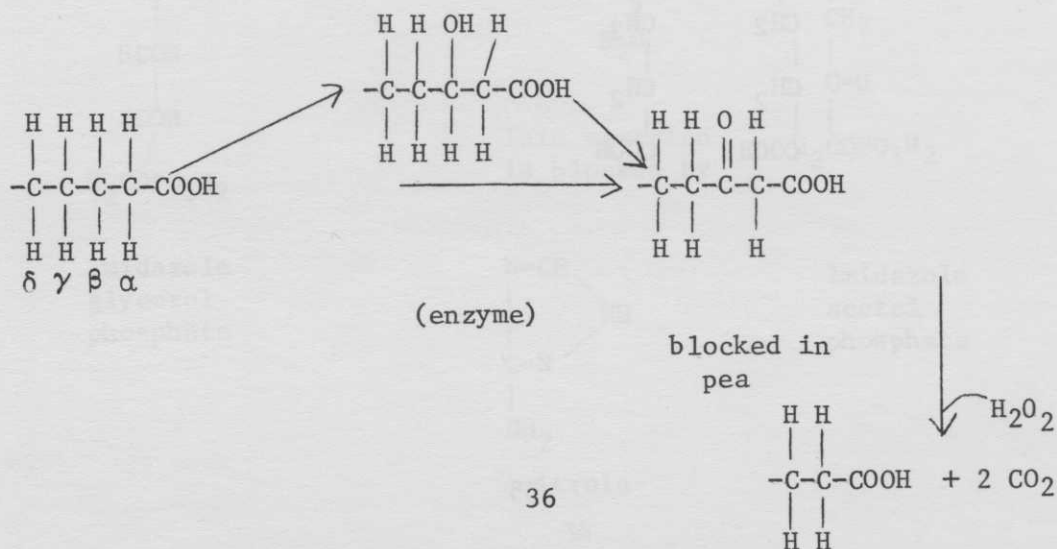
Members of the phenoxyalkanecarboxylic acid series with longer side chains than 2,4-D are inactive per se. If there is an even number of carbons in the side chain, the molecule is converted to 2,4-D by beta-oxidation (Synerholm and Zimmerman, 1947):



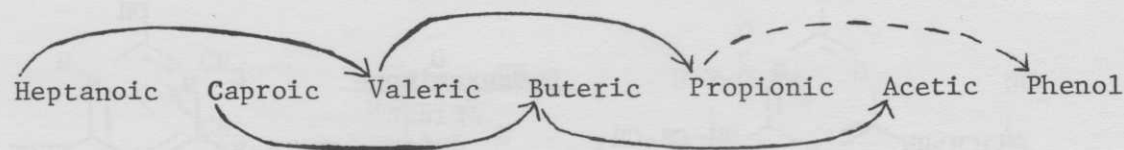
With odd number of carbons in the side chain and beta oxidation, benzoic acid is produced as the active agent:



Beta-oxidation mechanism appears as:

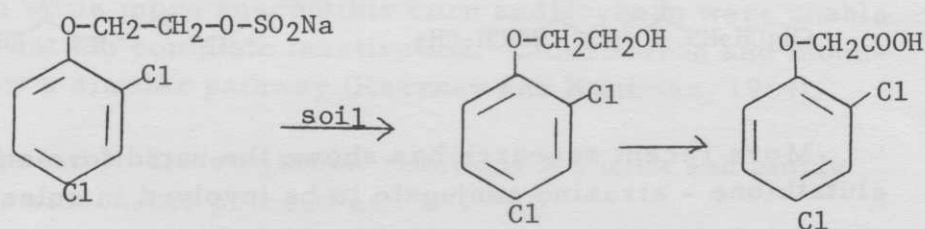


The following diagram shows the normal beta-oxidation of various n-phenoxyalkancarboxylic acids:



Some plants cannot carry out beta-oxidation or do so at a very slow rate and live while other plants convert the molecule to the active form rapidly and die. The practical uses appear with certain weeds in leguminous crops using butyric forms of phenoxy herbicides. MCPB and 2,4-DB were most promising as weed control materials.

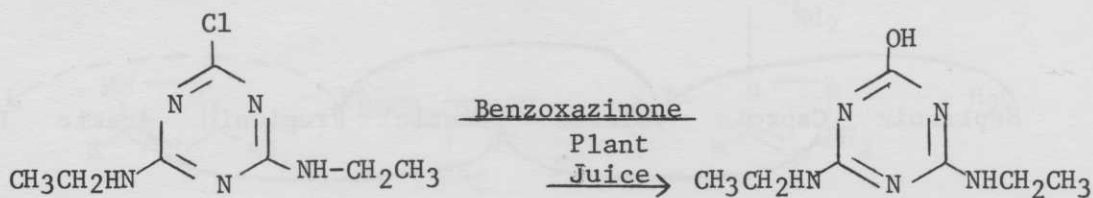
Sesone is also converted to 2,4-D in the soil:



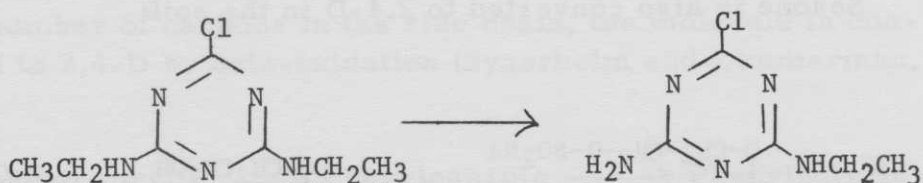
This conversion occurs in soil but not on foliage of higher plants. The control obtained is primarily preemergence (Kearney and Kaufman, 1969).

#### Conversion of Active to Inactive (Less Active) Forms of Chemical

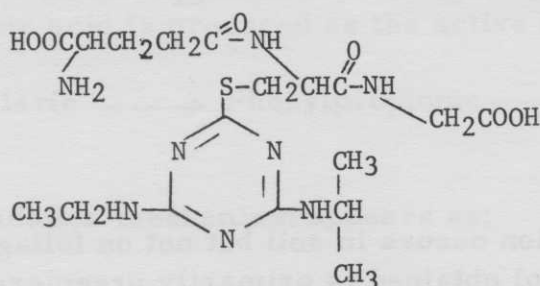
Early research on triazine inactivation suggest that 2-chloro derivatives were converted non-enzymatically in the presence of Benzoxazinone to 2-hydroxy forms.



Later, it appeared that the side chain was lost as a partial means for reducing the toxicity (Shimabukuro et al., 1970). This formed less toxic chemicals, but they were still somewhat active for reducing the photosynthetic rate.

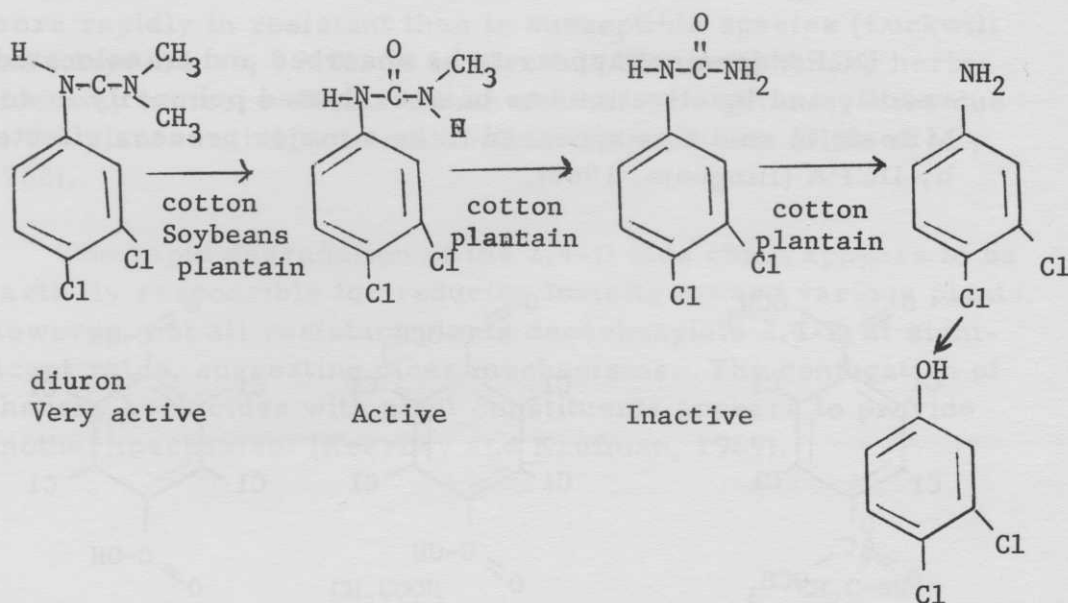


More recent research has shown the rapid formation of a glutathione - atrazine conjugate to be involved in selectivity:



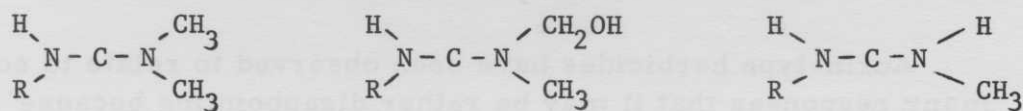
This conjugate was further metabolized to  $\gamma$  - L - glutamyl - s - (4-ethylamino - 6 - isopropylamino - 2 - s - triazine) - L - cysteine which is a dipeptide conjugate. Susceptible plants were low in glutathione s-transferase which appeared to be required for conjugation of atrazine and glutathione (Shimabukuro and Swanson, 1969).

Urea herbicide metabolism may also play an important role in selectivity (Swanson and Swanson, 1968). A demethylation pathway has been demonstrated:



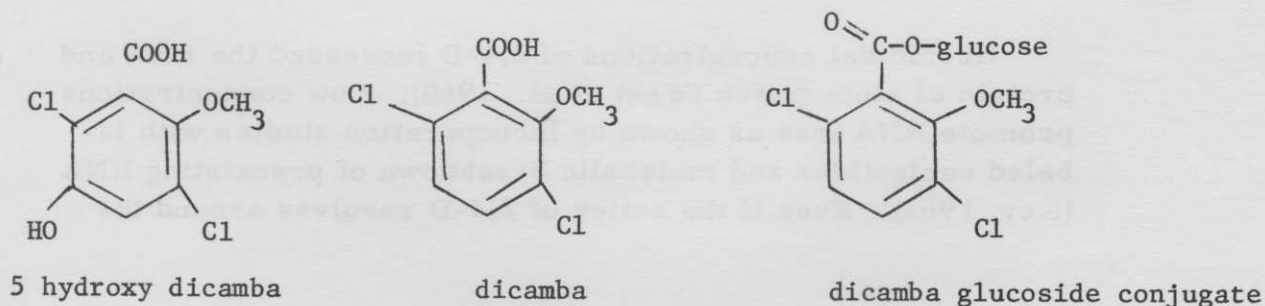
Plantain and cotton were quite effective for demethylation of diuron while more susceptible corn and soybean were unable to carry out the complete inactivation. Chloroxuron and monuron follow a similar pathway (Kearney and Kaufman, 1969).

Proposed N-demethylation reactions for urea and amide herbicide sidechains proceed as:



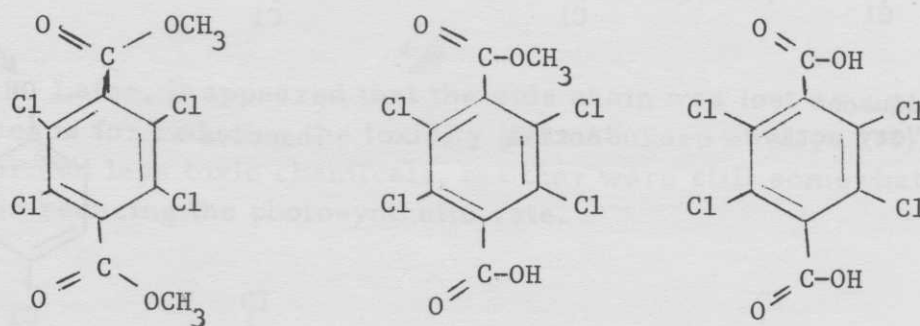
(urea herbicide side chain)

Certain grasses were found to hydroxylate dicamba and form a glucoside (Cooke, 1956):



This may be a major factor in selectivity for weed control in bluegrass. Bluegrass receives some initial effects which seem to diminish after periods of time. It metabolizes a high percentage of the dicamba in two days.

DCPA does not appear to be absorbed and translocated readily and inactivation has been evaluated primarily in soil. Mitosis in root tips appeared to be a major process affected by DCPA (Bingham, 1968).



(DCPA)

### Phenoxy Herbicides

Auxin-type herbicides have been observed to relate to so many responses that it may be rather disappointing because very little specific information can be said about the mode of selective action. Many metabolites and enzyme activities appear to change in response to treatment with 2,4-D. The evidence is gaining toward a postulation that 2,4-D is acting upon the RNA-DNA- protein system.

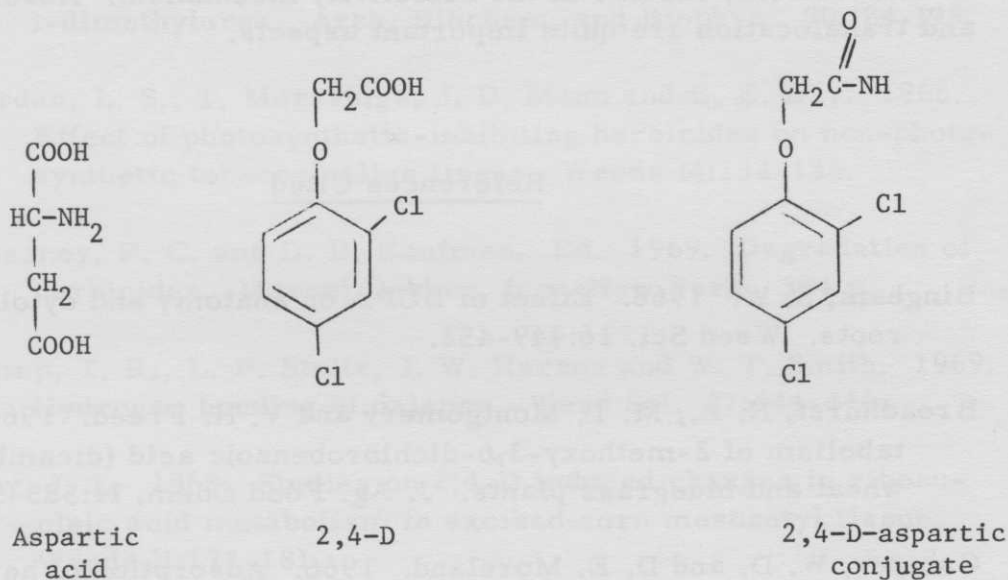
Herbicidal concentrations of 2,4-D increased the RNA and protein of stem tissue (West et al., 1960). Low concentrations promote RNA loss as shown by incorporation studies with labeled nucleotides and metabolic breakdown of preexisting RNA (Key, 1963). Even if the action of 2,4-D revolves around the



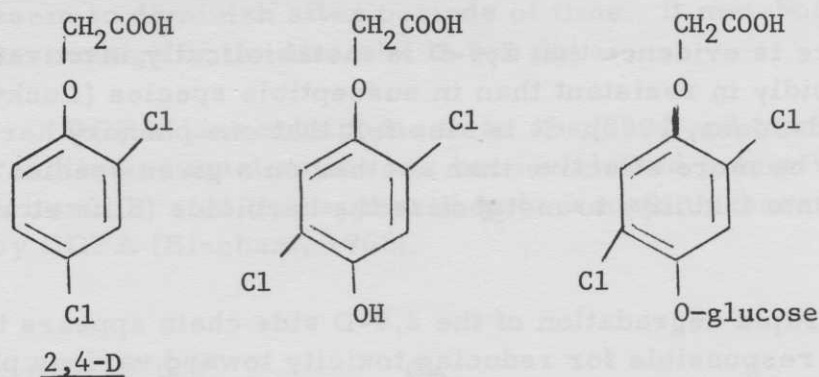
DNA-RNA-protein system, we still remain essentially without understanding of the mechanism of biochemical selectivity.

There is evidence that 2,4-D is metabolically inactivated more rapidly in resistant than in susceptible species (Luckwill and Lloyd-Jones, 1960). It is also felt that one phenoxy herbicide may be more effective than another on a given species due to the plants inability to metabolize the herbicide (Slife et al., 1962).

The rapid degradation of the 2,4-D side chain appears to be partially responsible for reducing toxicity toward various plants. However, not all resistant plants decarboxylate 2,4-D at significant rates, suggesting other mechanisms. The conjugation of phenoxy herbicides with plant constituents appears to provide another mechanism (Kearney and Kaufman, 1969).



Hydroxylation of the ring of 2,4-D prior to forming a conjugate has also been demonstrated:



Many conjugates similar to the above have been demonstrated under several plant situations and appear as a selective mechanism.

The metabolic aspects of plants upon the herbicide molecule are not the only factors in the selectivity mechanism. Absorption and translocation are quite important aspects.

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## Discussion Period

Dr. Ward: Have you used a material like DMSO to reduce the amount of herbicide needed? What's your thinking on using some material of this nature to get better penetration, or more rapid penetration of herbicides into plant tissue.

Dr. Bingham: My feeling on DMSO is that we're going to a product that is probably more hazardous than a parent herbicide, and it may be more of a problem than using higher rates of herbicides. But going to surfactants, or something that would increase the rate of penetration and translocation, is an area of research that needs further emphasis.

Dr. Switzer: Historically, herbicides for turf have been developed primarily by chemical companies. They devise a new structure and then test it on a great number of different species. Eventually, one is found that will work using this empirical approach. Do you think we are getting anywhere close to being able to design a herbicide for turf weed control? You mentioned a couple that are useful in the southern grasses. I would like to know how to design one to take bentgrass out of bluegrass. Do you think we are approximating this at all?

Dr. Bingham: I think chemical companies are certainly looking at structures, and they have been over the past 10 years or so. They are taking a close look at some of the herbicides we're using already, trying to design one that would be more effective than those we already have. It's entirely in the realm of possibility.

Dr. Hemphill: I assume you were referring to foliar applications in your studies--typical applications--with a normal entry by adsorption.

Dr. Bingham: For the Hill reaction studies, no. They're primarily through the root system.

Dr. Hemphill: In some electron microscopic studies we found different reactions from a given chemical by injecting, as contrasted to a foliar application. Where is this degradation or inactivation occurring?

Dr. Bingham: I think it occurs in many parts of the plant; on the way to the site as well as at the site of action. I really can't answer your question because we haven't done any work to pinpoint these sites. There has been some work at North Carolina State University, where they show adsorption of these materials to protein and various other compounds. This could take place anywhere we would have the protein. It's much more effective on plant protein than it was on animal protein.

Dr. Timmons: I was interested in the fact that so many of the metabolism detoxification mechanisms seem to involve oxidation. For example, you showed demethylation of uracils, ureas and hydroxylation of phenoxy compounds. These all seem to be oxidation mechanisms and may be contributing to selectivity of these compounds. One of the materials that, of course, is used with the insecticides is piperonyl butoxide, which prevents oxidation. I wonder if we might not get quite a different spectrum of activity and selectivity of herbicides if they were used with some of these synergists to prevent oxidation from occurring?

Dr. Bingham: It sounds like a very good point to me. I don't know if there has been any research on this. One of the prime effects with the arsenicals that is always noted, and it's in the text books, is on the phosphoglyceraldehyde dehydrogenase enzyme. This enzyme contains the SH group, or sulfhydryl group. Here you have arsenic acid reacting with this sulfhydryl group to give you a complex. In other words, you get a substrate or an enzyme inhibitor complex showing the enzyme connected through a sulfhydryl group to the arsenic group. This tends to remove the enzyme from the reaction. Possibly, this is a little bit different from what you have heard as one of the mechanisms. The reactive site on the enzyme is the sulfhydryl group which reacts with the substrate (3-phosphoglyceraldehyde) to form the enzyme-substrate complex. In the process of conversion to the phosphoglyceric acid, it produces reduced triphosphopyridine nucleotide, the plants source of energy. If arsenic complexes with the sub-

strate, it is converted to phosphoglyceric acid and bypasses the ATP production that normally occurs from oxidation of pyridine nucleotides.

How is resistance or susceptibility related? This hasn't been explained very well with these herbicides, except absorption or penetration and translocation in the amount that this reaction is depended on in the plant. Conversion of the arsenical herbicide to arsenic acid may also be at different rates in various plants. It is very mobile once it is converted. We do know that arsenic will react with many other enzymes that have this active SH site and cause reduced rates of enzyme action. It seems to be one of the major sites of action of arsenic acid.

#### Introduction

There are 25 to 100 herbicides commonly used in the U. S. today. The actual number is dependent on how you define "commonly used." Each of these herbicides has a different site of action and effect on the physiological processes of the plant. It seems likely that several herbicides have more than one site of action. Furthermore, the exact response elicited may be influenced by several different factors. For example, 2,4-D may stimulate, inhibit or have no effect on the rate of regeneration, depending on the kind of plant treated, the dosage used, the length of time after treatment when the response was made, the physiological age of the plant and the plant organ in which the measurement is made.

The herbicides to be considered are listed in Table 1. I am sorry I will not have any information of general interest about them. These herbicides are classified according to their mode of action. It should be noted that the primary mode of action has not been fully established for some of these herbicides. Furthermore, there are always problems associated with trying to lump different things into groups, whether the things being classified are plant species, rocks, or organic chemicals. There is always going to be some individuals that don't fit any category while others have characteristics that fit into more than one category.

Dr. Davis' paper was prepared by Dr. Ray Blaine of Auburn University.





## EFFECTS OF HERBICIDES ON PLANT PHYSIOLOGICAL PROCESSES

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### Introduction

There are 50 to 100 herbicides commonly used in the U. S. today. The actual number is dependent on how one defines "common use." Each of these herbicides has at least a slightly different effect on the physiological processes of the plant. It seems likely that several herbicides have more than one site of action. Furthermore, the exact response elicited may be influenced by several different factors. For example, 2,4-D may stimulate, inhibit or have no effect on the rate of respiration, depending on the kind of plant treated, the dosage used, the length of time after treatment when the measurement is made, the physiological age of the plant and the plant organ on which the measurement is made.

The herbicides to be considered are listed in Table 1 along with information of general interest about them. These herbicides are classified according to their apparent primary mode of action in Table 2. It should be noted that the primary mode of action has not been fully established for some of these herbicides. Furthermore, there are always problems associated with trying to lump different things into groups, whether the things being classified are plant species, rocks or organic chemicals. There always seem to be some individuals that don't fit any category while others have characteristics that fit into more than one category.

\*Dr. Davis' paper was presented by Dr. Ray Dickens of Auburn University.

Table 1. Alphabetical list of some turfgrass herbicides with the chemical name in brackets. The information provided opposite each letter is: A-some trade names and manufacturers, B-family of herbicide, C-type of mode of action, D-some of the recommended uses, and E-acute oral toxicity to rats.<sup>a/</sup>

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1. Atrazine [2-chloro-4(ethylamino)-6-(isopropylamino)-s-triazine].

- A. AAtrex, Gesaprim - Geigy Agricultural Chemicals.
  - B. S-triazine.
  - C. Photosynthetic inhibitor.
  - D. Pre-emergence control of crabgrass, goosegrass and most broadleaf weeds in established turf.
  - E. LD 50 - 3080 mg/kg for rats.
- 

2. Benefin [N-butyl-N-ethyl-a,a,a,trifluoro-2-6-dinitro-p-toluidine].

- A. Balan - Elanco Products Co.
  - B. Toluidine.
  - C. Mitotic inhibitor? Affects seed germination and root growth.
  - D. Pre-emergence control of annual grasses in established turf.
  - E. LD 50 - >10,000 mg/kg for rats.
- 

3. Bensulide [0,0-diisopropyl phosphorodithioate-S-ester with N-(2-mercaptoethyl) benzenesulfonamide].

- A. Betasan - Stauffer Chemical Co. and Pre-san-Mallinckrodt Co.
  - B. Amides.
  - C. Cell division inhibitor? Affects seed germination and root growth.
  - D. Pre-emergence control of annual bluegrass and summer annual grasses in established turf.
  - E. LD 50 - 770 mg/kg for rats.
-

4. Cacodylic acid [hydroxydimethylarsine oxide].
- A. Phytar 138 - Ansul Co.
  - B. Organic arsenic.
  - C. Respiration inhibitor?
  - D. Kills all grass plants for sod renovation and spot treatment.
  - E. LD 50 - 830 mg/kg for rats.
- 

5. CMA [Calcium methanearsonate].
- A. Various - Vineland.
  - B. Organic arsenic.
  - C. Respiration inhibitor?
  - D. Control sandbur and other annual grasses in established bermudagrass and certain other turf.
  - E. LD 50 - 1000-2000 mg/kg for rats. (This value is an estimate. No published value was found.)
- 

6. Dalapon [2,2-dichloropropionic acid].
- A. Dowpon (sodium salt) - Dow Chemical Co. and Radapon-Chemagro Co.
  - B. Halogenated aliphatic acid.
  - C. Growth regulator (2,4-D)-type effects and others.
  - D. Kills all grassy plants for sod renovation and spot treatment.
  - E. LD 50 - 7500 to 9500 mg/kg for rats.
- 

7. DCPA [dimethyl tetrachloroterephthalate].
- A. Dacthal - Diamond Shamrock Co.
  - B. Phthalic acids.
  - C. Cell division inhibitor? Affects seed germination and root growth.
  - D. Pre-emergence weed control of crabgrass and other annual grasses in established turf.
  - E. LD 50 - >3000 mg/kg for rats.
-

8. Dicamba [3,6-dichloro-O-anisic acid ].
- A. Banvel D (dimethylamine salt) - Velsicol Chemical Corp.
  - B. Benzoic acid.
  - C. Growth regulator (2,4-D)-type effects.
  - D. Postemergence weed control of henbit, chickweed and other annual broadleaf weeds in established turf.
  - E. LD 50 - >1000 mg/kg for rats.
- 
9. DSMA [disodium methanearsonate ].
- A. Ansar 184 - Ansul Co. and other manufacturers and trade names.
  - B. Organic arsenic.
  - C. Respiration inhibitor?
  - D. Postemergence weed control of crabgrass, dallisgrass, bahiagrass, nutgrass and johnsongrass in bermudagrass and zoysiagrass. Do not use in centipede, or St. Augustine, and except at low rates in Tifgreen bermudagrass.
  - E. LD 50 - 2800 mg/kg for rats.
- 
10. MAMA [Monammonium methane arsonate ].
- A. Ansar 157 - Ansul Co. and various other manufacturers and trade names.
  - B. Organic arsenic.
  - C. Respiration inhibitor?
  - D. Postemergence weed control of crabgrass, dallisgrass, nutgrass and johnsongrass in established bermudagrass and zoysiagrass. Do not use in centipede or St. Augustine.
  - E. LD 50 - 750 mg/kg for rats.
- 
11. MSMA [Monosodium methanearsonate ].
- A. Ansar 170 - Ansul Co. and various other companies and trade names.
  - B. Organic arsenic.
  - C. Respiration inhibitor?

- D. Postemergence control of dallisgrass, crabgrass johnsongrass, sandbur, bahiagrass and nutgrass in established turf. Do not use in centipede or St. Augustine.
  - E. LD 50 - 1800 mg/kg for rats.
- 

- 12. Paraquat [1,1'-dimethyl-4,4'-bipyridinium ion].
    - A. Ortho Paraquat - Chevron Chemical Co.
    - B. Bipyridinium quarternary salts.
    - C. Free radical formation in the light generating other toxic free radicals that inhibit sulfhydryl enzymes.
    - D. Postemergence control of winter annuals in dormant turf.
    - E. LD 50 - 150 mg/kg for rats.
- 

- 13. Siduron [1,(2-methylcyclohexyl)-3-phenylurea].
    - A. Tupersan - E. I. duPont de Nemours and Co.
    - B. Phenylurea.
    - C. Cell division inhibitor? Affects root growth.
    - D. Pre-emergence control of annual grasses in established turf of bluegrass, bentgrass, zoysia and fescue.
    - E. LD 50 - > 5000 mg/kg for rats.
- 

- 14. Silvex [2-(2,4,5-trichlorophenoxy) propionic acid].
    - A. Kuron (propylene glycol butyl ether esters) - Dow Chemical Co.
    - B. Chlorophenoxy.
    - C. Growth regulator (2,4-D)-type effects.
    - D. Control broadleaf weeds including burkhorn plantain, common chickweed, dandelion, etc. in established turf. Do not use in St. Augustine or centipede.
    - E. LD 50 - 650 mg/kg for rats.
- 

- 15. Simazine [2-chloro-4,6-bis(ethylamino)-s-triazine].
  - A. Princep - Geigy Agricultural Chemicals.
  - B. S-triazine.
  - C. Photosynthetic inhibitor.

- D. Pre-emergence control of crabgrass, goosegrass and most broadleaf weeds in a few turfgrasses.
  - E. LD 50 - 2000 mg/kg for rats.
- 

16. Terbutol [2,6-di-tert-butyl-p-tolyl methylcarbamate].
- A. Azak - Hercules Inc.
  - B. Carbamate.
  - C. Cell division inhibitor. Affects seed germination and root growth.
  - D. Pre-emergence weed control of annual grasses in established turf.
  - E. LD 50 - 300-1000 mg/kg for rats.
- 

17. 2,4-D [(2,4-dichlorophenoxy) acetic acid].
- A. Numerous trade names, formulations, and formulators.
  - B. Chlorophenoxy.
  - C. Growth regulator (2,4-D)-type effects.
  - D. Control broadleaved weeds in established turf. Do not use in centipede or St. Augustine.
  - E. LD 50 - 300-1000 mg/kg for rats.
- 

18. 2,4,5-T [(2,4,5-trichlorophenoxy) acetic acid].
- A. Numerous trade names, formulations, and formulators.
  - B. Chlorophenoxy.
  - C. Growth regulator (2,4-D)-type effects.
  - D. Control certain 2,4-D-resistant broadleaved weeds in established turf. Do not use in centipede or St. Augustine.
  - E. LD 50 - 300 mg/kg for rats.
- 

a/ Data supplied in this table is to supply general information and is not intended as a basis for recommendations for use.

Table 2. A classification of some common turfgrass herbicides according to their probable primary mode of action. <sup>a/</sup>

Type of Action	Herbicide
A. Inhibit photosynthesis	atrazine, simazine
B. Inhibit respiration	CMA, DSMA, MAMA, MSMA
C. Inhibit cell division	benefin, bensulide, DCPA siduron, terbutol
D. Disturb hormonal growth regulation	dalapon, silvex, 2,4-D, 2,4,5-T, dicamba
E. Produce free radicals that inactivate sulfhydryl enzymes	paraquat

<sup>a/</sup> The mode of action has not been fully established for some of these chemicals. These have been placed into categories with other herbicides having similar effects and for which the mode of action is known.

## Photosynthesis Inhibition

Described in the very simplest terms, photosynthesis is the process by which green plants make food and evolve oxygen while using carbon dioxide, water and light energy. It would be expected that a plant treated with a photosynthesis inhibitor would die of starvation, and that the length of time required to kill the plant would depend on the size of its food reserves and how fast it was using them. Plants killed by photosynthesis inhibitors do not fully match these expectations. Therefore, it is necessary to consider photosynthesis and the action of photosynthesis inhibitors in somewhat greater detail.

The complex series of biochemical processes grouped together and called photosynthesis can be subdivided into two categories, depending on whether or not the processes require light. These that require light are further subdivided into two categories which will be discussed later. Arnon (1960) has summarized his research and that of others on the light reaction of photosynthesis in an easily understandable article published in the *Scientific American*. Some changes have been made in his story of photosynthesis since that time but they will not significantly affect our consideration of the process (Fogg, 1968; Levine, 1969).

The dark reaction of photosynthesis uses ATP (adenosine triphosphate), NADPH (reduced nicotinamide adenine dinucleotide phosphate) and  $\text{CO}_2$  resulting in the formation of carbohydrates. The carbon of  $\text{CO}_2$  is thus said to be fixed. These dark reactions are not limited to green plants, but the great bulk of all carbon fixation occurs in the chloroplast and uses ATP and NADPH produced by the chloroplast in the light. When plants are treated with photosynthesis inhibitors, the amount of carbon fixed can be reduced to the amount that can be fixed in the dark, but the process is never completely stopped. It is apparent that these herbicides directly affect only the carbohydrate synthesis dependent on ATP and NADPH produced by the chloroplast in the light.

When light strikes a green plant it may be absorbed by the green pigment, chlorophyll, located in bodies called chloroplasts. Chlorophyll in the chloroplast is bound to protein membranes and



arranged in thin, nearly round, sheets which in turf occur in stacks; these packets are called grana. Apparently, in the order of 2,500 chlorophyll molecules function together as a unit in capturing the light energy used in photosynthesis. When a photon of light is absorbed, its energy is transmitted to an electron; the electron is ejected and the chlorophyll becomes oxidized.

Upon ejection, this highly energetic electron can enter either of two biological pathways, cyclic or non-cyclic photophosphorylation. In cyclic photophosphorylation, the electron is captured by an electron acceptor and passed along a chemical pathway that includes the cytochromes. Eventually it returns to chlorophyll. This explains why the process is called cyclic and the chlorophyll does not become more and more highly oxidized as light is absorbed and electrons ejected. As the electron travels this chemical pathway it gives up increments of energy that can be used in the conversion of ADP (adenosine diphosphate) to ATP. Ten years ago it was generally assumed that such a conversion only occurred in the mitochondrion.

In non-cyclic photophosphorylation, the ejected electron is captured and passed along a chemical pathway to a compound that leads to the splitting of water which furnishes the proton for the formation of NADPH from NADP. Hydroxyl ions (OH) resulting from this process combine to form water and oxygen and the extra electron again passes along a chemical pathway, including cytochromes, back to chlorophyll. During the passage along the electron transfer chain, energy is given up and ADP is converted to ATP. In noncyclic photophosphorylation, oxygen is released and ATP and NADPH, which may be used in carbon fixation, are formed.

Photosynthesis inhibitors block non-cyclic photophosphorylation at some point prior to the splitting of water (Cook, 1956; Van Overbeck, 1962; Wessels and van der Veen, 1956). Good (1961, 1962) has reviewed the work of others and included much additional work of his own in two papers on the photosynthesis inhibitors. He lists many different herbicides that are inhibitors and calculates the concentrations of each necessary to bring about a 50% inhibition. The part of photosynthesis invol-

ving the splitting of water is called the Hill reaction, and special techniques make possible direct in vitro measurements of this process with chloroplasts isolated from plant tissues. Good (1961) concludes that inhibition of the Hill reaction is apparently the primary mode of action of the anilides (which include the phenylureas), the alkylamides and the s-triazines. Atrazine and simazine in our list of turf herbicides are s-triazines. Ashton (1965) has given some more recent information on photosynthesis inhibitors.

Many field and laboratory observations confirm the anticipated results of such inhibition. The photosynthesis inhibitors are more effective in high than in low light intensity and are ineffective in the dark. They show maximum effect as light wavelengths matching the absorption spectrum of chlorophyll, and they are often not effective against non-green tissue. They greatly decrease carbon fixation and stop oxygen evolution. The chlorophyll in treated plants becomes oxidized. Supplying an oxidizable substrate from an external source gives some protection. Only one observation does not seem to fit. Sensitive plants treated with these compounds die much quicker than if they were not treated and placed in the dark to stop all photosynthesis. This observation led Sweetzer and Todd (1961) to postulate the formation of a phytotoxic material as a result of this block.

The photosynthesis inhibitors are most often used as pre-emergence herbicides. They are applied to the soil and kill the seedling only after the chemical has been absorbed by the roots and the plant has emerged from the soil. Failure to get good kill of sensitive species usually means that the chemical did not enter the roots; normally due to (1) lack of uniform application, (2) lack of rain to leach the chemical into the soil or (3) germination of the seed at a depth below the treated soil layer.

#### Respiration Inhibition

This presentation will be limited to those processes that occurs in the mitochondria (tiny organelles inside each cell) in which ADP is converted to ATP,  $O_2$  is consumed,  $CO_2$  and water are produced, and an energy source is oxidized. Effects of herbicides on respiration are usually measured in one of two ways.

First,  $O_2$  consumption may be followed as pressure changes in a closed system in which the  $CO_2$  produced is removed by a suitable absorbant. The pressure changes can be converted to the amounts of  $O_2$  used by utilizing suitable constants. In the other system, disappearance of  $O_2$  from solution is followed polarographically by means of an oxygen-sensitive electrode. The readings obtained may also be converted to amounts of  $O_2$  used. Measurements are made either on seeds, very small plants, portions of plants or mitochondria isolated from plants. Lotlikar, Remmert and Freed (1968) have reported the effects of 22 herbicides on the respiration of mitochondria isolated from cabbage.

When respiration inhibitors are applied to a plant there may or may not be an immediate decrease in  $O_2$  consumption. Often, there is an initial increase in  $O_2$  uptake. The plant is not directly dependent on  $O_2$  consumption per se, but rather on the conversion of ADP to ATP. It is often said that ATP is the universal currency that is called upon by all cells, both plant and animal, to drive energy consuming processes. Two of the more potent respiration inhibitors, pentachlorophenol and dinoseb (DNBP), are effective because they uncouple oxidative phosphorylation. In simple terms this means  $O_2$  is consumed and substrate oxidized but the energy released is not used in converting ADP to ATP. Because of the importance of this possibility, a thorough investigator will determine both the oxygen consumed and the amount of inorganic phosphorous used in converting ADP to ATP. The results are usually expressed as a ratio between these (P:O ratio), and a decrease in the P:O ration is considered to be evident of uncoupling. The ideal ratio when malate or citrate is oxidized is 3.0.

Respiration inhibitors cause very rapid killing. Without ATP, all life processes stop. The need for ATP is common to both plants and animals. Consequently, herbicides that are respiration inhibitors are often quite toxic to man. Respiration inhibitors are usually applied as foliage sprays, causing contact kill. The foliage-applied respiration inhibiting herbicides will usually not translocate to the roots since they also inactivate the phloem transport system.

Arsenate and arsenite are known to interfere with mitochondrial metabolism. The primary mode of action of the organic arsenic compounds is probably through inhibition of respiration, although I am not aware of any sufficiently definite study to confirm this proposal. It should be mentioned that some of the organic arsenics have a relatively low toxicity to mammals.

### Inhibition of Cell Division

All higher plants start their life history as a fertilized egg and subsequent cell division, cell enlargement and cell differentiation result in an embryo in the seed. Often, there is at least a short period when cell division stops while the seed is dormant. When the seed germinates, cell division starts again but it is primarily limited to certain areas called meristems. In dicots (broadleaved plants), these occur at opposite ends of the embryonic axis; one being the root tips or radicle and the other the stem tip or plumule. An understanding of the location of these meristems is necessary to the understanding of how inhibitors of cell division function.

There are two types of germination in dicots. First, we will consider the kind of germination that occurs in cotton or kidney beans (Fig. 1 and 2). The young root emerges from the seed in these plants. Existing cells elongate as new ones are being formed in the root tip. After the root has emerged and anchored the seed, the hypocotyl begins to elongate. It grows out in the form of a crook and, as it elongates, it drags the seed coat and cotyledons out of the ground. When light strikes the hypocotyl, the hook begins to straighten, the cotyledons expand and the old seed coat splits and falls off. The growth of the hypocotyl is mostly due to cell enlargement of pre-existing cells. It is only after the cotyledons start to expand that the plumule begins rapid cell division and growth. While the seed was in the ground the plumule was nestled between the two cotyledons, partially covered by a relatively impermeable seed coat.

In some dicots, such as English peas, the hypocotyl does not elongate (Fig. 3). The old seed and cotyledons remain in the ground. Growth of the plumule and epicotyl result in the

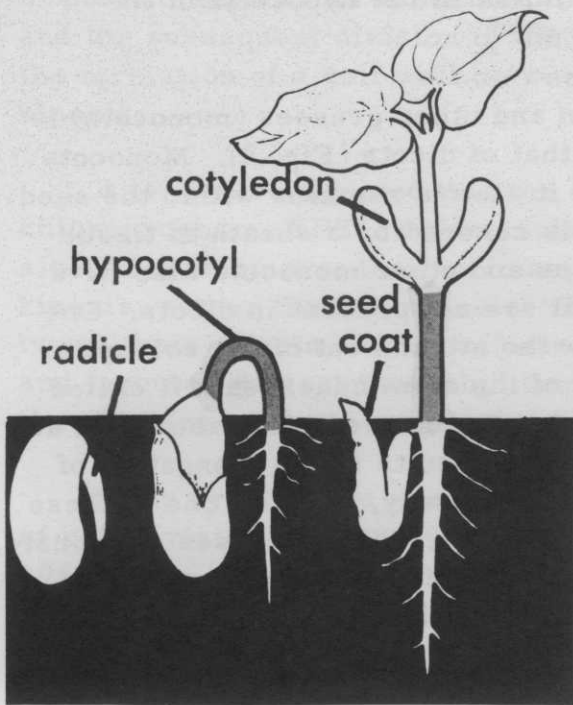


Figure 1

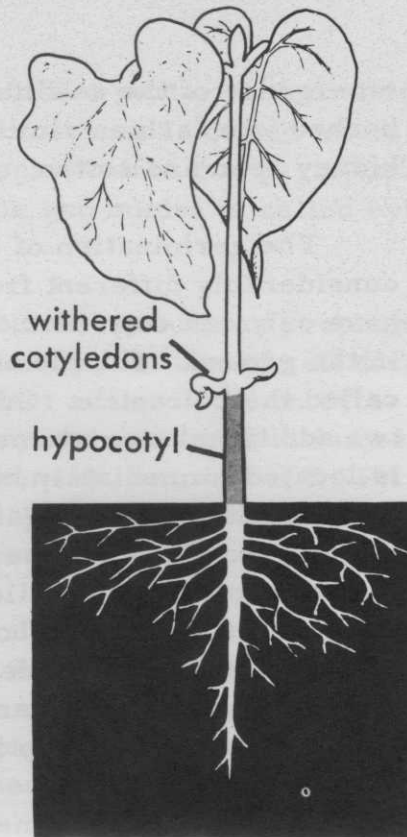


Figure 2

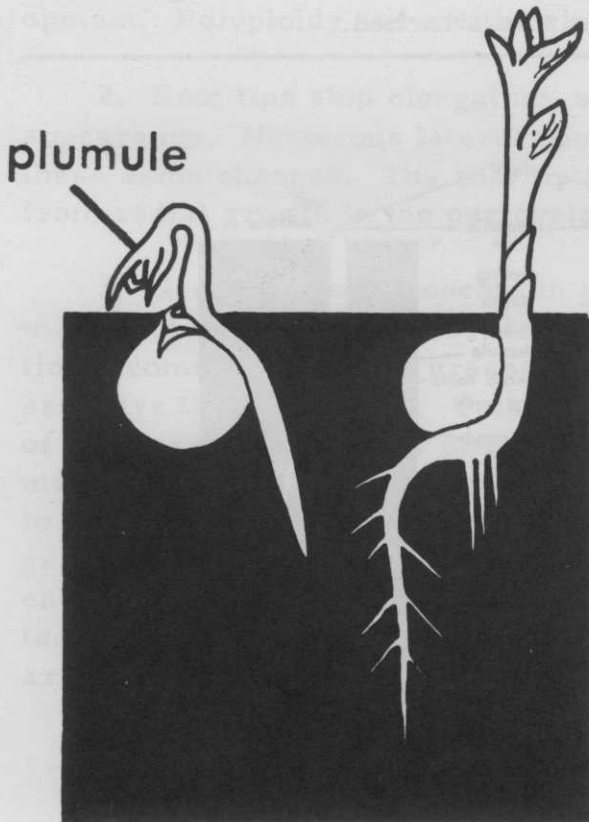


Figure 3

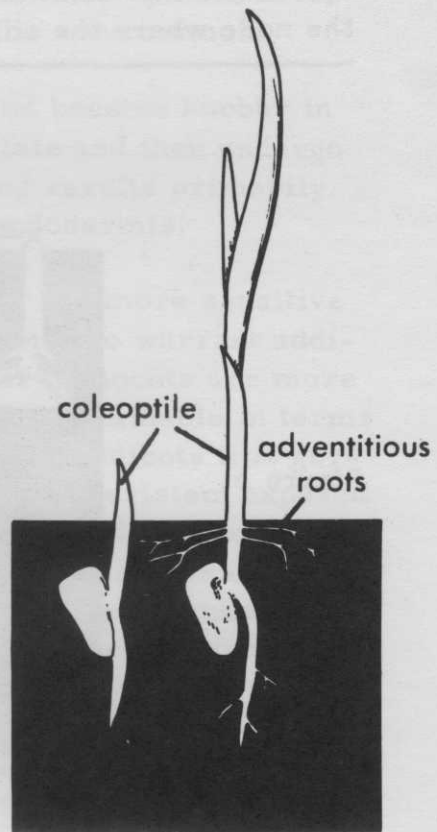


Figure 4

emergence of the seedling. Sometimes this epicotyl is also hooked in a fashion similar to that of the hypocotyl of the kidney bean and cotton.

The germination of corn and other grasses (monocots) is considerably different from that of dicots (Fig. 4). Monocots have only one cotyledon, and it always remains within the seed in the ground. The plumule is covered by a sheath of tissue called the coleoptile. Grasses and other monocots also have two additional meristems that are not present in dicots. One is located immediately below the attachment of the coleoptile and results in the elongation of the stem underneath it called the mesocotyl. The other is located immediately above the attachment of the coleoptile, and it results in the elongation of the node immediately above it. Actually, there is one of these meristems for each node of the stem. When grasses germinate, the root emerges first and then the mesocotyl begins to elongate, pushing the coleoptile up through the soil.

Elongation of the mesocotyl ceases when light strikes the coleoptile (Fig. 5). The stem above the attachment begins to elongate, the plumule continues expanding, the coleoptile splits and the shoot emerges. Secondary roots emerge from the node where the coleoptile was attached.

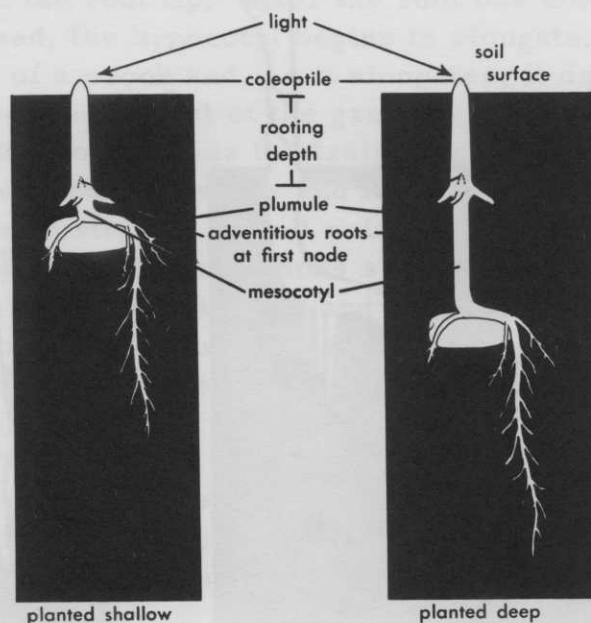


Figure 5.

Cell division is usually divided into two parts. The division of the nucleus and its associated chromosomes is called mitosis, and the subsequent division of the cytoplasm into two parts and the formation of a cell wall between the two nuclei is called cytokinesis.

It is well recognized that the carbamates, such as propham, chloroprotham, EPTC and vernolate, are inhibitors of cell division. Furthermore, their primary effect seems to be on cytokinesis, rather than on mitosis. The numerous similarities between their effects and the effects of benefin, bensulide, DCPA and terbutol suggest that inhibition of cell division may also be the primary mode of action of the latter group.

Many people have worked with herbicides causing inhibition of cell division (Doxey, 1949; Ennis, 1949; Ivens and Blackman, 1950; Mann, Jordan and Day, 1965; Mann and Storey, 1966; Sawamura, 1965). A review of these papers establishes the following as rather common effects of these herbicides:

1. They behave somewhat like the chemical colchicine in that they may cause a doubling of chromosome numbers. Affected cells increase in size and do not continue spindle development. Polyploidy and multinucleate cells are common.

2. Root tips stop elongating, swell and become knobby in appearance. Numerous lateral roots initiate and then undergo these same changes. The root tip swelling results primarily from radial growth in the pericycle and endodermis.

3. Grasses, and monocots in general, are more sensitive than dicots. One of these observations seems to warrant additional comment; that the grasses and other monocots are more sensitive than the dicots. This is probably explainable in terms of numbers and positions of the meristems. In dicots that germinate like cotton and kidney beans, the only meristem exposed to the chemically treated soil is the root tip, and then only if germination occurs in the treated layer. If the root manages to enter untreated soil, the plant will survive. The plumule is protected as it penetrates the treated soil. Cell division inhibitors are usually applied as pre-emergence herbicides to the surface

of the soil, or incorporated in the upper surface. It is not uncommon to see a dicot seedling emerge and then die because there is not a sufficient root system to maintain the growth of the plant.

However, grass not only has the root tip in the treated soil but also the plumule and meristems above and below the attachment of the coleoptile are relatively exposed.

The bulk of the root system, the adventitious roots, originate from this same node (Fig. 4). It is always near the surface and, thus, in the chemical treated soil because the epicotyl elongates until light strikes the coleoptile. Recent work has established the importance of the position of the chemically treated soil with reference to these meristems in affecting the efficiency of these herbicides.

Researchers are currently attempting to explain all herbicidal action in terms of their effects on protein synthesis. It is obvious that dividing cells must be making DNA and RNA and so it is not surprising to find that herbicides inhibiting cell division affect protein synthesis. It might be preferable to list interference with protein synthesis as the mode of action of these herbicides since this effect precedes the effect on cell division. However, there are many herbicides that affect protein synthesis that do not strongly inhibit cell division.

D. J. Wort in a book edited by Audus (1964) has summarized the effects of herbicides on protein synthesis. Mann, Jordan and Day (1965) and, later, Moreland et al. (1969) used radio-labeled amino acids to screen herbicides for their effects on amino acid absorption and incorporation into protein. Several herbicides were shown to influence these processes, but the full significance of these findings in relation to their herbicidal activity is not known.

#### Disturbance of Hormonal Growth Regulation

Those herbicides that effect hormonal growth regulation all have the ability to modify normal growth patterns. Some areas of cell division may stop functioning and new areas are often



initiated. The result is a highly distorted plant. These alterations in cell division clearly suggest alterations in protein synthesis, which has been confirmed. The mode of action of the growth regulating herbicides, such as 2,4-D, 2,4,5-T and MCPA, has been more thoroughly investigated than any other group of herbicides. But their precise mode or modes of action remains unknown.

From a practical standpoint, the following are important facts for all of the herbicides that I have placed in this category, with the exception of dalapon:

1. The herbicides, in general, are more effective against broadleaved weeds than against grasses.
2. They are usually applied as foliar sprays.
3. They are effective at very low rates of application.
4. They may be translocated from the leaves to the roots and cause death of underground organs.
5. Because they are translocated downward, they are effective against some perennials.
6. Because they are effective in very low doses and because many prized ornamentals are quite sensitive, drift of these herbicides can cause serious problems.
7. The degree of growth distortion is not an index of the ease of killing the plant. Many plants, such as cotton, can have quite noticeable distortion without being killed or seriously reducing the yield.

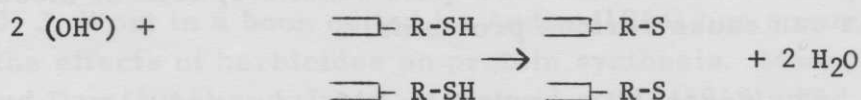
It is perhaps a mistake to include dalapon in the same group with dicamba, silvex, 2,4-D and 2,4,5-T. It is more effective against grasses than against broadleaf plants and requires high application rates to induce kill. Work done with microorganisms by Hilton et al. (1959) indicates that one major site of its action may be inhibition of pantothenate synthesis; however, there is

some doubt about this as the primary mode of action in higher plants. In other respects, dalapon is similar to other growth regulating herbicides.

#### Free Radicals Effects on Sulfhydryl Enzymes

The final group of chemicals are the bipyridinium salts, which include paraquat. Paraquat could have been included in the list of photosynthesis inhibitors but it is apparent, from its very rapid killing power, that this is not its primary mode of action. The current status of our knowledge of the action of the bipyridiniums is well covered in a paper by Zweig et al. (1969).

When applied as a foliar spray, paraquat quickly kills all green parts of the plant it contacts that are exposed to light. Electrons made available during photosynthesis, as described earlier, are used to convert the bipyridinium salt to its free radical form. This free radical, in turn, causes the formation of other free radicals. The herbicide thereby becomes reoxidized and is again ready to capture another electron and repeat the process all over again. Since oxygen is also necessary for the compound to be toxic, it is assumed that  $\text{H}_2\text{O}_2^\circ$  and  $\text{OH}^\circ$  are among the free radicals produced. If this is true, the toxic action of paraquat is quite similar to that of ionizing radiation and one of its primary reactions would be the inactivation of sulfhydryl enzymes as diagrammed below.



The following are important considerations in field applications of paraquat:

1. The compound is very tenaciously adsorbed and is inactivated quickly in soils containing clay.
2. The herbicide kills only the plant parts it contacts. It has essentially no residual activity and is not appreciably translocated.

3. It is much more effective in the light than in the dark and against green than non-green tissues.

4. The slight toxicity in the dark and against non-green tissue is thought to be due to free radical formation caused by reduction mechanisms associated with respiration (Andus, 1964).

5. Of the commonly used herbicides, paraquat is one of the most toxic to man.

#### Summary

I have tried to cover some of the more significant aspects of the primary modes of action of common herbicides. Herbicides were sometimes, for convenience, placed into categories without sufficient information about their primary mode of action. An attempt has been made here to show how a knowledge of the mode of action can be used to explain how herbicides act in the field.

Acknowledgement. We wish to give credit to the text "Botany", by Wilson and Loomis, Holt, Rinehart, and Winston, for Figures 1, 2, 3, 4 and 5.

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## Discussion Period

Dr. Daniel: Do you have any observations on potassium azide? It's been tested a little on some things.

Dr. Dickens: We've done some testing on forage crops, but not on turf. Dr. Harry Amling has done some work with horticulture crops and it appears to do a pretty good job--something similar to calcium cyanide. I've stayed away from it because of the toxicity. I don't think it will ever be approved for homeowner use.

Dr. Hemphill: We have used this in hopes of getting rid of some of the cottonfield-type bermuda, but unfortunately it's just a knockdown and it comes back very shortly.

Dr. Dickens: Was this incorporated in the soil?

Dr. Hemphill: No, this was a surface foliar application.

Dr. Dickens: Ours was incorporated and kept watered in.

Dr. Switzer: I'd question whether or not the rapid burn effect from DNBP, paraquat or any of these others is directly related to its effect on the respiration system.

Dr. Dickens: I'd question that myself.

Dr. Switzer: I'd rather think this is a matter of permeability effect. If you put it on at a low enough rate you are going to have an effect on mitochondrial respiration, but I don't think the quick burn is a result of respiration.

Dr. Dickens: It's too fast, I feel, to be the cause.

Dr. Bingham: I would like to comment about dinoseb on the mitochondria. The effect seems to take place on the membrane where the electron normally travels through the cytochrome system in the membrane. Dinoseb tears up the membrane and allows these electrons to freewheel through the membrane. Only a very small amount of ATP is formed once you get this

freewheeling. Ordinarily, about three ATP's are formed for each oxygen supplied with an electron. Very little ATP is formed if the membrane is torn.

Dr. Ahrens: I think an interesting observation on dinoseb, or DNBP, when it is taken up through roots, is that it obviously does destroy membranes. It can move with transpiration water, pass out of leaves intact, and injure other leaves that it touches. It is the first herbicide that I have ever seen do that.

I'd like to hear some discussion from others on the relative hazard of paraquat. I'm one of those who doesn't feel it is very hazardous when used properly. We've had a lot of people scared away from it, I feel, to other things that might be more toxic, like dinoseb. It's such a useful tool; the best chemical hoe that we have. I'd like to hear some other comments on it.

Dr. Dickens: I think you hit it on the head when you said, "when properly used." That's the thing I worry about.

Dr. Dewey: I might comment on paraquat, since I am probably responsible for a lot of the concern and publicity that it was given. We had observed this material being used on a rather large scale, and in many instances with no precautions being taken whatsoever. This was particularly true with the defoliation of potato vines, where the materials were applied by air and the flagmen in the fields were standing in the drift. We also had people that were rather reckless--using knapsack sprayers in orchard situations. Consequently, in going through the literature, we found that there were many accidental deaths resulting from the inhalation of droplets or accidentally swallowing the material. Since the action was irreversible, with no antidote, and the length of time it took for fatalities to occur varied anywhere from 16 hours to 21 days, it seemed that the least we could do was to call attention to the problem and to take proper precautionary measures. It was this objective that we had in mind when we started giving this matter publicity. It got a little bit out of hand as it was passed from one person to another, as usually happens. But shortly after that, paraquat containers came out with a poison label. All we were really asking was that people adhere to the rules and the warning that were already on the container, but were not being observed. Actually, we were

doing this because we felt this material had a great future. We wanted to make certain that we did not encounter a series of accidents that would cause the loss of its use. It was not our intent to try to run paraquat out of business on a scare philosophy.

Mr. Seely: When I was in Australia a year and a half ago, the people were very much interested in the fact that we were not using paraquat. They were using it on wide scale basis with no problems whatsoever. As a consequence, they were wondering why we were all concerned about it. Actually, I would agree that we need to use caution with materials which are highly toxic, such as dinoseb, which has an LD<sub>50</sub> of only 40. We are using it in very large quantities and it's increasing rapidly, since this is a very rapidly dissipated material. We don't anticipate any problems in registering these materials, as compared to some of the more persistent compounds.

Dr. Timmons: I know that things like dinoseb, trifluorobenzimidazoles from Fison, ioxynil and other phenols are all oxidative phosphorylation inhibitors or uncouplers. Ioxynil is a broadleaf control among grassy species. I am curious if these other materials are also primarily broadleaf controls in grasses and if they are, why are they?

(No response)

Dr. Newman: While paraquat is absorbed onto clays very rapidly and is inactivated, is there any real evidence to show just exactly what happens to that molecule after it is absorbed? Is it degraded, or isn't it? What is the fate of this thing as a result of continuous use? I think this is a question in some people's minds.

Mr. Seely: I can't answer this directly, but I can give you some indirect information on it. We have been making continual applications of the material for a number of years in the same general areas. Although we have no direct studies indicating that the material has become active, plant growth on the treated areas has been on the downgrade now for the last three or four years, as contrasted to those which are not getting the material. This would imply that some of the material is becoming available. We're still getting a very rapid tie up of an immediate ap-



plication in the soil, but apparently some of the material is becoming available. I think it is being slowly released off the colloid.

Dr. Burt: We have used it for edging, around flower beds and things like that on our sandy soils, and have had residual for as much as 12 months--retarding, pegging down of turfgrasses. Our results are similar to those of Mr. Seely.

Mr. Scheer: I am aware of the fact that the efficiency of paraquat can be increased through addition of certain surfactants at certain concentrations. Does anyone here have any experience on this subject?

Dr. Dickens: There has been some work done on various concentrations, but I can't tell you what the effects were--both in the amount of dilutant and the percentage concentration. In fact, they've both been worked on. I don't recall what the situation was on that.

Dr. Hemphill: I've always had the impression that paraquat was degraded or inactivated very quickly in the soil. I used it on a gravel driveway to kill some bluegrass and weeds, and it killed the bluegrass turf for about one foot into the turf area. This was put on with a watering can; it wasn't spray drift. Evidently, it does stay around for quite awhile and will move in the soil.

Dr. Green: I think Dr. J. B. Weber at North Carolina State University has done quite a lot of work on adsorption on soils. Paraquat and diquat, because they are cations, are adsorbed pretty much like calcium, sodium and hydrogen, except that their affinity is much greater than these ions. There is a different selectivity of these compounds for different clays--montmorillonite, for example. Most low-land soils containing montmorillonite will tend to adsorb paraquat and diquat to a great extent. Kaolinite, the more weathered clays, and sand with their low exchange capacity will tend to adsorb the compounds less. Over a period of time these exchangeable cations can be released back into the soil solution through exchange with metallic cations.

Dr. Dickens: If I'm not mistaken, Ortho or Chevron had quite a problem in recovering these cations. In other words, they put a given amount on, it didn't come out of the bottom of the column and they couldn't find it in the column on some of the clay minerals. They finally found it with an x-ray spectrograph in between the lattice of the individual clay molecules. Of course, your expanding type or montmorillonite clays would trap more in this respect, too.

Dr. Kaufman: This is a very biodegradable compound and, from my own viewpoint, I consider it to be one of the more readily degradable compounds. Because it is very tightly adsorbed, it is not available for organisms. Also, the work Jerry Webber had done indicates that it is not available for degradation. The moment it becomes available, it does seem to be readily degraded now. In some other work Dr. Heeling is doing at Beltsville, which is not published yet, there are indications that with continued use of this, there may be a saturation of the soil. Once you get to a certain level, it's no longer adsorbed and it will leach, as well as become available for toxic purposes.

## UNIQUE APPROACHES TO WEED CONTROL

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### Introduction

Although the title of this paper is "Unique Approaches to Weed Control," I would like to point out that the approaches to be discussed are not original with our research group. Information presented is largely taken from the literature. However, they are unique in the sense that few investigators are using them.

Three approaches will be discussed. First, if we could make desirable plants, in our case turfgrasses, more competitive, the desirable plants with a better competitive advantage would crowd out the undesirable plants, the weeds. Or alternatively, if we could make the weeds less competitive, then once again the desirable plants would crowd out the undesirable plants. When we follow good cultural practices, such as proper mowing, fertilization and irrigation, we encourage dense, vigorous turf; however, other forces are at work to counteract part of this effort. Turf diseases, insects, nematodes and traffic represent some of these forces. With more competitive turfgrasses, the effects of many of these negative factors could be greatly reduced. In the last few years a large amount of research has been done on CO<sub>2</sub>-assimilation in plants. Black et al. (1969) have suggested that efficient CO<sub>2</sub>-assimilating plants are much more competitive than non-efficient CO<sub>2</sub>-assimilating. An example of an efficient CO<sub>2</sub>-utilizing plant is crabgrass and an example of a non-efficient of CO<sub>2</sub>-utilizing plant is Kentucky bluegrass.

The second topic to be discussed is chemical-genotype interactions. We are all aware of instances where disease organisms have developed resistance to antibiotics, where houseflies have developed resistance to DDT and where certain weeds have developed resistance to herbicides. We would like to turn this thing around. That is, develop turfgrass varieties which are resistant to a specific herbicide. Then the resistant varieties could be treated with the herbicide and the weeds in turf would be killed without damaging the turf.

The third topic to be discussed is the interaction between chemicals and enzymes and/or enzyme systems. We would like to develop a pre-emergence herbicide that is active only on germinating seeds. This pre-emergence herbicide would not be active on roots, stems or leaves of emerged plants. Jones and Varner (1967) have described a bioassay for gibberellic acid using barley half-seeds. One advantage of this type of system is that one would be studying the effects of chemicals on seeds prior to the start of cell division.

#### Improving Competitive Ability of Turf Plants

Over the past 20 years, information has been accumulating in the literature which enables one to classify plants into efficient plants and non-efficient plants according to their ability to assimilate CO<sub>2</sub> (Black et al., 1969). The photosynthetic characteristics of efficient and non-efficient plants are given in Table 1. Black et al. (1969) have suggested that plants with the capacity to photosynthesize at high rates (efficient plants) are more competitive than those with a low photosynthetic capacity (non-efficient plants). Such plants as bermudagrass, crabgrass, corn, sorghum, johnsongrass, sugar cane and pigweed are examples of efficient plants, and all of these are very competitive. Kentucky bluegrass, tall fescue, wheat, oats, barley, rice, soybeans and spinach are examples of non-efficient plants.

In order to emphasize the competitive nature of efficient plants, the column with the photosynthetic characteristics of efficient plants has been labeled crabgrass and the column for non-efficient plants has been labeled bluegrass. Thus, the data given in Table 1 are ranges for efficient and non-efficient plants

Table 1. Characteristics of efficient and non-efficient plants.

	Bluegrass	Crabgrass
Light Saturation	1000-3000 ft-c	> 5000 ft-c
CO <sub>2</sub> Assimilation Rate	15-35 mg CO <sub>2</sub> /sq dm/hr	50-80 mg/sq dm/hr
Optimum Temperature	10°-25° C	30°-40° C
Photorespiration	Present	Absent
Compensation Point	> 30 ppm CO <sub>2</sub>	< 5 ppm CO <sub>2</sub>

and are not specific for crabgrass and Kentucky bluegrass. While looking at Table 1, it should be remembered that here in central Ohio on a hot, bright summer day, the light intensity is above 8000 ft-c and the temperature at least 32°C. It can be seen from Table 1 that on a bright summer day, both Kentucky bluegrass and crabgrass are light saturated; i.e., they both are photosynthesizing at their maximum rate. However, it must be noted that crabgrass, the efficient plant, has a maximum rate of CO<sub>2</sub> assimilation of 50-80 mg CO<sub>2</sub>/sq dm of leaf area per hour, while Kentucky bluegrass, the non-efficient plant, has a maximum rate of only 15-35 mg CO<sub>2</sub>/sq dm hr.

Not only high light intensity, but also high temperature favors the higher rates of CO<sub>2</sub> assimilation of crabgrass over bluegrass, as can be seen in their optimum temperature for photosynthesis. Once again, on a hot summer day, 32°C is in the optimum temperature range for efficient plants, which have an optimum temperature of 30°-40°C. Since non-efficient plants have a range of 10°-25°C, a temperature of 32°C is above their optimum temperature and their rate of CO<sub>2</sub> fixation will be reduced because of the excessively high tempera-

ure. Photorespiration, which is an increase in  $O_2$  uptake or  $CO_2$  release under conditions of high light intensity and  $O_2$  levels above 2%, is present in non-efficient plants but is not present in efficient plants. Photorespiration is a wasteful process. The plants are releasing  $CO_2$  without conserving energy (Jackson and Volk, 1970).

Another characteristic of non-efficient plants is their compensation point. Their compensation point is above 30 ppm  $CO_2$ , while efficient plants have a compensation point of less than 5 ppm  $CO_2$ . What this means is that, if you place crabgrass and Kentucky bluegrass together in a closed system, both grasses will fix  $CO_2$  until the concentration of  $CO_2$  in the chamber reaches the compensation point of Kentucky bluegrass. Although the crabgrass will continue to fix  $CO_2$  the Kentucky bluegrass will start to evolve  $CO_2$ , resulting in the death of the Kentucky bluegrass.

The effect of light intensity on  $CO_2$  fixation is shown graphically in Figure 1. For non-efficient plants, the rate of  $CO_2$  fixation levels off and is constant for light intensities above 3000 ft-c. The rate of  $CO_2$  fixation for efficient plants continues to increase for light intensities greater than 5000 ft-c. Not only do efficient plants have a higher level of light saturation, but they also have much higher rates of  $CO_2$  assimilation at all but the very lowest light intensities. This figure emphasizes the fact that, on a bright summer day when the light intensity is at least 8000 ft-c, crabgrass can capture vastly more light energy than Kentucky bluegrass.

A graphic presentation of the effects of temperature on  $CO_2$  fixation is shown in Figure 2. The rate of  $CO_2$  fixation for the non-efficient plant is roughly constant between  $15^\circ$  and  $25^\circ C$ , with a decrease in rate above and below these temperatures; while the rate of  $CO_2$  fixation for efficient plants continues to increase to above  $40^\circ C$ . Not only do efficient plants have a much higher optimum temperature but, again, their rate of  $CO_2$  assimilation is much greater at all but the lowest temperatures. On a bright summer day with temperatures around  $35^\circ C$ , crabgrass is fixing  $CO_2$  at a maximal rate. Due to the excessively high temperatures, Kentucky bluegrass is fixing  $CO_2$  at a reduced

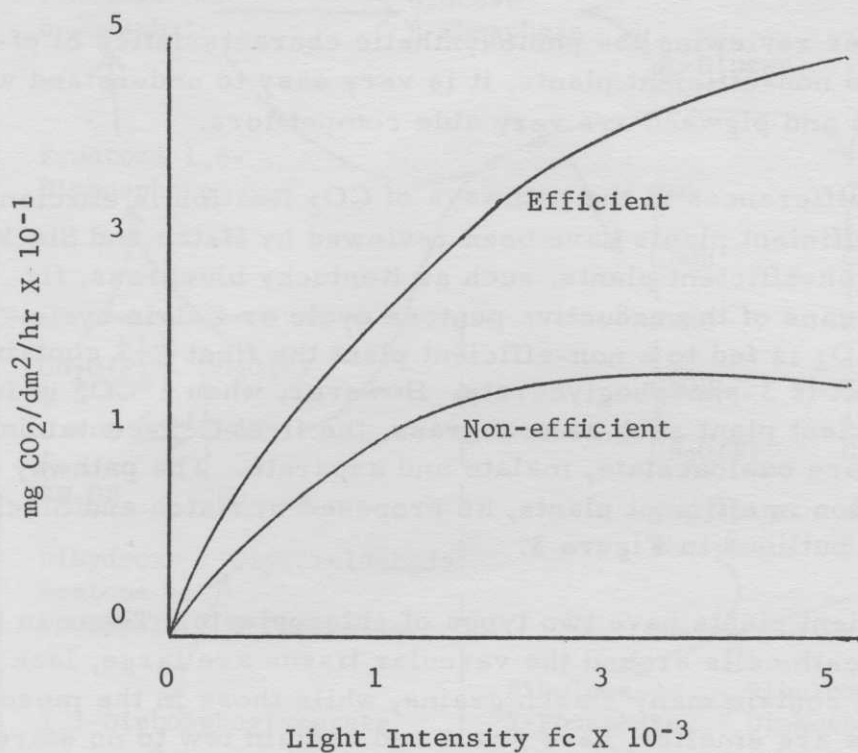


Figure 1. General response of photosynthesis to increasing intensity of light for efficient and non-efficient plants. Adapted from Black et al. (1969).

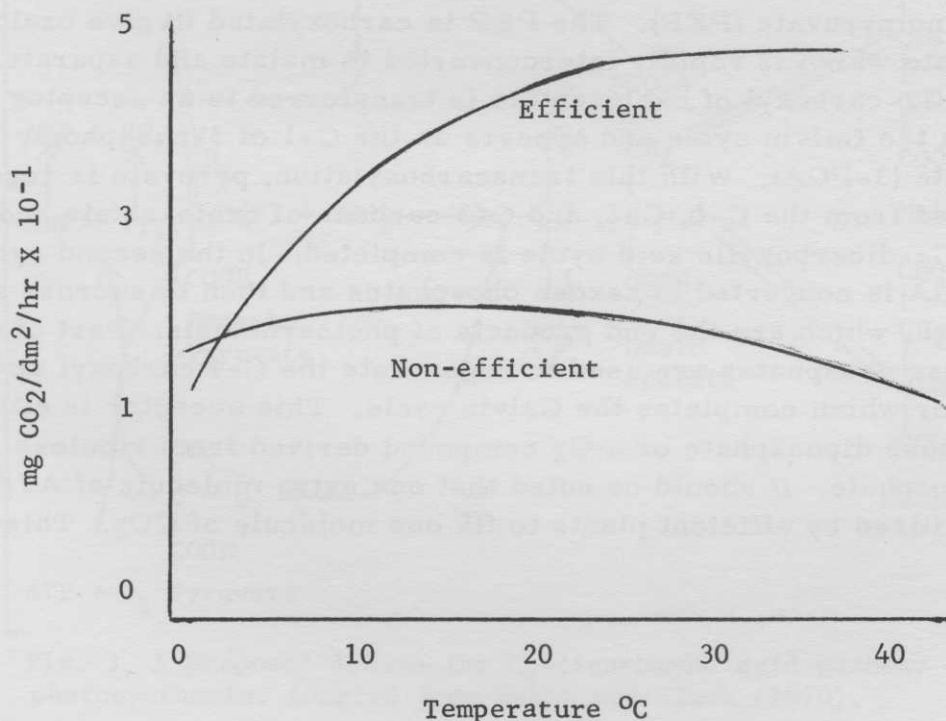


Figure 2. General response of photosynthesis to increasing temperature for efficient and non-efficient plants adapted from Black et al. (1969).

rate. After reviewing the photosynthetic characteristics of efficient and non-efficient plants, it is very easy to understand why crabgrass and pigweed are very able competitors.

The differences in the pathways of CO<sub>2</sub> fixation in efficient and non-efficient plants have been reviewed by Hatch and Slack (1970). Non-efficient plants, such as Kentucky bluegrass, fix CO<sub>2</sub> by means of the reductive pentose cycle or Calvin cycle. When <sup>14</sup>CO<sub>2</sub> is fed to a non-efficient plant the first C<sup>14</sup> containing product is 3-phosphoglycerate. However, when <sup>14</sup>CO<sub>2</sub> is fed to an efficient plant such as crabgrass, the first C<sup>14</sup>-containing products are oxaloacetate, malate and aspartate. The pathway of CO<sub>2</sub> fixation in efficient plants, as proposed by Hatch and Slack (1970), is outlined in Figure 3.

Efficient plants have two types of chloroplasts. Those in the bundle sheath cells around the vascular tissue are large, lack grana and contain many starch grains, while those in the mesophyll cells are smaller, have grana and contain few to no starch grains (Laetsch, 1968). By means of non-aqueous density fractionation, Hatch and Slack (1970) have isolated these two types of chloroplasts from corn. They have shown that the mesophyll chloroplasts contain the C<sub>4</sub>-dicarboxylic acid cycle enzymes and that the bundle sheath chloroplasts contain the Calvin cycle enzymes. According to the scheme proposed by Hatch and Slack, pyruvate reacts with ATP and inorganic phosphate to form phosphoenolpyruvate (PEP). The PEP is carboxylated to give oxaloacetate which is rapidly interconverted to malate and aspartate. The C<sub>4</sub>-carboxyl of oxaloacetate is transferred to an acceptor from the Calvin cycle and appears as the C-1 of 3-phosphoglycerate (3-PGA). With this transcarboxylation, pyruvate is regenerated from the C-1, C-2, and C-3 carbons of oxaloacetate and the C<sub>4</sub>-dicarboxylic acid cycle is completed. In the second cycle, 3-PGA is converted to hexose phosphates and then to sucrose and starch, which are the end products of photosynthesis. Part of the hexose phosphates are used to regenerate the C-4 carboxyl acceptor which completes the Calvin cycle. This acceptor is either ribulose diphosphate or a C<sub>2</sub> compound derived from ribulose diphosphate. It should be noted that one extra molecule of ATP is utilized by efficient plants to fix one molecule of CO<sub>2</sub>. This



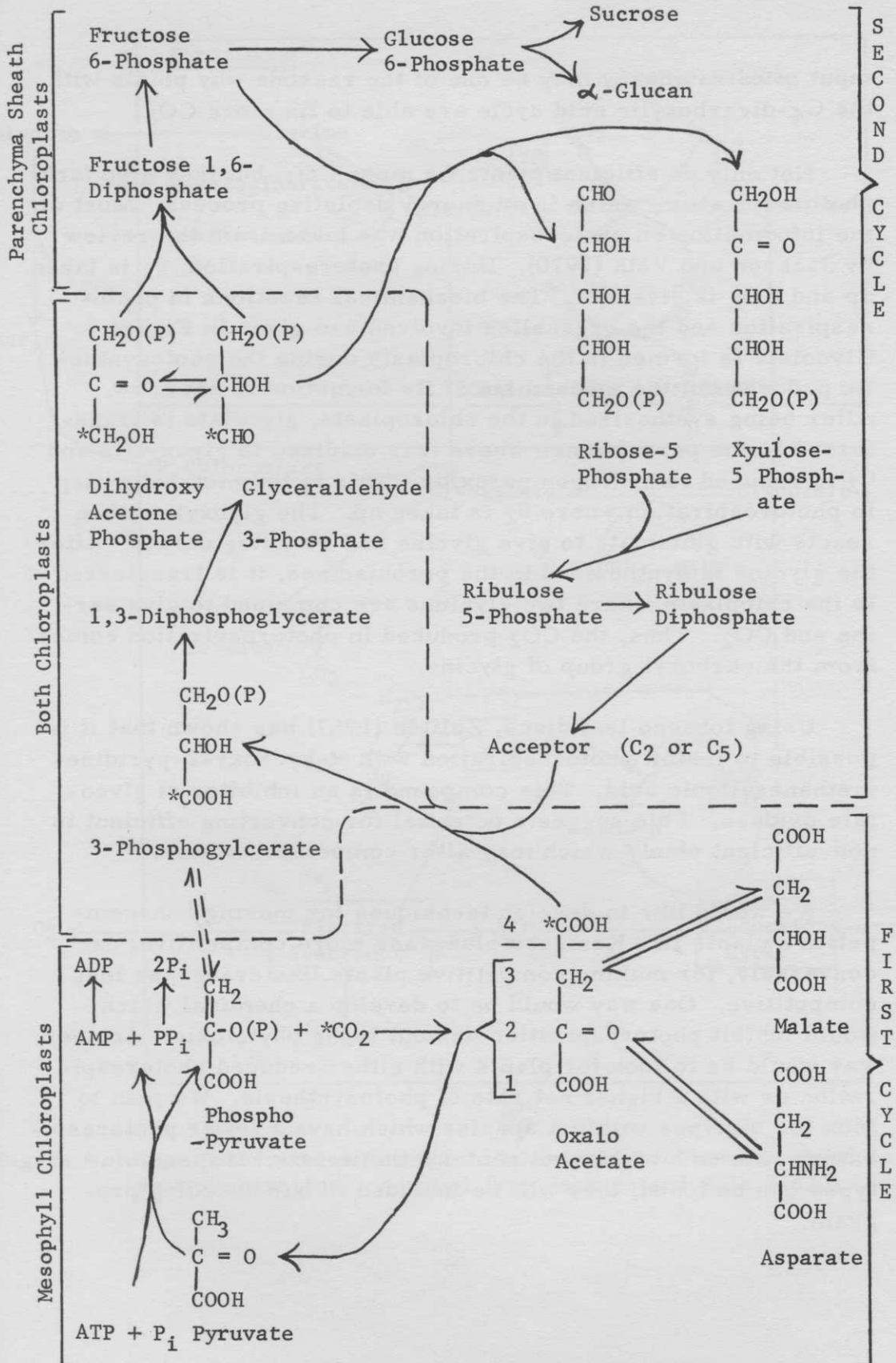


Fig. 3. A proposed scheme for C<sub>4</sub>-dicarboxylic acid pathway of photosynthesis. Adapted from Hatch and Slack (1970).

input of extra energy may be one of the reasons why plants with the C<sub>4</sub>-dicarboxylic acid cycle are able to fix more CO<sub>2</sub>.

Not only do efficient plants fix more CO<sub>2</sub>, but they also lack photorespiration, which is an energy depleting process. Most of the information on photorespiration was taken from the review by Jackson and Volk (1970). During photorespiration, O<sub>2</sub> is taken up and CO<sub>2</sub> is given off. The biochemical reactions in photorespiration and the organelles involved are given in Figure 4. Glycolate is formed in the chloroplasts during the photosynthetic process but the mechanism of its formation is not known. After being synthesized in the chloroplasts, glycolate is transferred to the peroxisomes where it is oxidized to glyoxylate and O<sub>2</sub> is reduced to hydrogen peroxide. This is the metabolic step in photorespiration where O<sub>2</sub> is taken up. The glyoxylate then reacts with glutamate to give glycine and α-ketoglutarate. After the glycine is synthesized in the peroxisomes, it is transferred to the cytoplasm where two glycines are combined to give serine and CO<sub>2</sub>. Thus, the CO<sub>2</sub> produced in photorespiration comes from the carboxyl group of glycine.

Using tobacco leaf discs, Zelitch (1967) has shown that it is possible to inhibit photorespiration with α-hydroxy-2-pyridine-methanesulfonic acid. This compound is an inhibitor of glycolate oxidase. This suggests potential for converting efficient to non-efficient plants which may alter competitive status.

We would like to develop techniques for making non-competitive plants like Kentucky bluegrass more competitive; or conversely, for making competitive plants like crabgrass less competitive. One way would be to develop a chemical which would inhibit photorespiration without being phytotoxic. Another way would be to look for plants with either reduced photorespiration or with a higher net rate of photosynthesis. We plan to look for biotypes within a species which have a lower photorespiratory rate on a higher net photosynthetic rate. If these biotypes can be found, they will be included in our breeding program.

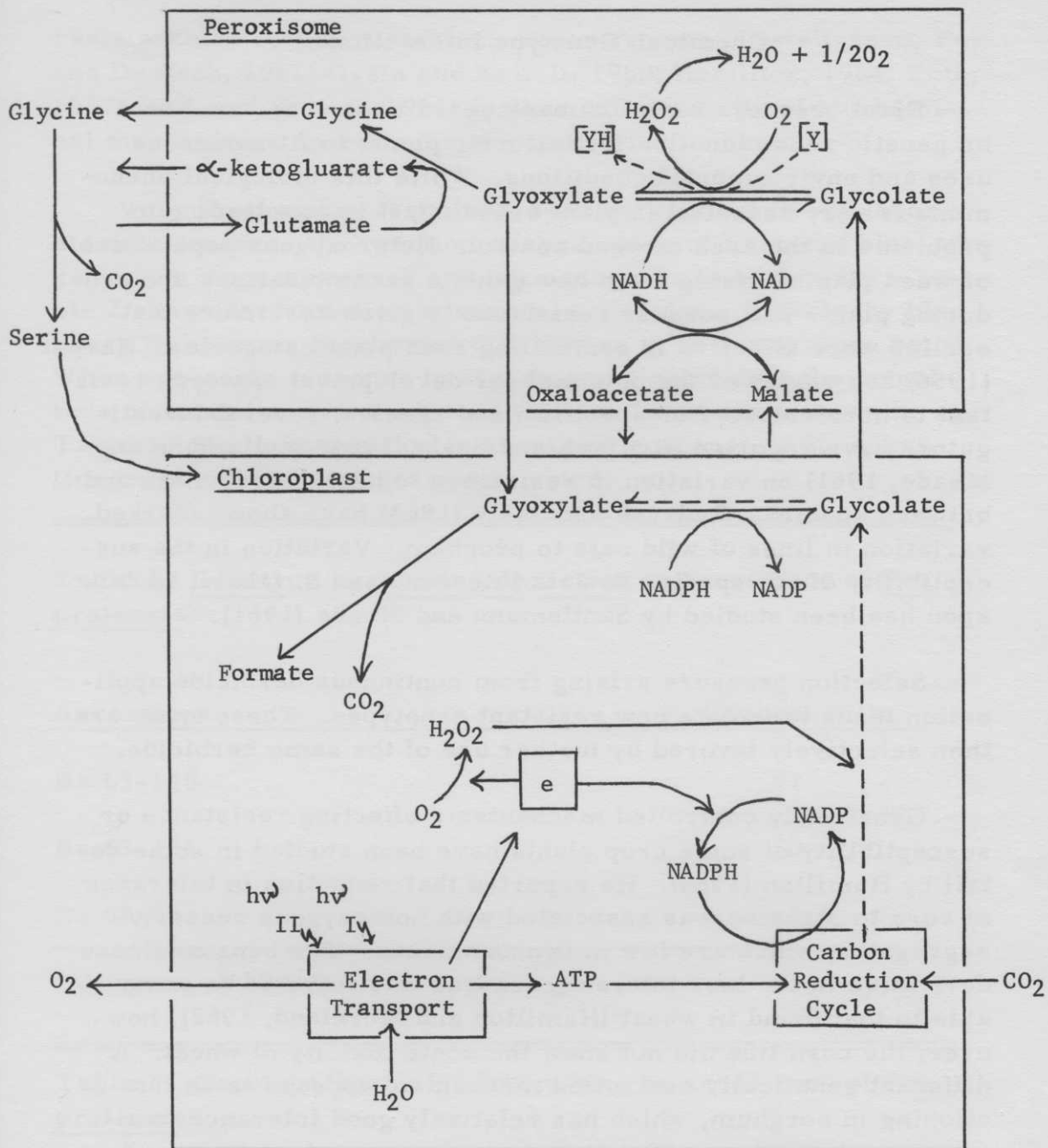


Figure 4. A proposed scheme for the biochemical reactions involved in photorespiration. Adapted from Jackson and Volk (1970).

## Chemical/Genotype Interactions

Plant breeders have for many years used variation based on genetic recombination for tailoring plants to fit numerous uses and environmental conditions. While this biological phenomena is very essential in plant breeding, it is now leading to problems in the area of weed control. Heterozygous populations of weed plants arising from new genetic recombinations are producing plants that possess resistance to given herbicides that earlier were effective in controlling such plant categories. Harper (1956) has reviewed the potential for development of weeds resistant to herbicides. For specific weed species, several investigators have reported (Rydrych and Seely, 1964; Santlemann and Meade, 1961) on variation in resistance to herbicides within and between species. Rydrych and Seely (1964) have shown marked variation in lines of wild oats to propham. Variation in the susceptibility of the species Setaria lutescens and S. faberii to dalapon has been studied by Santlemann and Meade (1961).

Selection pressure arising from continuous herbicide application tends to isolate new resistant genotypes. These types are then selectively favored by further use of the same herbicide.

Genetically controlled mechanisms effecting resistance or susceptibility of some crop plants have been studied in some detail by Hamilton (1964). He reported that reduction in tolerance of corn to atrazine was associated with homozygous recessive segregates, which are low in benzoxazinone. The benzoxazinone derivative in the less tolerant corn line was found to be comparable to that found in wheat (Hamilton and Moreland, 1962); however, the corn line did not show the acute toxicity of wheat. A different genetically controlled mechanism appears to be functioning in sorghum, which has relatively good tolerance to simazine. Yet it does not contain benzoxazinone derivatives and excised roots do not convert simazine to hydroxysimazine, as is the case of tolerant lines of corn. Acute toxicity may be related to photooxidations or accumulation of an oxidant as a result of Hill reaction inhibition, according to Hamilton (1964). He further suggested that since carotenoids seem to play a role in preventing harmful photooxidation, they might be involved in

resistance of corn to simazine. Other reports (Castelfranco, Foy and Deutsch, 1961; Gysin and Kniisli, 1960; Hamilton, 1964; Roth, 1957; Roth and Kniisli, 1961) further detail results of biochemical mechanisms operating in the corn-triazine case.

Very preliminary tests have been carried out in our laboratories to assess the reaction of accessions of Kentucky bluegrass, St. Augustinegrass and bermudagrass to herbicides. Table 2 shows the variation in several accessions of Kentucky bluegrass to linuron. Significant differences in response were noted. When accession response to atrazine was evaluated, the magnitude of variation was much less than for linuron, as shown in Table 3. Similar variation in accession response of St. Augustinegrass and bermudagrass was noted.

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Table 2. Genotype/herbicide interaction on accessions of Poa pratensis.

Accessions	Percent Kill*
Ba 63-148	97
Ba 63-151	50
Ba 63-68	0

\* Linuron at 10#/A

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Table 3. Genotype/herbicide interaction on accessions of Poa pratensis.

Accessions	Percent Kill*
Ba 67-242	100
Ba 62-31	90
Ba 67-247	80

\*Atrazine 10#/A

Conclusions from this preliminary work are sufficiently encouraging to warrant further attention to research in this area. A second phase will evaluate hybrids developed from susceptible and resistant accessions.

### Chemical-Enzyme Interactions

The third unique approach to weed control is the study of the interaction between chemicals and specific enzymes and/or enzyme systems. An example of the type of interaction that we are interested in is the effects of chemicals on the initial steps of germination. The idea behind this type of study is to develop a herbicide that has only pre-emergence activity and attacks metabolic reactions common only to the germination phase of growth. Some pre-emergence herbicides are mitotic inhibitors, and they inhibit the root growth of plants as well as the emergence of seedlings. A herbicide that is specific for some biochemical reaction or reactions in the initial stages of germination prior to cell division, probably would not have herbicidal activity on growing plants.

As shown in Figure 5, the barley half-seed bioassay for GA<sub>3</sub>, as described by Jones and Varner (1967), is an example of this type of a test system. In the barley half-seed bioassay, the distal end of the barley seed is incubated in a culture solution containing GA<sub>3</sub>. The amount of  $\alpha$ -amylase produced in the barley half-seed is directly proportional to the concentration of GA<sub>3</sub> in the culture medium. In the study of the effects of chemicals on the germination of seeds, both a half-seed and a whole-seed bioassay system would be used. Both half-seeds and whole-seeds would be incubated in culture media with and without the chemical of interest, as well as with and without GA<sub>3</sub>. After incubation, the  $\alpha$ -amylase would be extracted from the seeds and then the amount of enzyme extracted assayed.

Penner (1968) showed that benzyladenine stimulated the synthesis of  $\alpha$ -amylase in excised cotyledons of squash; whereas, GA<sub>3</sub> had no effect. The use of both squash and barley in a bioassay for chemical effects appears to be desirable since enzyme synthesis is promoted in one by cytokinins, and in the other by gibberellins. Also, since squash seeds contain a large amount of oil,

Figure 5. A proposed bio-assay procedure for studying interactions of chemicals and enzyme systems in seed germination.

Bio-assay system		
Steps	Whole seed	Half seed
Treat with chemical	X	X
Incubate	X	X
Enzyme extract	X	X
Enzyme assay	X	X

they are not dependent on stored carbohydrates for growth. Either of the above two differences may explain why squash seeds are tolerant to chloramben, while barley seeds are not.

If chemically treated seeds lack  $\alpha$ -amylase activity, there are three possible reasons for this lack of activity. One, the chemical is an inhibitor of  $\alpha$ -amylase. Two, the chemical is inhibiting the synthesis of  $\alpha$ -amylase by inhibiting either RNA or protein synthesis. Or three, the chemical is inhibiting the synthesis of the phytohormone by the embryo.

Hopefully, this type of bioassay system would yield a highly selective pre-emergence herbicide that would prevent the germination of seeds, but would not affect mature plants. This selective pre-emergence herbicide would not affect the vigor of the grass plants in an established lawn, nor would it affect the establishment of a lawn using sod. By eliminating the germination of weed seeds, such as crabgrass, the desirable turfgrasses would be more competitive.

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## Discussion Period

Dr. Schmidt: On what basis do you claim that the low photorespiration would necessarily be beneficial? I can see in cold weather where it may be an advantage to have a plant that is photorespirant.

Mr. Stottlemeyer: I'm not talking about dark respiration. During photorespiration the plant is releasing CO<sub>2</sub> without conserving energy, and this is an inefficient process which one would think is detrimental to the plant. If the plant doesn't respire, then CO<sub>2</sub> isn't released and energy is conserved. The plant can always store excess fixed carbon as starch. What would you suggest is the advantage of photorespiration to the plant?

During respiration in fatty seeds, the fatty acids are broken down into acetate and this acetate is utilized via the glyoxylate cycle, which is essentially a modified citric acid cycle. Is this the glyoxylate pathway that you are thinking of? This is a different system.

Dr. Schmidt: The point that I want to make is that in grasses, such as bluegrasses, which is definitely a photorespirator, you will have a build-up of carbohydrates in spite of the fact that you may have an increase of photorespiration, even during cold weather. So this would be contrary to the fact. I think we have to be careful when we label this as being detrimental. We may want to select grasses that have low photorespiration, but again they must be ecologically adapted.

Mr. Stottlemeyer: The main disadvantage of photorespiration is that it is most evident when you have low CO<sub>2</sub> and high temperatures. High temperatures are a problem in the summertime. It appears that high temperatures are the problem when one tries to grow Kentucky bluegrass in such places as Washington, D. C. and St. Louis. Bluegrasses just fade out in these areas in the summertime. If you can get a plant that doesn't waste its energy supply, then it may be more competitive and better able to compete with such plants as bermudagrass and crabgrass, which are efficient plants.

Dr. Schmidt: At lower temperatures, the respiration in light exceeds that in dark, but at temperatures above 40C., the reverse is true. We have to look at two bases--not only photorespiration, but also photosynthesis. CO<sub>2</sub> compensation point is dependent upon both factors.

Dr. Ledebøer: Is photorespiration the limiting factor that we have on the cool season grasses; the fact that they do increase their photorespiration during high temperature? The compensation point goes up so high that we lose due to this fact. I would have to agree with Mr. Stottlemeyer. Since photorespiration takes place to this degree, it can probably be earmarked as a beneficial process here if the photorespiration is rather low. I don't think we can find plants among cool season grasses where it is completely absent.

Dr. Schmidt: I'm trying to point out that you have to look at the ratio between photosynthesis and photorespiration. Nugget, for example, which is a northern ecotype, we find doing quite well for us in hot temperatures and yet this grass has a very high photorespiration rate. On the other hand, it has a high photosynthetic rate. So you have low compensation point on this basis. If you're going just with photorespiration rate, this doesn't fit the trend. The point I'm trying to make is that you have to look at both factors.

Dr. Ledebøer: To expand this a little further into management of these grasses, have you speculated at all into management practices which can lower the photorespiration rate of these grasses? Have you found any evidence to this? In Dr. Schmidt's work with these grasses, I believe, that they absorb most of their nutrients during cooler temperatures and, as such, increase the amount of stored hydrocarbohydrates, later letting the grass metabolize these carbohydrates in such a manner as the environment dictates. Is there any evidence to this effect in the search that you have made?

Mr. Stottlemeyer: I must point out that, at the present time, we've just made some preliminary studies on CO<sub>2</sub> assimilation. Evidently Dr. Schmidt has done a lot more work in this area than we have. Although we haven't gotten heavily involved in this work, we are definitely planning to start in the near future.



## PERSISTENCE AND DEGRADATION OF COMMONLY USED TURF HERBICIDES IN OUR ENVIRONMENT

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### Introduction

Many pesticides are released into our environment to control weeds, plant pathogens and insects. Parts of all pesticides enter into the environment and become an integral part of it. Therefore, knowledge of the behavior and persistence of all pesticides in our environment is essential if we are to develop sound and safe pest control practices.

Nearly all pesticides applied to our environment ultimately reach the soil. When a pesticide comes in contact with the soil, several processes may act to bring about its dissipation from soil. Generally, organic pesticides are dissipated more readily than inorganics, although some exceptions probably exist (Sheets, 1964b). Processes known to decrease the concentrations of pesticides include the formation of insoluble compounds and complexes, leaching, dilution in soil, mechanical removal (wind, water and plants), fixation and adsorption to soil, microbial degradation, photodecomposition, chemical reactions and volatilization.

One of the controversial aspects of our present environmental situation concerns the continued use of pesticides. The chlorinated hydrocarbon insecticides have come under severe criticism due to their relatively long persistence in the environment, biomagnification through certain organisms and their frequent detection in the food chain. In contrast, the organic herbicides have received relatively little criticism, until recently, primarily due to their low mammalian toxicity and short persistence under

most conditions. The purpose of this presentation is to examine the persistence and degradation of commonly used turf herbicides in our environment. The criteria for selection of the herbicides discussed in this presentation were recommendations included in references (Anon, 1968a; Anon, 1968b) and from personal observation of the author as to what was available on the shelves of several local emporia. Common and chemical names of these herbicides are presented in Table 1.

Table 1. Common and Chemical Names of Turf Herbicides Discussed in Text

Common Name	Chemical Name
atrazine	2-chloro-4-ethylamino-6-isopropylamino- <u>s</u> -triazine
benefin	<u>N</u> -butyl- <u>N</u> -ethyl- $\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro- <u>p</u> -toluidine
bensulide	<u>0,0</u> -diisopropyl phosphorodithioate <u>S</u> -ester with <u>N</u> -(2-mercaptoethyl) benzenesulfonamide
bromoxynil	3,5-dibromo-4-hydroxybenzoxynitrile
cacodylic acid	hydroxydimethylarsine oxide
2,4-D	(2,4-dichlorophenoxy) acetic acid
dalapon	2,2-dichloropropionic acid
DCPA	dimethyl tetrachloroterephthalate
dicamba	3,6-dichloro- <u>o</u> -anisic acid
2,4-DP, dichlorprop	2-(2,4-dichlorophenoxy) propionic acid
DMPA	[ <u>0</u> -(2,4-dichlorophenyl) <u>0</u> -methyl isopropylphosphoramidothioate]

Table 1. Continued.

Common Name	Chemical Name
DMTT, dazomet	tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione
DSMA	disodium methanearsonate
MAMA	monoammonium methanearsonate
MCPA	(4-chloro- <u>o</u> -tolyl)oxy acetic acid
methyl bromide	methyl bromide
MSMA	monosodium methanearsonate
neburon	1-butyl-3-(3,4-dichlorophenyl)-1-methylurea
paraquat	1,1'-dimethyl-4,4'-bipyridinium salts
PMA	(aceto) phenylmercury
potassium cyanate	potassium cyanate
siduron	1-(2-methylcyclohexyl)-3-phenylurea
silvex	2-(2,4,5-trichlorophenoxy) propionic acid
simazine	2-chloro-4,6-bis(ethylamino)- <u>s</u> -triazine
SMDC, metham	sodium methylthiocarbamate
2,4,5-T	(2,4,5-trichlorophenoxy)acetic acid
terbutol	2,6-di- <u>tert</u> -butyl- <u>p</u> -tolyl methylcarbamate

## Persistence

The importance of a process in causing the dissipation of a pesticide from soil depends on the physical and chemical properties of the pesticide, soil properties and prevailing environmental conditions. Inactivation or decomposition of a pesticide, which is active for only a few days to a few weeks, is largely attributable to a single process (Sheets, 1964b). Adsorption of some pesticides to soil particulate matter, for example, is rapid and sufficiently complete to render them immediately inactive when they enter the soil. Some pesticides disappear from soil within a few days to a few weeks by volatilization or by chemical reactions and subsequent volatilization. Degradation by soil microorganisms and leaching from soil may account for dissipation of a major part of some pesticides that disappear rapidly. The longer a pesticide persists, the greater the probability that several processes become involved in its inactivation and disappearance from soil (Small and McCants, 1962). The relative persistence of the commonly used turf herbicides is illustrated in Figure 1.

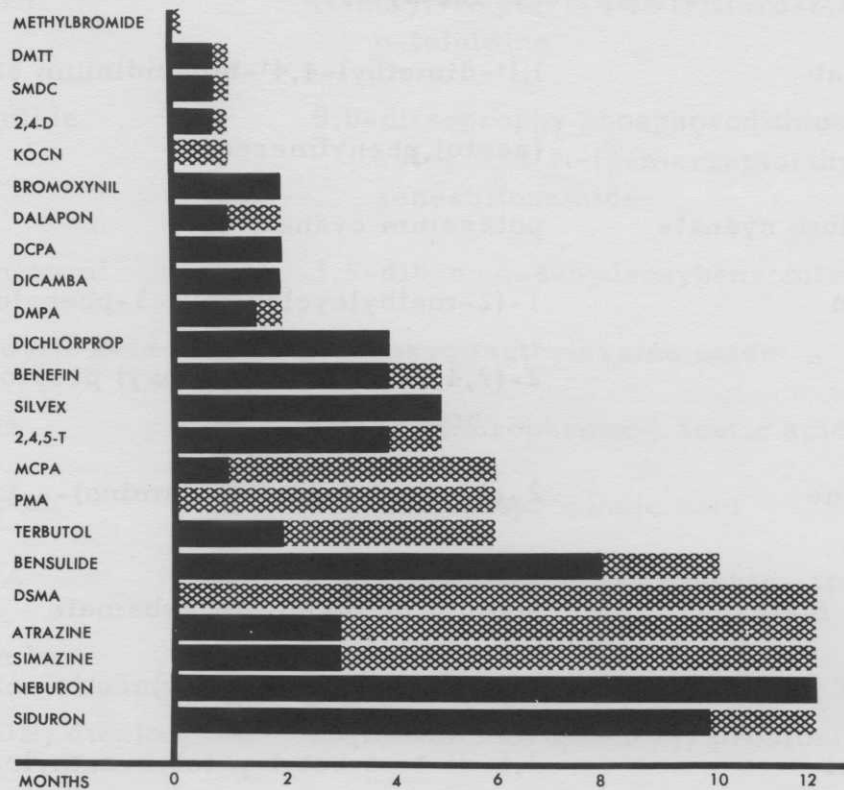


Figure 1. Average persistence of turfgrass herbicides. (The solid bar represents the average persistence period; the thatched bar represents exceptional periods of persistence. These averages are based solely on a broad literature survey and are, therefore, not indicative of any single soil type).



## Degradation

Microbiological, chemical, photochemical and physical reactions are active in the decomposition of many pesticides. Free of the soil environment, microbial reactions can be studied in detail at the cellular and enzymic levels. Investigations with sterile soils and model systems have revealed that purely chemical systems also play a role in decomposing pesticides. Extensive investigations of representative compounds within a particular group of pesticides have elucidated certain classes of reactions which have underlying similarities from a chemical and biochemical standpoint. In a few cases, a thorough understanding of these reactions has allowed us to predict the type of decomposition product that could be produced within certain classes of compounds and the ease with which they are mediated.

The least understood transformations of pesticides in soils are those reactions catalyzed by the purely chemical systems as compared to the biochemical systems mediated by soil microorganisms. The major difficulty in distinguishing chemical from biochemical reactions has been to obtain a sterile soil system that has not undergone extensive physical and chemical destruction due to autoclaving or other methods of sterilization. As a consequence of the difficulty of obtaining intact sterile systems in which to study chemical reactions, a large majority of the pesticide transformations have been ascribed to soil microorganisms. The principal biochemical reactions associated with microbial metabolism of pesticides include dealkylation, dehalogenation, amide or ester hydrolysis, oxidation, reduction, aromatic ring hydroxylation, ring cleavage and condensate or conjugate formation. Many of these reactions, the enzymes, the pathways and the intermediate products involved in pesticide metabolism have been described in detail. Although many of these reactions have been demonstrated as occurring in soils, most of the information has been obtained through pure culture investigations.

A. Methyl bromide. Methyl bromide ( $\text{CH}_3\text{Br}$ ) is a gas and is quite volatile. It is applied as a gas beneath a cover and its activity is dependent upon gaseous diffusion. The diffusion rate

of gases is influenced by molecular weight, temperature, continuity of air spaces, presence of codiffusing gases and distribution of fumigant between air, water and solid phases of soil. The latter distribution is influenced by temperature, moisture, air space, clay and organic matter (Goring, 1963).

Little is known about methyl bromide degradation in soil. Under conditions of fumigation, methyl bromide adsorbed by wheat underwent decomposition with the formation of inorganic bromide (Bridges, 1955; Winteringham et al, 1955). Some free methanol was produced by hydrolysis. Methyl bromide was found to be active in methylating the histidine and lysine of wheat protein (Bridges, 1955; Winteringham et al, 1955).

B. SMDC. Due to its high degree of volatility, SMDC is most frequently used as a fumigant. Although its most extensive use is for controlling soil-borne plant pathogens, it has also been used as a herbicide, particularly for killing weed seeds in soil. SMDC chemically decomposes in soil to several products, including methyl isothiocyanate, which is the primary toxicant (Gray, 1962; Lloyd, 1962; Munnecke, Domsch and Eckert, 1962; Turner and Corden, 1963) (Table 2). The chemical reactions of SMDC and its decomposition products have been examined under varying conditions of soil environment (Turner and Corden, 1963). In dilute alkaline (pH 9.5) solutions, SMDC decomposed to methylisothiocyanate and elemental sulfur, and in acid solutions, carbon disulfide, hydrogen sulfide, methylamine, methyl isothiocyanate and N,N-dimethylthiuram disulfide were found.

Table 2. Decomposition Products of SMDC

Structure	Chemical Name	Common Name or Designation
$\begin{array}{c} \text{H} \quad \text{S} \\   \quad    \\ \text{CH}_3\text{N} - \text{C} - \text{S} - \text{Na} \end{array}$	sodium <u>N</u> -methyldithio-	SMDC
	carbamate	
$\text{CH}_3\text{N} = \text{C} = \text{S}$	methyl isocyanate	MIT

Table 2. Continued.

Structure	Chemical Name	Common Name or Designation
$\text{CH}_3\text{NH}_2$	methylamine	
$\text{S} = \text{C} = \text{S}$	carbon disulfide	$\text{CS}_2$
$\text{H} - \text{S} - \text{H}$	hydrogen sulfide	$\text{H}_2\text{S}$
$\begin{array}{c} \text{H} \quad \text{S} \\   \quad    \\ \text{CH}_3\text{N} - \text{C} - \text{NH}_2 \end{array}$	methyl thiourea	MTU
$\begin{array}{c} \text{H} \quad \text{S} \quad \text{H} \\   \quad    \quad   \\ \text{CH}_3\text{N} - \text{C} - \text{NCH}_3 \end{array}$	<u>N,N'</u> -dimethylthiourea	DMTU
$\begin{array}{c} \text{H} \quad \text{S} \quad \quad \text{S} \quad \text{H} \\   \quad    \quad \quad    \quad   \\ \text{CH}_3\text{N} - \text{C} - \text{S} - \text{C} - \text{NCH}_3 \end{array}$	<u>N,N'</u> -dimethylthiuram monosulfide	DMTM
$\begin{array}{c} \text{H} \quad \text{S} \quad \quad \quad \text{S} \quad \text{H} \\   \quad    \quad \quad \quad    \quad   \\ \text{CH}_3\text{N} - \text{C} - \text{S} - \text{S} - \text{C} - \text{NCH}_3 \end{array}$	<u>N,N'</u> -dimethylthiuram disulfide	DMTD

Most of these products will react with one another forming additional products. Methylamine and carbon disulfide react, forming methyl isothiocyanate which in turn can react with SMDC, yielding N,N-dimethylthiuram disulfide, and with methylamine or  $\text{H}_2\text{S}$ , forming N,N-dimethylthiourea. Since the effectiveness of SMDC as a soil fumigant is dependent on its conversion to methylisothiocyanate (Turner and Corden, 1963), production of N,N-di-

methylthiourea and N, N-dimethylthiuram disulfide reduces its effectiveness. These relatively nonvolatile decomposition products may represent a potential hazard for contamination of soil, water and plants with undesirable residues (Kaufman, 1967). Although other potential products of SMDC decomposition--e.g., CS<sub>2</sub> and H<sub>2</sub>S--are also toxic compounds, their high degree of volatility would tend to preclude their accumulation in soil.

C. DMTT. DMTT behavior in soil is quite similar to that of SMDC. The principal toxicant of DMTT is actually its degradation product, methyl isothiocyanate (Figure 2). Activation or degradation of DMTT in soil is dependent on moisture and is a function of time and temperature (Torgeson, Yoden and Johnson, 1957). Methyl isothiocyanate release occurs as a first order reaction and increases with soil pH over the range of 2.3 to 6.5, but decreases up to values of pH 7.7 (Munnecke, 1963). It decreased with increased clay or peat content, and was not dependent upon soil microorganisms.

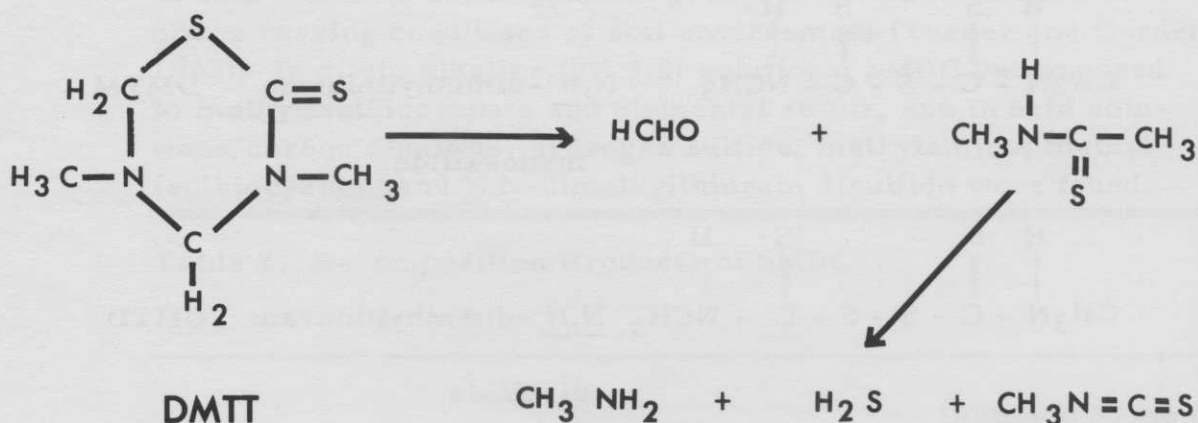


Figure 2. Degradation pathway of DMTT.

Formaldehyde and methylamino methylthiocarbamate are the first degradation products. Methylamino methylthiocarbamate further degrades to methylamine, hydrogen sulfide and methylisothiocyanate. As with SMDC degradation products, many of the DMTT products react with one another and form additional products. Methylamine and hydrogen sulfide react with formaldehyde and form methylamino methanol, dimethylamino methane, and 1,3,5-trithiocyclohexane which eventually degrades to CO<sub>2</sub>, NH<sub>3</sub>, SO<sub>2</sub> and H<sub>2</sub>O. Methyl isothiocyanate will also react with water and form CO<sub>2</sub>, H<sub>2</sub>S and methylamine (Torgeson, Yoden and Johnson, 1957). Methyl isothiocyanate also reacts with ammonia, amines or sulfhydryls (Munnecke, 1963; Munnecke and Martin, 1964; Torgeson, Yoden and Johnson, 1957).

D. Dalapon. Dalapon is frequently recommended for controlling spot infestations of weed grasses (Anon, 1968a). Although it is readily susceptible to biodegradation by soil microorganisms, loss of dalapon by volatility has also been recorded. Kutschinski (1964) reported high dalapon losses at high temperatures when dalapon was applied to the soil as an acid. Day (1961) and Day, Jordan and Russell (1963) suggest a sufficiently rapid loss to eliminate significant soil residues in their studies with some esters of dalapon. Foy (1960) observed that the dalapon acid volatilized rapidly from an aluminum surface at room temperature, whereas negligible amounts of the sodium salt form disappeared in 64 hours under the same conditions. It would seem likely that the volatility of dalapon from soil would depend on the chemical form and the presence and magnitude of physical interactions between the molecules and soil particles. Since there is little interaction of dalapon with soil particles (Kearney et al, 1965), volatility at any given temperature would primarily be a function of the chemical form of the molecule and air movement.

Dalapon degradation by soil microorganisms is accompanied by chloride ion liberation (Kaufman, 1964). The dehalogenation of dalapon was demonstrated with extracts of an Arthrobacter spp. isolated from soil (Kearney, Kaufman and Beall, 1964a; Kearney, Kaufman and Beall, 1964b). The enzyme catalyzed the conversion of dalapon to pyruvic acid. This reaction presumably proceeds by the intermediate formation of 2-

chloro-2-hydroxypropionate which would spontaneously yield the keto acid, pyruvate (Figure 3). Further metabolism involved the formation of alanine, CO<sub>2</sub>, and presumably Krebs cycle intermediates (Kearney, 1966).

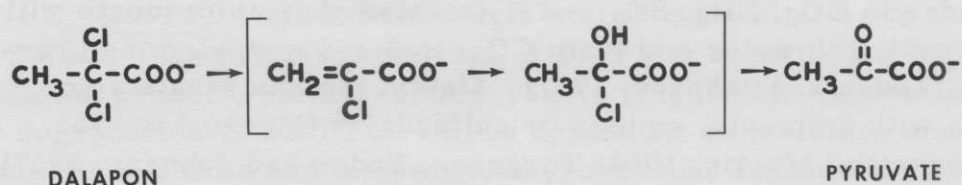


Figure 3. Enzymatic degradation of dalapon.

E. Phenoxyalkanoates. The phenoxyalkanoic acids constitute the largest and most common class of herbicides used for control of turfgrass weeds. Phenoxyalkanoate herbicides most commonly used include 2,4-D, 2,4-DP, 2,4,5-T, MCPA and silvex. The phenoxyalkanoates are also perhaps the most intensely studied group of pesticides. The advent of the dioxin controversy has undoubtedly added additional impetus to the phenoxyalkanoate investigations.

Nearly all of the phenoxyalkanoates are metabolized to some extent by soil microorganisms. Five metabolic steps have been established as general processes involved in the metabolism of phenoxyalkanoates (Kearney, Kaufman and Alexander, 1967) (Figure 4). These reactions include: (1) conversion of nonfatty-acid side chains to the corresponding fatty acids; (2)  $\beta$ -oxidation of compounds with long fatty acid moieties, yielding products with shorter alkanolic acid moieties; (3) cleavage of the ether linkage between the side chain and the ring; (4) ring hydroxylation, and (5) ring cleavage. Several of these reactions are known to occur in soil. The enzymology of most of these reactions has also been clarified.

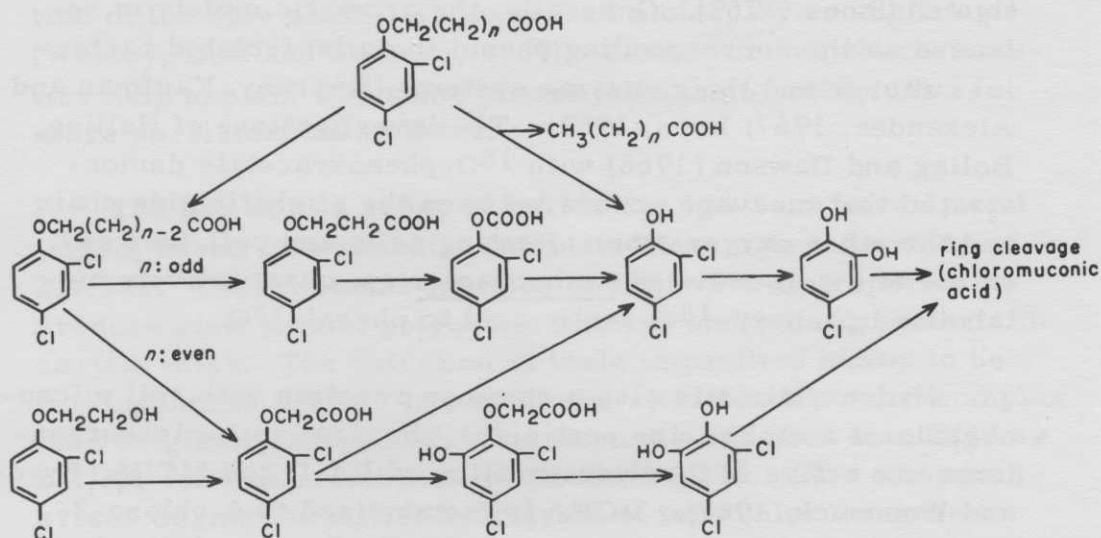


Figure 4. Degradation pathways of phenoxyalkanoates.

Esters of phenoxyalkanoates are known to be converted to their corresponding phenoxyalkanoic acids (Loos, 1969). The herbicidally inactive molecule sesone (2-(2,4-dichlorophenoxy)ethyl sodium sulfate) is activated microbiologically in moist soil (Loos, 1969; Vlitos, 1952; Vlitos, 1953). Sesone is first converted to the 2,4-dichlorophenoxyethanol and subsequently to 2,4-D (Vlitos, 1952; Vlitos, 1953). A similar reaction occurs with the phosphite herbicide 2,4-DEP (tris 2-(2,4-dichlorophenoxy)ethyl phosphite).

$\beta$ -Oxidation is known to occur with phenoxyalkanoic acids having more than two carbon atoms in the fatty acid side chain (Loos, 1969). Whether or not this phenomenon would occur with the two 2-propionate substituted compounds silvex and 2,4-DP is not known. The 2-propionate substituent could be considered a methyl substituted acetate group. The introduction of methyl substituents to the aliphatic acid group of long-chain phenoxyalkanoates considerably retards the  $\beta$ -oxidation of these compounds by some microorganisms (Webley, Duff and Farmer, 1959). This could explain the generally greater period of persistence of silvex and 2,4-DP than their corresponding acetate forms 2,4,5-T and 2,4-D, respectively.

Cleavage of the ether linkage has been extensively investigated (Loos, 1969). Generally, the aromatic moiety is released as the corresponding phenol in soils, isolated bacterial cultures and their enzyme systems (Kearney, Kaufman and Alexander, 1967; Loos, 1969). The investigations of Helling, Bollag and Dawson (1968) with  $^{18}\text{O}$ -phenoxyacetate demonstrated that cleavage occurs between the aliphatic side chain and the ether oxygen atom. Resting cells and cell-free extracts of a soil-isolated *Arthrobacter* sp. quantitatively metabolized phenoxy- $^{18}\text{O}$ -acetic acid to phenol- $^{18}\text{O}$ .

Hydroxylation is also a common reaction with soil microorganisms metabolizing pesticides. Several soil microorganisms are active in the hydroxylation of 2,4-D and MCPA (Byrde and Woodcock, 1957). MCPA is metabolized to 4-chloro-2-methyl-5-hydroxyphenoxyacetic acid (Faulkner and Woodcock, 1965). 2,4-D is also hydroxylated in the 5-position. It is also hydroxylated in the ortho position coupled with a chlorine shift to 2,5-dichloro-4-hydroxyphenoxyacetic acid. Another organism metabolizes MCPA to several products, including one believed to be the 6-hydroxy-MCPA (Gaunt and Evans, 1961).

The steps involved in ring cleavage of phenoxyalkanoate herbicides have been elucidated (Loos, 1969; Menzies, 1969). The catechols produced from 2,4-D and MCPA are cleaved and yield the corresponding chloromuconic acids. These presumably are attacked by reactions involving a dehalogenation and the formation of simple organic acids that serve as substrates for diverse groups of soil microorganisms. Similar mechanisms are believed to function in the metabolism of other similar pesticides having the basic aromatic structure.

Extensive investigations have been conducted to determine the effect of molecular structure on the breakdown of phenoxyalkanoate herbicides (Loos, 1969). The type, place and number of substituents are all known to affect the recalcitrance of phenoxy compounds. In general, phenoxy compounds with meta substituents on the ring are slowly degraded. Substitutions in para position largely overcame the deactivating effect of other substituents. Methyl substituents increased recalcit-



rance in comparison to halogen substituents. Methyl substitution of the side chain also increased molecular recalcitrance (Webley, Duff and Farmer, 1959). These various characteristics help explain why some phenoxyalkanoate herbicides are more persistent than others.

The use of this group of herbicides has been severely criticized, based on a recently completed teratogenicity study of 2,4,5-T. Experimental samples of 2,4,5-T were reported to produce cleft palate, polycystic kidneys and fetical effects in certain mice. The detection of toxic impurities known to be teratogenic in 2,4,5-T has made the situation far more complex than originally suspected. One impurity has been identified as 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). This compound arises during the initial hydrolysis of tetrachlorobenzene to 2,4,5-trichlorophenol. The phenol subsequently reacts with chloroacetic acid to form 2,4,5-T. Previously, the hexachlorodibenzo-*p*-dioxin was implicated in the chickedema factor, but later the tetrachloro isomer was shown to be equally toxic to chicks (Higginbotham et al, 1968). Whether 2,4,5-T or TCDD is the teratogen is not clear at this time.

F. Dicamba. Dicamba is quite mobile in most soils. It moves close behind the forward penetration front of water in both surface (Friesen, 1965) and subirrigated (Harris, 1964) soil columns. Its adsorption to high organic matter soils is greater than for clay or sandy soils, and adsorption to clays is greatest onto kaolinite clays (Burnside and Lavy, 1966). Although dicamba has relatively low adsorption potential, its volatilization is reduced by soil contact. At equivalent temperatures and relative humidities, nearly half of the radioactivity of  $^{14}\text{C}$ -dicamba was lost from planchets during an 11-week period, whereas loss by volatilization from a silty clay loam was negligible over an 8-week period.

Degradation of dicamba occurs more rapidly in acid (pH 5.3) than in alkaline (pH 7.5) soils (Corbin and Upchurch, 1967) high in organic matter. Soil microorganisms are active in degrading dicamba (Wurzer and Corbin, 1968), via the decarboxylation mechanism to 2,5-dichloroanisole (Menzies, 1969) (Figure 5).

Subsequent soil degradation products have not been reported. Liberation of chloride ion from dicamba in soil was not detected (Sheets and Kaufman, 1965). Alternation of the methoxy substituent has been suggested but has not been substantiated (Swanson, 1969).

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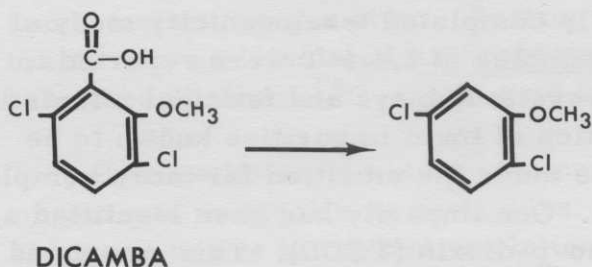


Figure 5. Degradation of dicamba.

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Degradation products observed in plants include 5-hydroxy-2-methoxy-3,6-dichlorobenzoic acid, 3,6-dichlorobenzoic acid, 3,6-dichlorosalicylic acid and 3,6-dichlorogentisic acid, in addition to one or more conjugate forms (Broadhurst, Montgomery and Freed, 1966; Swanson, 1969). Hydrolysis products of the conjugate forms include intact dicamba, 5-hydroxy-2-methoxy-3,6-dichlorobenzoic acid and 3,6-dichlorosalicylic acid. Formation of these hydrolysis products suggests conjugation through the carboxyl, methoxy and a hydroxy substituent. The fate of these materials in our environment is unknown.

G. Bromoxynil. Bromoxynil and ioxynil (3,5-diiodo-4-hydroxybenzotrile) have been introduced recently as herbicides. They were reported in 1963 (Carpenter and Heywood, 1963; Wain, 1963) as potential postemergence herbicides. Bromoxynil for use in controlling chickweed (Stellaria spp.) was observed on the shelf of a local emporium. More information is available on the degradation of ioxynil than bromoxynil. However, their close similarity in structures suggests analogous modes of degradation.

Photolysis of the 3,5-dihalogeno-4-hydroxybenzotriles may be a factor in their herbicidal action as the herbicidal action of ioxynil and bromoxynil has been shown to be more enhanced in light than in dark (Ugochukwu and Wain, 1965). Irradiation with

ultraviolet light for 20 hours in benzene converted ioxynil to 3,5-dibromyl-4-hydroxy-benzonitrile, with the possible involvement of free radicals.

More than 78 per cent of the ioxynil in solution was adsorbed by the soil when 100 ml of a 1000-ppm solution was shaken with 50 g of an acid soil (Jones and Hatch, 1937). Almost 90 per cent was removed from solution when limed peat was used. Lime apparently precipitates the herbicide as the relatively insoluble free phenol, rather than removing it by adsorption to soil components. Nearly complete degradation was achieved in 19 days in a nonsterile soil, whereas no degradation was detectable in a sterile soil. It was proposed that the microbial degradation of ioxynil in the soil produces the corresponding amide and then the acid (Figure 6), with dehalogenation also possible (Jones and Hatch, 1937). Similar mechanism could be expected to occur with bromoxynil.

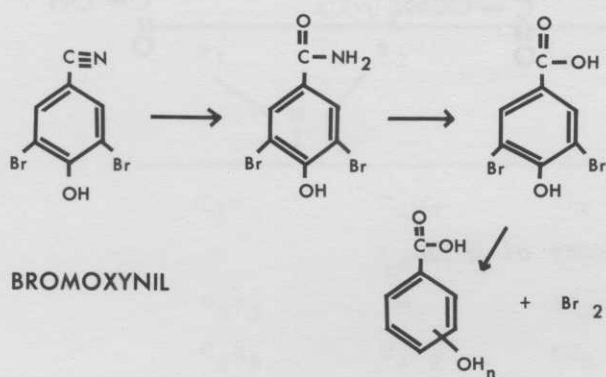
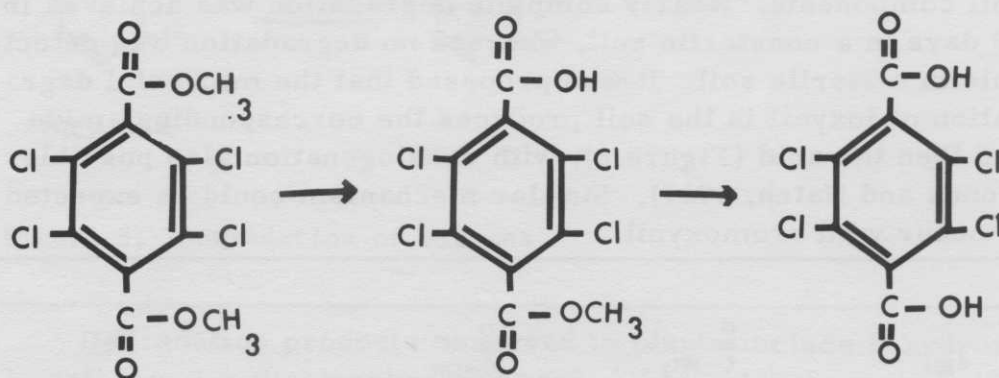


Figure 6. Degradation pathway of bromoxynil.

H. DCPA. DCPA is a benzoic acid derivative which has given excellent control of crabgrass when applied in the early spring before crabgrass has germinated (Anon, 1968b). Very little information is available about its lability in our environment. Crosby and L. Ming-yu (1969) predicted that irradiation of DCPA at wave lengths longer than 290 mu would produce only 2,3,5,6-tetrachloroterephthalic acid (Figure 7). The monomethyl and free dicarboxyl analogues have been tentatively

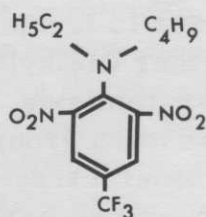
identified after application of DCPA to soil (Gershon and McClure, 1966; Skinner, Stallard and Priddle, 1964). The monoethyl derivative was found to undergo decarboxylation under the conditions of gas chromatography, according to Skinner, Stallard and Priddle (1964). Further degradation in soil of the dicarboxyl product 2,3,5,6-tetrachlorophthalic acid would probably involve decarboxylation.



DCPA

Figure 7. Degradation pathway of DCPA.

I. Benefin. Dinitroanilines have been used as dye intermediates for several decades. Both fungicidal (Clark and Hams, 1953) and herbicidal activity (National Research Council, 1955) have been described. Their use in turfgrass application is for crabgrass control. Both aerobic and anaerobic degradation pathways have been postulated for benefin (Probst and Tepe, 1969). Evidence supporting the postulated pathways exists in positive identification of certain of the proposed intermediates as well as the establishment of similar pathways for the benefin analogue trifluralin (a,a,a-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) (Figure 8).



BENEFIN

DEGRADATION PRODUCTS

ALKYL GROUPS			NITRO GROUP POSITIONS	
R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	2	6
C <sub>2</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>9</sub>	CF <sub>3</sub>	NO <sub>2</sub>	NO <sub>2</sub>
H	C <sub>4</sub> H <sub>9</sub>	CF <sub>3</sub>	NO <sub>2</sub>	NO <sub>2</sub>
C <sub>2</sub> H <sub>5</sub>	H	CF <sub>3</sub>	NO <sub>2</sub>	NO <sub>2</sub>
C <sub>2</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>9</sub>	CF <sub>3</sub>	NO <sub>2</sub>	NH <sub>2</sub>
H	H	CF <sub>3</sub>	NO <sub>2</sub>	NO <sub>2</sub>
H	C <sub>4</sub> H <sub>9</sub>	CF <sub>3</sub>	NO <sub>2</sub>	NH <sub>2</sub>
H	H	CF <sub>3</sub>	NO <sub>2</sub>	NH <sub>2</sub>
H	C <sub>4</sub> H <sub>9</sub>	CF <sub>3</sub>	NH <sub>2</sub>	NH <sub>2</sub>
H	H	CF <sub>3</sub>	NH <sub>2</sub>	NH <sub>2</sub>
OH	OH	CF <sub>3</sub>	NO <sub>2</sub>	NO <sub>2</sub>
C <sub>2</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>9</sub>	CF <sub>3</sub>	NH <sub>2</sub>	NH <sub>2</sub>

Figure 8. Degradation products of benefin.

Dealkylation followed by progressive reduction of the nitro groups appears to be the major pathway for aerobic degradation (Probst and Tepe, 1969). The initial dealkylation step occurs both in soil and photochemistry. The initial dealkylated compound is apparently the intermediate in dual pathways of degradation. One pathway converts the initial dealkylated metabolite to a,a,a-trifluoro-5-nitro-N-butyltoluene-3,4-diamine by reduction of one nitro group prior to further dealkylation. The alternate pathway involves further dealkylation and formation of a,-a,a-trifluoro-2,6-dinitro-p-toluidine, followed by subsequent sequential reduction of the nitro groups to amines. An additional product isolated from benefin treated soils which has not been reported for other dinitro-aniline herbicides was a,a,a-trifluoro-2,6-dinitro-p-cresol. Polar products are formed during the degradation of benefin and probably arise through the formation of aromatic amines.

Although certain of the products observed during anaerobic degradation are the same as those observed under aerobic degradation, their order of appearance is different. Reduction of the nitro groups followed by dealkylation appears to be the major anaerobic degradation pathway. The formation of polar products also is characteristic of the anaerobic degradative pathway. The key reaction affecting the rate of anaerobic degradation of dinitro-aniline herbicides is the formation of the first reductive products which serve as the intermediates in the formation of extractable polar products and nonextractable products (Probst and Tepe, 1969).

Photodecomposition and volatility are also known to affect the dinitroaniline compounds. Improved herbicidal activity of trifluralin by soil incorporation when compared to surface application (Pieczarka, Wright and Alder, 1962) suggests possible loss by either volatilization or photodecomposition. The vapor pressure of trifluralin ( $1.99 \times 10^{-4}$  mm Hg at 29.5°) suggests that volatility could be a factor under some field conditions (Probst and Tepe, 1969). Photochemical decomposition is characteristic of substituted aromatic compounds (Crosby and Mingyu, 1969; Scheinbaum, 1964). The photodecomposition sequence of trifluralin involved dealkylation. The chemical structure similarity of trifluralin and benefin and benefins instability to light suggests a similar pathway of decomposition (Probst and Tepe, 1969).

J. Terbutol. Terbutol is a recent newcomer to the field of carbamate herbicides. It is a methylcarbamate and, as such, represents a new class of carbamate herbicides. Terbutol has found some usage as a pre-emergence crabgrass control.

Although very little is known about the degradative mechanisms of methylcarbamate herbicides, certain analogies have been made with degradative mechanisms observed with certain methylcarbamate insecticides (Kaufman, 1967). Spencer (1965) suggested that methylcarbamates were subject to several possible points of metabolic attack, including hydrolysis of the ester linkage and oxidation of the N-methyl group, a ring substituent, or the ring itself. Products resulting from an initial attack at the ester linkage would probably be the enol, carbonate ion and alkylamine, with methylisocyanate as a possible intermediate. (Aeschlimann and Reinert, 1931; Casida and Augustinsson, 1959; Casida, Augustinsson and Jansson, 1960). Methylcarbamic acid also could be formed as an intermediate, rather than the methylisocyanate. In either case, the subsequent products would be methylamine and CO<sub>2</sub>.

Whether or not the degradation of terbutol would occur by this mechanism is questionable because of possible steric inhibition by the presence of the bulky tert-butyl groups in close proximity to the ester linkage. Evidence of such a steric effect has been obtained (Kaufman, 1970). We observed a competitive inhibition between numerous methylcarbamate compounds and isopropyl *m*-chlorocarbanilate (chlorpropham) and a chlorpropham-hydrolyzing enzyme. Failure of terbutol to act in a competitive fashion was attributed to steric inhibition. Because of this apparent steric inhibition of hydrolysis of the ester linkage, it was suggested (Kaufman, 1967) that terbutol might be more persistent in soil than other carbamate herbicides.

K. Neburon and Siduron. Neburon and siduron are both phenylurea herbicides. Neburon contains two alkyl substituents, an *n*-butyl group and a methyl group, whereas siduron contains a single 2-methylcyclohexyl substituent on the amine group of the urea linkage. Numerous processes are known to

affect the degradation of phenylurea herbicides in soil (Sheets, 1964a). Although no systematic studies have been carried out, urea herbicides appear to be sufficiently stable under normal temperature and soil conditions to resist hydrolytic breakdown or oxidation by purely chemical means (Geissbuhler, 1969; Hill et al, 1955). No unequivocal examples of the reduction of urea herbicide phytotoxicity in the field, due to the action of sunlight, have been reported. Considerable circumstantial evidence indicates, however, that light represents an important factor in the applicability and environmental fate of these herbicides (Ashton, 1965; Comes and Timmons, 1965). Among the most common urea herbicides, neburon was more stable to light than 3-phenyl-1,1-dimethylurea (fenuron), 3-(p-chlorophenyl)-1,1-dimethylurea (monuron), or 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron) (Jordan, Day and Clerx, 1963).

Photochemical products of monuron in solution resulted in replacement of the aromatic chlorine by a hydroxyl group and elimination of dimethylamine to give 4-chlorophenyl isocyanate (Crosby and Ming-yu, 1969). Presumably, the corresponding products would be formed during photochemical degradation of siduron or neburon.

N-Dealkylation is the major degradation pathway of urea herbicides by soil microorganisms (Geissbuhler, 1969). N-Dealkylation results in the formation of the corresponding alcohols and phenylureas. Subsequent degradation products of the phenylureas would be CO<sub>2</sub>, NH<sub>3</sub>, and the corresponding aniline. Degradation of neburon would result in the eventual formation of 3,4-dichloroaniline, CO<sub>2</sub>, NH<sub>3</sub>, methanol and n-butanol (Figure 9). The alcohols would be readily degraded by soil microorganisms. Recent evidence has demonstrated that the 3,4-dichloroaniline moiety is recalcitrant (Bartha, Lanzilotta and Pramer, 1967) to biodegradation. Further, it may be condensed to 3,3',4,4'-tetrachloroazobenzene (Bartha and Pramer, 1967). More recent evidence, however, would indicate that very little, if any, azobenzenes would be formed from aniline-based herbicides which are degraded only very slowly (D. D. Kaufman, unpublished data).



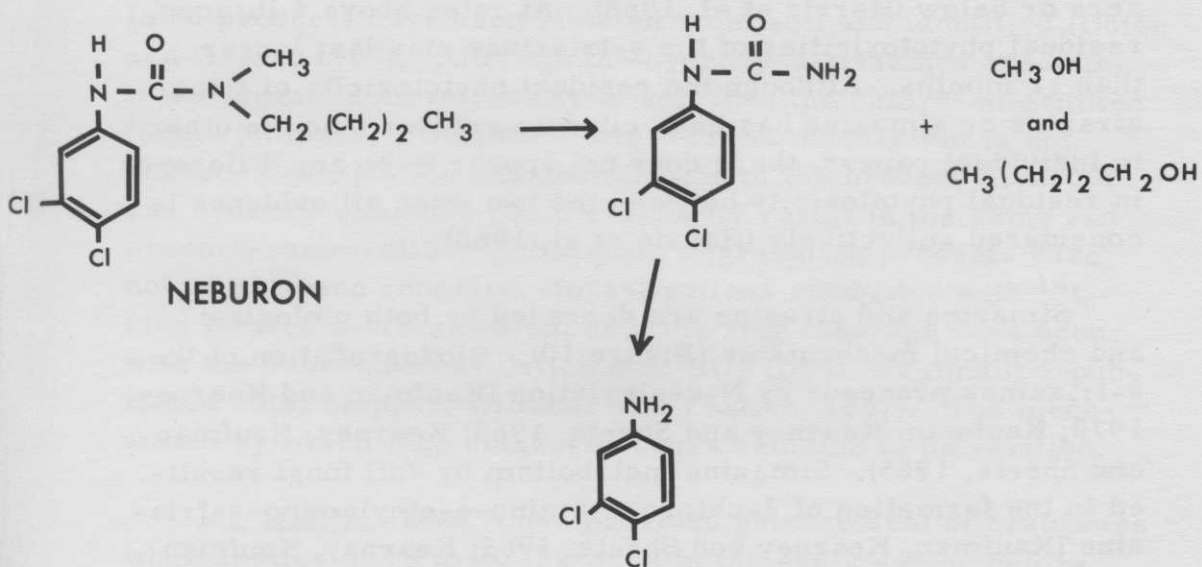


Figure 9. Degradation pathway of neburon.

A similar degradation pathway could be expected with siduron. Degradation products might include  $\text{CO}_2$ ,  $\text{NH}_3$ , aniline and 2-methylcyclohexanol. The presence of the bulky 2-methylcyclohexyl group as a substituent, however, may preclude dealkylation as a major degradation pathway for this compound and other degradative mechanisms may be more important. The long persistence period of 12 months or more could indicate the inability of soil microorganisms to readily degrade siduron.

L. s-Triazines. The s-triazines, atrazine and simazine, are also used as turfgrass herbicides. In southern states, atrazine has been used for pre-emergence control of crabgrass, goosegrass and most broadleaf weeds in established turf. In the Pacific Northwest, grass seed producers have used both atrazine and simazine for producing high quality seed, free from weed seed contamination.

The s-triazines are generally recognized to be among the more persistent herbicides. Residual phytotoxicity of s-triazines has been observed from 3 to 12 months at rates of 4 lb/acre or below (Harris et al, 1968). At rates above 4 lb/acre, residual phytotoxicities of the s-triazines may last longer than 12 months. Although the residual phytotoxicity of either atrazine or simazine has been cited as greater than the other in individual papers, there does not appear to be any difference in residual phytotoxicity between the two when all evidence is considered collectively (Harris et al, 1968).

Simazine and atrazine are degraded by both biological and chemical mechanisms (Figure 10). Biodegradation of the s-triazines proceeds by N-dealkylation (Kaufman and Kearney, 1970; Kaufman, Kearney and Sheets, 1965; Kearney, Kaufman and Sheets, 1965). Simazine metabolism by soil fungi resulted in the formation of 2-chloro-4-amino-6-ethylamino-s-triazine (Kaufman, Kearney and Sheets, 1965; Kearney, Kaufman and Sheets, 1965), whereas atrazine was metabolized to both 2-chloro-4-amino-6-ethylamino-s-triazine and 2-chloro-4-amino-6-isopropylamino-s-triazine (Kaufman and Blake, 1970). Subsequent metabolism of 2-chloro-4-ethylamino-s-triazine resulted in further dealkylation or deamination or both, followed by a dehalogenation of the molecule with the eventual formation of ammelide (Kearney, Kaufman and Sheets, 1965).

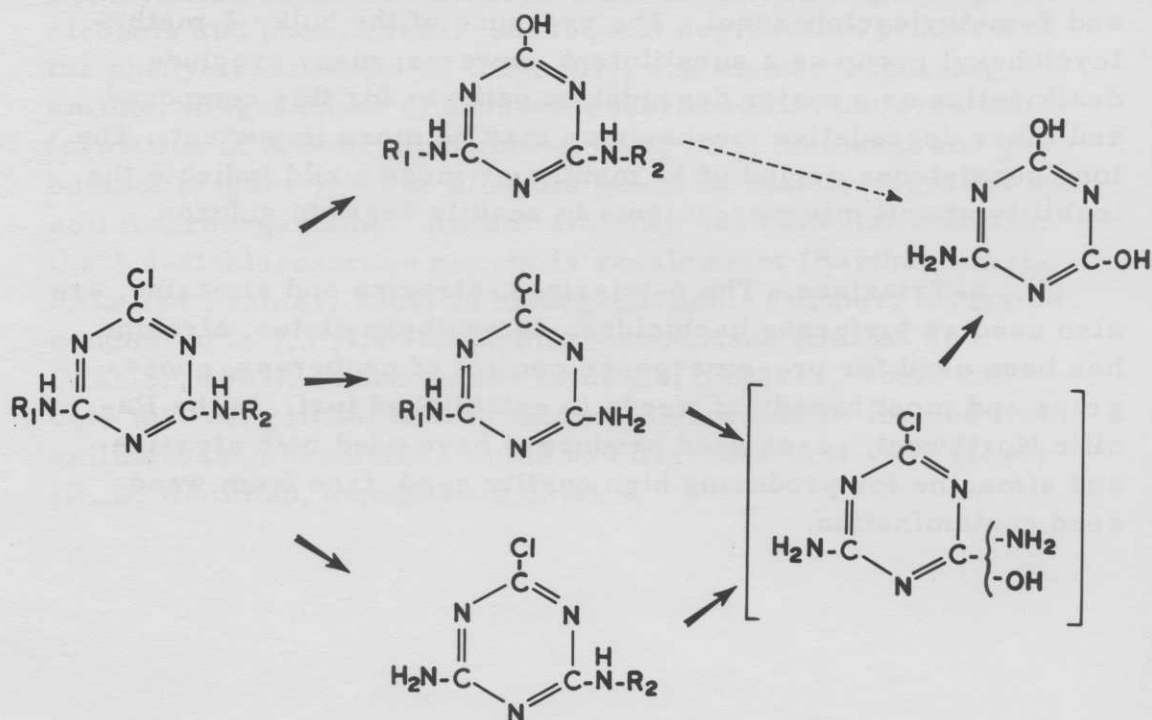


Figure 10. Chemical and biochemical degradation pathways of chloro-s-triazines.

Chemical degradation of simazine and atrazine occurs by dehalogenation with the formation of the corresponding 2-hydroxy-s-triazines. This process appears to be the major degradative mechanism occurring in soil (Harris, 1967); however, dealkylated products have been isolated from soil and identified (Obien and Green, 1969). Although the hydroxy-s-triazines are known to be degraded more readily in soil than the chloro-substituted forms (Skipper, 1970), their degradation mechanism is not known. Dealkylation and deamination of the hydroxy atrazine and hydroxy simazine could eventually result in the same end product--ammedlde. Subsequent degradation products have not as yet been reported. Investigations conducted with  $^{14}\text{C}$ -ring labeled s-triazines indicate the ring cleavage does occur with the subsequent evolution of  $^{14}\text{CO}_2$  (D. D. Kaufman; unpublished data; Skipper, Gilmour and Furtick, 1967). The mechanism by which ring cleavage occurs remains to be verified.

M. DMPA. DMPA has provided good control of crabgrass when applied at 15 to 20 lbs/acre in the early spring before crabgrass has germinated (Anon, 1968b). It is moderately susceptible to photolysis, and persists for 6 to 8 weeks in soil at recommended rates. Very little is known about the degradation of DMPA in soil. Several sites of attack are possible on the molecule. Hydrolysis to 2,4-dichlorophenol and O-methyl isopropyl phosphoramidothioate is apparently the major mode of degradation. A soil fungus, Aspergillus clavatus, degraded both DMPA and trace amounts of 2,4-dichlorophenol which appeared in the culture media (Fields and Hemphill, 1966). The growth of other soil fungi was stimulated by O-methyl isopropyl phosphoramidothioate.

N. Bensulide. Bensulide is also used for the control of crabgrass, but lawn grasses cannot be reseeded for 6 to 12 months following application, depending upon the amount of rain and soil type. We know very little about the mode of degradation of bensulide in soil. It appears to be more persistent than most organophosphate pesticides.

O. Paraquat. Paraquat has been used in southern regions for post-emergence control of winter annuals in dormant turf. It is registered for weed control during establishment of grass seed crops (Calderbank, 1968; Weed Science Society of America,

1967). Paraquat acts primarily as a contact herbicide. It is very rapidly adsorbed by plant foliage, and is resistant to removal by rain.

Very little is known about the persistence of paraquat in soils. Paraquat is unique among herbicides in its soil behavior in that it is very rapidly and strongly adsorbed on soil and, hence, completely inactivated by soil. It cannot be removed from soil by ordinary leaching, washing or solvent extraction. Refluxing with 18 N sulfuric acid is necessary to remove paraquat from soil (Calderbank, 1968). Most soils supposedly have sufficient capacity in the top inch of soil alone to bind many hundred times the normal field rates of application of paraquat.

Free of the soil, loss of paraquat can occur via photochemical decomposition or microbial degradation. Photochemical degradation of paraquat resulted in the formation of two major products, 4-carboxy-1-methylpyridinium chloride and methylamine hydrochloride (Slacle, 1965). Carbonyl compounds were suspected as transitory intermediates. These same products were shown to result from photochemical degradation of paraquat on the surface of plants in daylight (Slade, 1966). The ultimate fate of these compounds in our environment is not known at present.

A wide variety of microorganisms are capable of degrading paraquat (Baldwin, Bray and Geoghegan, 1966; Calderbank, 1968). Reduction of paraquat to colored free radicals has been observed in fungal and bacterial cultures. Only one product has been tentatively identified as resulting from microbial decomposition: 4-carboxy-1-methyl pyridinium chloride (Bozarth, Funderburk and Curl, 1966). Other products remain to be identified.

P. KOCN. Potassium cyanate (KOCN) has been used for post-emergence of crabgrass as well as being a fungicide. It decomposes rapidly in aqueous systems to potassium carbonate and ammonia and does not accumulate in soil (Thomson, 1967). Both of these degradation products could ultimately be of some fertilizer value.

Q. PMA. The degradation of several organomercurials has been reported (Menzies, 1969). PMA is degraded in soil and lost as metallic mercury vapors (Kimura and Miller, 1964). PMA is degraded more rapidly in nonautoclaved soil than in autoclaved soil, suggesting the role of biological processes. Essentially the same products, however, were recovered from both autoclaved and nonautoclaved soils. Presumably, the biological and chemical degradation pathway would be the same (Figure 11).

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### PMA

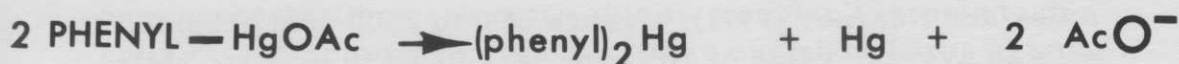
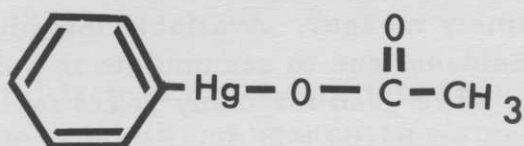


Figure 11. Degradation pathway of PMA.

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Booer (1944) postulated that organic mercury compounds reacted by base exchange with soil clays to form an intermediate compound. In the case of PMA, the intermediates would be a diphenylmercury and a mercury clay compound. The diphenylmercury compound would accumulate in soil, whereas metallic mercury would result from degradation of the clay complex. The metallic mercury would be rendered innocuous by formation of mercury sulfide. These results were not completely confirmed in later studies by Kimura and Miller (1964),

who found that PMA was degraded in soil and lost as the metallic mercury vapor. They recovered 14-16 per cent of original PMA applied as the mercury vapor. Approximately 60-70 per cent was recovered as the intact PMA. Although the remaining mercury residues were recoverable, they were not characterized.

R. Arsenicals. In recent years the organic arsenicals have been used to control certain perennial weeds. DSMA, MSMA, MAMA and cacodylic acid are important examples of this class of compounds. DSMA, MAMA and MSMA are commonly used in turfgrass for post-emergence control of crabgrass (Anon, 1968a). Cacodylic acid kills all grasses and is generally used only for sod renovation and spot treatments (Weed Science Society of America, 1967). Information on the persistence of arsenicals in soil is extremely meager. Available information indicates that arsenic residues tend to accumulate in soil. Lead and calcium arsenate were used for many years for insect control in tobacco, cotton, orchards and other crops. Arsenic residues in the surface 8 inches of orchard soils ranged from 23.2 to 580 ppm of  $As_2O_3$  in 21 samples collected in the northwest (Jones and Hatch, 1937). In a more recent survey by Woolson, Axley and Kearney (1971), a range of 0 to 2500 ppm arsenic, with an average value of 165 ppm, was found in orchard soils which were first treated about 40 years ago and some of which are still under treatment today. These samples were collected from the states of Washington, Idaho, Montana, New York, Oregon, Florida, Indiana, Maryland and Maine. Subsequent crops have often failed to survive on these abandoned orchard soils.

Schweizer (1967) has calculated that at normal rates of application of DSMA in Mississippi (equivalent to 6 kg per hectare per year), more than 50 years would elapse before arsenic residues would reach toxic levels in cotton. In contrast, rice is very susceptible to DSMA residues and phytotoxic levels may be reached in the time range of 3 to 80 years, depending on soil type.

Metabolism of most organic herbicides leads to the formation of less toxic compounds. Metabolism of DSMA ( $LD_{50}$  700 to 1000) and MSMA in soil yields the inorganic arsenate ( $LD_{50}$  40 to 100)--a compound that is 10 to 25 times more toxic (Von Endt,

1968). Both methylation and demethylation reactions may occur in the course of microbial metabolism of arsenicals. Challenger (1951) postulated that methanearsonic acid, cacodylic acid and trimethylarsine resulted from progressive methylation of arsenious acid. Demethylation of DSMA and MSMA resulted in the formation of the inorganic arsonate (Von Endt, 1968).

Arsenic reactions in soil are complex. Consequently, it would be erroneous to assume that equal applications to different soil types would yield the same degree of residual phytotoxicity. Arsenic exists in four principal forms in soils; i.e., the water soluble, calcium, aluminum and iron arsenates. Preliminary experiments at Beltsville assessing the phytotoxicity of each of these four fractions suggest that water soluble and possibly calcium arsenate exhibit phytotoxicity (Woolson, Axley and Kearney, 1971).

Several factors govern the fate and behavior of arsenic in soil. The availability of arsenic to plants is partly mediated by soil pH. Arsenic becomes less available for plant uptake as soil pH increases with the formation of insoluble calcium arsenates. Soils of high clay content with increased iron and aluminum concentrations are more able to complex arsenate than soils of lighter texture. Since arsenic and phosphorus are chemically similar, the availability of arsenic for plant uptake is proportional to the phosphorus content of the soil (Everett, 1963). The susceptibility of individual plant species is an important factor in assessing arsenic toxicity in soils. Methods of inactivating toxic arsenic residues in soils are currently under investigation at Beltsville (Woolson, Axley and Kearney, 1971).

S. Formulation effects. So far we have discussed the persistence and degradation of these chemicals as though they were the only pesticide present in soil, or that they were applied as technical grade materials. This is not the case, however, in actual practice. Most frequently pesticide chemicals are applied in combination with either fertilizers or other pesticides or both. Further, they may be applied as simple or complex ester, or salt formulations. It is well known that the behavior pattern of pesticides may change radically with changes in formulation.

Several of the commonly used turfgrass herbicides are available in numerous salt or ester formulations (Table 3), and are generally linked to the pesticide molecule through the carboxyl group of the pesticide. As reported earlier, soil microorganisms are capable of degrading certain esters of 2,4-D (Vlitos, 1952; Vlitos, 1953), presumably through simple hydrolysis. However, some evidence for transesterification and some type of beta-oxidation has been suggested in certain plants (Helling, Bollag and Dawson, 1968; Trichell, Morton and Merkle, 1968). Subsequent to hydrolysis, 2,4-D would be subject to the degradative mechanisms described earlier. Manometric evidence has been obtained that microorganisms can oxidize the alcohol moiety of the isopropyl and butyl esters of 2,4-D (Aly and Faust, 1964).

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Table 3. Common Ester and Salt Formulations for Turfgrass Herbicides

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Esters	isopropyl isooctyl 2-ethylhexyl butoxyethanol propylene glycol
Salts	dimethylamine diethanolamine triethylamine octylammonium dodecylammonium <u>N</u> -oleyl-1,3-propylenediamine

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Considerable information exists on the volatility of esters of 2,4-D and related compounds (Adams, Jackson and Barnesberger, 1964; Baskin and Walker, 1953; Day, Johnson and Dewlen, 1959; Flint, Alexander and Funderburk, 1963; Hilton, Jensen and Hull, 1963; Jensen and Schall, 1966). Esters of 2,4-D can be divided into two groups based on volatility; the isooctyl (the propylene glycol butly ether) and the butoxyethanol (low volatile esters). These are about 10 to 20 times less volatile



than the lower alkyl esters of 2,4-D, which include the isopropyl and N-butyl ester (Flint, Alexander and Funderburk, 1963). Usually, phenoxyacetic esters that contain five carbons or less in the alcohol moiety are considered "highly volatile," whereas those that contain more than five are "low volatile" esters (Baskin and Walker, 1953). A further refinement in the definition of "highly volatile" comes from a sophisticated approach using gas liquid chromatography to measure vapor pressure of 24 esters of 2,4-D and 2,4,5-T (Hilton, Jansen and Hull, 1963). A "highly volatile" ester is defined as any phenoxy herbicide with a vapor pressure greater than  $1.5 \times 10^{-4}$  mm Hg at 25°C. It is not known whether or not these criteria can be applied to other pesticide formulations.

Although considerable information is known about phytotoxic interactions of pesticide combinations, very little is known about their interactions which may affect behavior in soil. We have recently been working on the biodegradation of pesticide combinations in soil and have observed several striking effects in terms of altered persistence (Barnett et al, 1967; D. D. Kaufman, unpublished data). For example, the persistence of phenylcarbamate herbicide chlorpropham (isopropyl m-chlorocarbanilate) is increased in soil in the presence of several methylcarbamate insecticides. This phenomenon was explained by a competitive inhibition of the chlorpropham-hydrolyzing enzyme of soil microorganisms by certain methylcarbamates. We have also observed that the herbicide, dicamba, may be partially degraded more rapidly in soils treated with 2,4-D (D. D. Kaufman, unpublished data). The importance of this observation in the field, however, has not been determined.

### Mobility

The placement of a pesticide on its intended target-area has created few environmental problems. Movement of the pesticide from its site of application, however, is one cause of environmental contamination. Thus, mobility data are useful in evaluating the persistence of applied chemicals, as well as in defining conditions associated with pesticide usage.

Herbicides move by leaching, water or wind erosion, and by volatility. We have already discussed volatility where applicable in connection with individual compounds. Movement of

herbicides over soil surfaces occurs by water or wind erosion. Topography, permeability, and precipitation are important factors influencing surface runoff (Helling and Turner, 1968). Steep topography, low permeability and intense precipitation tend to accelerate runoff losses and herbicide mobility.

Formulation, rate of application and rainfall intensities influenced 2,4-D runoff on a cultivated, fallow, Cecil sandy loam (LeGrand, 1966). The isooctyl and butyl-ether ester formulations were far more susceptible to removal in runoff than the amine salts. Losses of 2,4-D were positively correlated with the rate applied, were greatest early in each storm, and decreased with the storm duration. Vegetative cover also influences surface movement. Initial losses of dicamba in runoff water were greater on sod than on fallow plots; whereas 2,4,5-T losses were about equal (Barnett, 1967).

Herbicide leaching implies the vertical movement by capillary and gravitational water of a dissolved molecule in the soil profile. According to LaGrand (1966), leaching occurs in the zone of aeration above the water table. Helling and Turner (1968) have developed a soil thin-layer chromatographic technique for characterizing the mobility of pesticides in soil. Differences in the effect of soil type on pesticide mobility have been observed. In lieu of a standard soil, they presented a system of five classes of pesticides arranged on the basis of mobility. The mobility scheme comprised the following  $R_f$  ranges: Class 1, 0-0.09; Class 2, 0.10-0.34; Class 3, 0.35-0.64; Class 4, 0.65-0.89, and Class 5, 0.90-1.00. Based on a review of the literature and the work of Helling (unpublished data) and Helling and Turner (1968), the commonly used turfgrass herbicides could be assigned to classes of decreasing mobility as follows: Class 5, dicamba, dalapon; Class 4, 2,4-D, 2,4-DP, MCPA, silvex, 2,4,5-T; Class 2, bensulide, bromoxynil, DSMA, neburon, siduron; Class 1, benefin, paraquat, terbutol, and Class 3, atrazine, simazine.

### Summary

We have discussed some of the chemical, biochemical and physical ways by which pesticides are dissipated from our environment. Differences and similarities exist in how these various processes affect major chemical classes of pesticides.

Although we know very little about the fate and behavior of some pesticides, considerably more information exists for many pesticides. You may recall that very few of the degradative pathways discussed involved complete mineralization of the pesticide to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc. The fate and toxicology of many of the degradation intermediates is unknown. Our knowledge of the ultimate fate of phenolic, aniline and heterocyclic ring structures in soil is very meager. Adsorption, absorption, leaching, runoff, wind erosion, volatility, chemical and biochemical reactions, and photodecomposition are all processes which affect both the persistence and degradation of turfgrass herbicides in our environment. One or two of these processes often predominate in effecting loss of a particular herbicide from soil. Properties of the soil, the herbicide and the environment variables act directly and indirectly, and interact in many combinations to influence herbicide behavior.

Pesticides are not significantly different in principle from other chemical substances that are an integral part of our civilization's environment. Their ultimate disposal, just as any other chemical, may produce particular problems if they persist. There is no reason, however, why modern technology cannot provide less hazardous materials and more adequate and safe disposal techniques. Such techniques will require continued research on the nature of the degradation of chemicals under the various environments. It will also require adequate attention to the hazards to man and other elements of the environment during the degradation process.

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## Discussion Period

Dr. Switzer: When studying the average persistence of turfgrass herbicides, what rates did you use? (Editor's Note: These studies are represented in Fig. 1)

Dr. Kaufman: These are all at variable rates. Really, I took a literature review. I did qualify that, in making these averages, I only used recommended rates for each compound. There are no excessive rates involved. On the other hand, there could be a different rate of application with dalapon, as opposed to any other chemical.

Dr. Switzer: I was thinking of DCPA, particularly, as opposed to bensulide. My experience has been that bensulide and DCPA have about the same residual activity at comparable rates. Yet, your graph indicated that DCPA has a half life of maybe two months, whereas bensulide was four or six months. I just wondered if the rates for bensulide were comparable to DCPA.

Dr. Kaufman: I really can't recommend on that, except to say that they were recommended rates of these compounds.

Dr. Bingham: You indicated that 2,4-D seemed to travel almost as far into the soil as dicamba. We have the problem with dicamba getting into the root systems of many plants, like ornamentals. If 2,4-D goes in the soil to this depth, too, why don't we have the same problem?

Dr. Kaufman: I would say it was a matter of degradation. From my own viewpoint as a microbiologist, I think of 2,4-D as being a readily degradable compound. This has been demonstrated. It is a very degradable compound. Dicamba, in contrast, is not readily degraded. We have looked for a long time for an organism that would degrade this compound. In the fusion system, it is at least resistant to microbial degradation, using a chloride ion as a major degradation. We were only using chloride ion liberation. In a situation where you have 2,4-D leaching it, the effect should be the same as dicamba. It wouldn't be taken up.

Dr. Bingham: I wondered if this thin layer system gave you similar results that you would find in the field situation. Maybe something like 2,4,5-T. Is this degrading as fast as 2,4-D? Could we get differences with the various phenoxy's?

Dr. Kaufman: Difference of what--persistence?

Dr. Bingham: Yes, and also the effect on ornamentals or plants that have shallow root systems. Is the difference between dicamba and phenoxy herbicides on ornamental plants following turf applications more related to uptake and translocation differences, than degradation?

Dr. Kaufman: I think there is very definitely a difference in the persistence, at least in terms of microbiology. There would be a difference in the persistence of 2,4,5-T. It is much more persistent to degradation. There is a lot known about structure effects here, and anytime you put something in another position--obviously the phenoxy compound should be in the 3 or 5 position--you impart resistance to degradation.

## PRACTICAL TOXICOLOGY IN CONSUMER USE OF TURFGRASS HERBICIDES

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### Introduction

My contact with people, relative to herbicides, is an indirect one. I'm not a turf man, nor a herbicide specialist. Many of those using herbicides, in my opinion, feel that herbicides really are not pesticides. They feel they are more like water, but perhaps smell differently. Some of the research people working with herbicides evidently have similar ideas.

### Toxicity Studies

The basis of toxicology goes back to the relationship of dose to response. Typically, we speak of acute oral doses; chronic or sub-acute doses involving repeated doses over an extended period; dermal doses to the skin, and inhalation. All of you are familiar with expressions of toxicities of this type. Oral, chronic, dermal, eye irritation, birth defects, etc., are all a part of the toxicology information needed to obtain registration of a pesticide. Preliminary chronic or sub-acute toxicities usually consist of 90 day feeding studies, and at least 21 days for inhalation, using guinea pigs. Inhalation studies are usually based on exposure to vapors, and generally have not included exposure to aerosol droplets or other particulate matter, unless the formulation studied happens to be specifically for use as an aerosol.

With the need for establishing tolerances for all compounds, chronic tests are the rule. However, in the past this was not so, particularly with herbicides and fungicides. Two year chronic oral studies are now standard, usually using rats, sometimes dogs, and occasionally monkeys. Occasionally third generation animal

studies for effects on reproduction are now required. Probably even more tests of this sort will be required in the future - using mice. We may also use egg embryo tests to detect teratogenetic effects. Cost of such tests are high because of the number of animals required and the extended time involved.

Wildlife toxicity is also an integral part of our toxicity studies. In the past, this has not been true. The standard procedure presently involves three species of fish and three species of birds. People interested in wildlife often ask why toxicity tests are not conducted on eagles, the osprey and several other birds. Obviously tests can't be run on everything, and animals have to be selected that are readily available in fairly large numbers. We don't have all the answers, but must proceed on a calculated risk basis just as we do when we cross the street.

Feeding studies have long been required for pesticides used on food crops prior to registration, but non-food uses sometimes escaped. These are now a part of the routine for all pesticides, regardless of use. In the future more of the answers relative to warm blooded animals will be needed. This, of course, involves increasingly refined analytical techniques. In the late 1940's, a sensitivity of 2 ppm for DDT was considered good. Anything less than this was considered as zero. Now we are working in parts per billion and parts per trillion levels and still sometimes seeking to go lower, particularly with water contamination problems and effects on wildlife.

The importance of reading the label has been stressed to avoid fatal accidents. Unfortunately, many of the children involved in such accidents cannot read and the parent or an adult has failed to comply with the label. I am now about at the point where I think it's an effort in futility. People just don't read labels.

#### Classes of Toxicity

Pesticide products have been grouped into four classes, depending on their toxicity for labeling purposes. Class I pesticides are highly toxic, based on oral toxicities to 50% of the

TABLE 1.

## FEDERAL INSECTICIDE FUNGICIDE AND RODENTICIDE ACT - CATEGORIES OF TOXICITY

CATEGORY	ROUTE OF ADMINISTRATION				
	SIGNAL WORD ON THE LABEL	ORAL (mg/kg) <sup>1</sup>	Probably Oral Dose for a 150 lb. man	DERMAL (mg/kg) <sup>1</sup> 24 hr. exposure	
			LD50	LC50	
I (HIGHLY TOXIC)	DANGER - skull and crossbones - POISON	0 to 50	a few drops to a teaspoonful	0 to 200	0 to 2,000
II (MODERATELY TOXIC)	WARNING	over 50 to 500	over one teaspoonful to one ounce	over 200 to 2,000	over 2,000 to 20,000
III (SLIGHTLY TOXIC)	CAUTION	over 500 to 5,000	over one ounce to one pint or one pound	over 2,000 to 20,000	
VI (RELATIVELY NONTOXIC)	none*	over 5,000	over one pint or one pound	over 20,000	

NOTE: \*None required based on acute toxicity; however, nature of product and use pattern may require appropriate precautionary statements

LD50 - the dose level which will kill 50% of test animals. Minimum of 14 days observation. Animals fasted for oral studies.

LC50 - the air concentration which will kill 50% of test animals exposed for a period of 1 hour. Minimum of 14 days observation. Vapor or gas may be expressed in ppm.

1 Equivalents: 1000 milligrams (mg) 1 gram (g); 28.3 grams 1 ounce; 1 kilogram (kg) 2.2 pounds (lb)

2 Equivalents: 1 liter (l) 1.06 quarts; 1000 micrograms (ug) 1 milligram (mg)

animals exposed, usually rats, of doses of 50 milligrams per kilogram or less; inhalation of not over 200 ppm and skin adsorption of 200 ppm. (Please refer to Table 1 for a summary of categories of toxicity.) If our proposed new restricted legislation in New York passes, all Class I poisons will be on the restricted list and will not be available to the general public. They will be sold only by vendors having permits and purchased only by people that have use permits. But the uses of these materials will not be limited, they can be used for any of the labeled uses.

Some herbicides are highly toxic and are in Class I; i.e., the dinitros, endothall and sodium arsenite. Pesticides in Class I have labels bearing the signal words "Danger-Poison" and/or the skull and crossbones.

Class II pesticides have moderately high toxicities, 50 to 500 milograms per kilogram, and have the word "Warning" on the label. Materials like diquat, paraquat and pentachlorophenol are examples of herbicides in this category. The warning on the label is much milder than on the Class I pesticides. The label of a product in this category warns against inhaling, cautions against getting it on the skin, taking it internally, and keeping it out of the reach of children. Generally, this category of materials is thought, even by responsible industry, to be too toxic for general availability to the average homeowner. As a matter of practice we do not presently recommend to the general homeowner audience anything but Class 3 and Class 4 compounds, with few exceptions which we call specialized uses.

Class 3 compounds bear the signal word "Caution." The principle problem with Class 3 pesticides is not from general exposure of the user, but from storing them in unmarked containers, so they are later misused. There is a need to treat all pesticides with respect. As long as pesticides are treated as poisons, difficulty can be avoided.

Class 4 pesticides do not require any warning or signal word on the label and are considered to be relatively safe; that is, as safe as a pesticide can be. Examples of these types of materials are dalapon, simazine and amitrole. In spite of the fact that amitrole is a Class 4 material, one that we think is relatively safe,



the Food and Drug Administration has refused to issue a tolerance for the material because of possible carcinogenicity. This action has been petitioned by the American Cyanamid Company and Amchem Products, Inc., and a fact finding committee has been appointed. This is one of the types of problem that will be encountered more and more. It's the sort of thing that should make us very careful in our presentation to the public if we are to maintain our credibility. We must not say that they are harmless materials. Better means for reevaluating materials as our standards change are needed.

### Evaluating Data on Pesticides

One of the difficulties encountered is the failure to recognize that the standards by which judgements have to be made are changing. As a result, we have been losing our credibility. One of the reasons is that oftentimes industry has taken the attitude that the benefits over the risks are proved beyond any doubt. Likewise, we have expected our critics to prove us wrong beyond any doubt. On the other hand, people that have criticized the industry, like the Environmental Defense Fund and others, have taken the attitude that the slightest shred of evidence is ample to raise a question and is of sufficient reason to keep a pesticide off the market. In dealing with this problem, the need to protect the environment and also to make certain that pesticides are available, must be recognized. Data must be evaluated as fairly as possible and let the chips fall where they may. If there is a reasonable doubt or question, and there are alternate methods, then the only prudent thing is to use these alternative methods. We must readjust our thinking and make changes as they occur rather than wait for them to be forced upon us.

When a chemist or conservationist starts making judgements on whether or not DDT is carcinogenic, I think he's out of his field. I likewise feel he's out of his field if he starts talking about oxygen production and algae in the ocean when he hasn't gotten beyond the test tube stage. The judgements on public health, such as carcinogenicity, teratogenicity and mutagenicity, should be made by people working in this field. The Food and Drug Administration and Public Health Department have these responsibilities. Also, other professional groups are capable and responsible. For

example, a five man committee of the American Medical Association reported in its May 11, 1970, Journal that the proof of DDT being a carcinogen is not complete and is something that still has to be established.

I don't know, frankly, how much action has been taken on warm blooded animals, or the effect carbamates have on mitosis. If there hasn't been any action, then someone had better instigate some research immediately. Also, I think that we, as plant scientists, probably shouldn't be talking too much about the harmless nature of these kinds of materials, relative to mitotic effects, if we do not have evidence.

Our state and federal agencies are not always sensitive to the needs of the public and accepting responsibility or assuming leadership. The Pesticide Regulation Division is opposed to the idea of the legislative activity of the states. But why are the states doing it? One of the reasons is because a need is not being met. As a result, the states have been forced to take action of their own. This is undoubtedly going to result in a certain amount of chaos. Much of this could have been avoided six to eight years ago if we had been sensitive to some of the facts which were as evident then as they are today, and responded with some action to curtail the uses of materials like DDT and dieldrin. We must change our attitude or we will continually find ourselves in situations of this sort.

#### Pesticides and Public Health

We must be more critical of pesticides and their effects on health and the environment. Who has any more right to be critical of pesticides than we? We are working with licensed and experimental materials all the time. If we aren't going to be concerned--we who are working with them, the ones that know the most about them--then I think we are not meeting our responsibilities. We must assume this responsibility and evaluate these conditions more carefully. There are few uses that are so great that they would take precedence over the public health. The public is now saying that our standards have been too lax; that they don't like some of the decisions we have made. If we aren't going to be sensitive to their needs and respond accordingly, they're going to take the decisions out of our hands.

The fact that PRD and FDA are both being transferred to a new Environmental Protection Agency is strong evidence of this.

We tend to talk to our own groups, tell how wild the other guy is, and sympathize with one another. Other groups, in turn, do the same thing. Unfortunately, as long as this situation exists, problems will continue. We must communicate with one another to obtain understanding. If an effort isn't made to see that the bird watcher is aware of the purposes and the need for pesticides, he's not going to care until it affects him personally.

### Control of Pesticides

I wonder how many of you have stopped to think about how the pesticide industry image has been brought about. We talk about registrations of pesticides; how difficult they are to obtain and how much more pest control we need. As of three years ago, the regulations necessary in this country to register a pesticide are more stringent than those required for most of our food additives and many of our drugs. This does not mean that the problem of safety to health has been resolved. In fact, our present state affairs is ample evidence that we have not solved them.

One of the reasons for the present difficulties is that pesticides are extremely well controlled and researched up the point of marketing. However, from the market place to their final use there is little control and anything can happen. The Pesticide Regulations Division does not label some of our more toxic materials for home garden use. Nor do they intend them for homeowner use, but the homeowner can purchase them at the commercial outlets. This is, of course, one of the reasons for the legislation to restrict the sale of highly toxic Class I materials.

Our image really has been created, not by what we've done prior to marketing, but what happens to the pesticide afterwards. Who ends up using most of the pesticides? Is it the highest paid man, the manager or the most knowledgeable? Usually it's the most poorly paid, poorly educated individual on the team. If we wish to continue to operate this way, we have only one alternative. We must go to the safest possible materials and sacrifice good control.

We all tend to resist the idea of a prescription type of operation, as practiced by the veterinarian or medical doctor. But neither the veterinarian nor the M.D. is in the spot with prescription medicines that we're in at the present time with pesticides. Both are using materials that are in many instances just as dangerous, although they aren't used on quite the broad scale or quantity. However, the basic problem is very similar.

To correct the situation, more control is needed for the people who use pesticides, making sure that they are better informed. We can control the materials which these people use. For example, of the 18 million people in the state of New York, only two out of every hundred are in agriculture or associated agricultural businesses. The rest of the public feel they don't need pesticides in spite of the fact that probably 80% to 90% of these people use them in their homes. They do not think of these materials as being agricultural chemicals and the same as those that they are criticizing; i.e., DDT. Most of them wouldn't admit or don't know that they ever used DDT, although they probably have the aerosols that contain it under the kitchen sink. If they do realize they have it, they are inclined to think that the small amount they have doesn't contribute to the problem.

Some trout from Lake George have been found with residues of DDT as high as 146 ppm. There is no agriculture in the area. Most of the DDT used in the area was by the State Conservation Department, but they haven't used any since 1962. In spite of this, the levels have continued to increase in these fish. This means that the tourists and cottage owners living around the lake are the only other possible place that DDT could have come from, unless it's fall-out from the air.

It's not going to be easy for us to change our outlook, but if we are going to be realistic, we must change. We've been on the defensive for several years and where has it gotten us? If this continues, we're going to lose all of our opportunities to influence pesticide decisions. The only way we can gain respect and influence what pesticides can be used and the part they can play is to willingly admit our mistakes or the possibility of harmful effects, and try to establish credibility.

## Lack of Communications

The question is how to get the facts to a mass audience. Most of you remember 2,4,5-T reports from Globe, Arizona. About one third of the inside page of the first section of the New York Times was devoted to 2,4,5-T and all the distortions that occurred to man, animal, plants, etc. Three or four weeks later, on about page 78 of Section 4, down in the lower left hand corner of the right hand page, there was a three inch article pointing out that a task force sent to investigate the 2,4,5-T incident found the facts not to be substantiated, except for minor distortion of a few plants. Most audiences I have talked to all have seen the original report, believe it, but almost none have seen the article appearing three weeks later reporting these were not the facts. Is this responsible reporting? Is this the way to acquaint the public with the facts of the issue?

The point is, the news media are selling news. Many do not seem to be interested in factual stores--the pros and cons--so the man on the street can make a sound decision. They're interested in what's going to sell the newspaper, or news program. Usually, this is something that's different and will catch his attention.

One of the biggest challenges that the universities and industry have in the future is how they inform the public adequately to make a fair decision. If we can get the facts to them, I have confidence that the right decisions will be made. If they do not have these facts, they have no alternative but to believe what is released by the news media.

## Discussion Period

Dr. Alley: You say we are the ones that are getting ourselves into a corner from pesticide recommendations. I don't believe this is so. I think everyone of us working with any form of pesticide have tried to tell the public all along what we know about them.

Dr. Dewey: Your comments are well taken. As you know, there are three kinds of pollution: pesticide, political and emotional. In some instances the political and the emotional aspects are much greater than our actual pesticide pollution. One of the most discouraging things is to see the utter chaos that exists in PRD and FDA. This is the result of decisions not being made by the technical people that have the information. I dare say that 2,4,5-T is a case of point. This is a subject of great interest and I am not well enough informed to discuss it. However, I've yet to see the scientific paper on which the final judgement was made.

Many of us have often said that these materials were not harmful and that we didn't think there was any health problem. You may honestly still feel this way, but I wonder if maybe what we should say is that this is an area outside our realm of responsibility. Health aspects are established by FDA, or the appropriate health agency.

We've had reports of captan being teratogenic. It isn't a herbicide, so we can talk about it a little more impartially. There have been several articles in the New York Times on the characteristics of this particular material. The FDA reduced the tolerance 50% but, as near as I can determine, this reduction was not based on the hazard of teratogenicity. It was based on the fact that the levels being used were only about one-half as great as they originally anticipated. The residue levels were low enough so that higher tolerances were not needed. This is the decision of the government groups charged with this responsibility. Let's put the responsibility where it belongs. If they've made a mistake, why should we adsorb it? At the same time, I think the public will recognize that we are being more honest about the situation, and this will improve our credibility.

Dr. Appleby: You mentioned briefly that we had made mistakes in the past that tend to create a credibility gap between scientists and the general public. Can you offer a quick example in the herbicide area?

Dr. Dewey: Just off hand, no. But I think we have some problems coming up. For example, compounds requiring carcinogenic studies are (maleic hydrazide) and amitrole. Compounds requiring further teratogenic studies are 2,4-D, amitrole, 2,4,5,-T and cacodylic acid. Consider the dioxins. The USDA says it needs additional information on 2,4-D, 2,4-DB, 2,4-DP, (sesone), dicamba, toxaphene, 2,4,5-T, tricamba, erbon and silvex. If we say that there is no hazard to these materials, and later they are judged hazardous, we will find ourselves in a position that is difficult to defend. We had better recognize some of these facts and be a little more realistic in our approach. We have been the experts, up to a point, because we've been working with only one type of audience. They have been receptive to us because we were giving them something they needed. Right or wrong, it's better than nothing. But the public doesn't quite see it this way. I think this kind of approach has already involved us in some of these problems.

Dr. Ahrens: We had been talking about the safety of herbicides, when used as directed--never in terms of safety for eating. I don't know of anybody in the herbicide field who has ever promoted the careless use of a herbicide or stated that it could be taken internally. I think we are in danger in our own thinking if we say that just because a compound is a poison, or because it's teratogenic, it isn't safe. I don't believe that. You have to prove, in the first place, that it occurs where it might cause injury when used in a particular situation. I don't think you can talk in terms of the hazard of a compound per se. It must be related to the use.

Dr. Dewey: I agree, basically, with what you're saying. Many times we have failed to recognize that there are misuses, and I think this is something we have to count on. I agree that maybe these materials aren't a hazard when properly used. But the point is that we are really not in a very good position to be making this judgement. We had better let the expert in this field decide on the level of hazard.

In 1956-1957, while serving on the National Committee of the Entomological Society of America, Public Relations Committee, we thought that we shouldn't talk about insecticides as poisons. Rather we should refer to them as pesticides, or anything but poisonous materials. I think it was the biggest mistake we could have made. As a result, we have people using these materials and thinking they are safe because they bought them in the supermarket.

Mr. Simmons: We've learned to live with pesticides from the standpoint of acute oral LD<sub>50</sub>. Now we're learning these things have other effects. It isn't unreasonable to expect chemicals to have these side effects, but we seem to be evaluating them from a standpoint of a desirable and undesirable, regardless of rate, rather than at a no effect and an effect level at a given rate. Are we going to move towards a decision making procedure using effects at specific rates as the guideline in the acceptance of a pesticide?

Dr. Dewey: Now I think you're really getting into the basis for the difficulty we're encountering. It all goes back to the Delaney Clause. If any material causes carcinogenicity, the Delaney Clause would be used to eliminate its use. The response to a chemical is dependent on the dose administered. If you use enough table salt, or many other household items, you can create all kinds of problems. But the Delaney Clause has not been applied across the board with many chemicals. At the present time, neither the public nor our legislative groups are willing to accept the concept of dose response information to make judgments on things like cancer.

I recently met with a group of medical toxicologists and they spent two-thirds of their time arguing about the ridiculous situation that exists relative to the Delaney Clause and cancer. One of the difficulties is that our standards and rules have changed. Warm blooded pesticide toxicity used to be limited to residues in food or acute toxicity, as you mentioned. Today our rules are changing. They now involve the more subtle effects, but no one has established what these standards are yet. Until these standards are established, industry is up in the air, and nobody knows where they're going or what the judgements are going to be based



upon. This is one reason why I say, let's not be caught making statements out of our area of responsibility. Let's recognize the people that are responsible for these areas.

Dr. White: We're in an unrealistic situation, I think. At least an extraordinary situation where the experts aren't the ones refereeing the game. We talk as experts and we are, but who accredits experts and who is our spokesman--outside of each one of us as an individual. As an individual, I am faced with the whole series of environmental organizations that exist in the United States. Where's the spokesman for our group? How do we proceed to narrow the credibility gap, if you will? We can't go on the way we are. Anyone can get up and call themselves an expert. I would like your comments on that. How should we proceed as a group now? Should we, for instance, be the ones who are drumming the boards for standards, rather than the people who are inciting the riot, or what?

Dr. Dewey: I believe we are experts in the use of the material for the intended purpose. It becomes available to us only after it has cleared certain hurdles. The hurdles are constantly being changed, but nobody knows to what extent. We're sort of under a blindfold running down the track.

One thing we should strive for is better standards. If we're going to have an Environmental Protection Agency, I think it behooves us, through our agencies, to try to obtain recognition that matters of this sort should not be settled on a political and emotional basis, but should be judged on factual basis. If possible, we should set up a buffering system between the political appointee in office and the staff that's doing the work, and makes the decision. The political appointee should be protecting the technical staff so decisions are based on fact and careful consideration. Many congressmen won't agree with this approach, but I believe this is presently one of our problems.

Another thing lacking in our system, and is probably one of the reasons why we're in trouble with 2,4,5-T, is that many of the operations and standards were set 20-25 years ago. The technology, tests and standards are much more strict today than they were at that time. Yet, we have no built-in mechanism for re-

evaluating some of these materials to make sure that they adhere to present day standards. So what happens? All at once someone files a claim in court, perhaps valid today, but ignored 20 years ago, bringing chaos to the whole area. We may need to plug into our system a method of reviewing and updating our standards in these areas. For example, our methods of assaying and determining possibilities of carcinogenicity, teratogenicity and mutagenicity are relatively new. There were practically no tests for teratogenicity in 1960. We still do not have a refinement which the toxicologists are willing to accept. They are not in agreement on what is adequate.

Dr. White: How do we change the rules?

Dr. Dewey: In many instances, recognition of the problem is half the battle. We are trying to work through the Association of Land Grant Colleges. I think our associations and our own attitudes have to be changed, and we have to have some unison of agreement in this area if we are going to be effective.

Dr. Green: The greatest misuse, in some cases, seems to be in crops where industry can't afford to do the toxicology work; consequently, they refuse to develop compounds. If users don't have restrictions, or somebody is not watching closely, they will use a material that isn't registered. The public consumes the product without knowing. Is it unreasonable to suggest that the federal government take the responsibility for standardizing toxicology studies and actually do the work, particularly in crops which may not be of great enough economical importance for industry to go through all the procedures necessary for registration?

Dr. Dewey: I agree that this is really one of the problems. If you are from the northeast where there is a great diversity of crops, you can appreciate how great this problem is becoming. At the present time we have a regional IR-4 project, which is a means set up at the federal level for the purpose of registering minor uses of pesticides. I think we are going to find this is inadequate. In fact, it's already inadequate. We have tried to furnish information at levels where we thought problems of this sort would be taken into account, or at least considered

and recognized. I don't believe the problem of minor uses or minor crops is recognized adequately at the federal level. The individual state certainly can't do it. Industry cannot be expected to spend sums for registration which are greater than they are going to realize in returns. Either we must change our approach or perhaps leave the responsibility up to the federal government. Presently, data has to be developed for each crop individually. Maybe we should be a little more liberal in this area and register uses on the basis of similar crops so research would not have to be duplicated for each crop. In many instances it is even hard for our Experiment Stations to justify; yet the information must come from somewhere if we continue to require it.

For example, I recently requested a DDT label at the federal level for some uses which we recommend in New York. One of these was for use on blackberries and raspberries. These crops represent only 1,200 acres in the whole state, and we're only talking about a single application. The federal government would not accept this because the research was based on strawberries, but would accept a 10,000 acre usage on fresh market sweet corn for about 9 applications at 1 lb/acre/application. This seems ridiculous to me! We should spend more research time working on sweet corn trying to find suitable alternatives, rather than working on blackberries to find a one pound usage involving a total 1,200 lbs., as compared to 90,000 lbs. on sweet corn. This is the kind of logic that seems to be completely overlooked.

Dr. Daniel: Who do the practitioners using agricultural products have in Washington to represent them? This came out very clearly at the American Seed Trade Meetings in 1970. A lot of people feel that, in the Department of Agriculture, they haven't had someone to champion the producer's cause. How do we performers, producers and users represent our golf course superintendents in Washington, so our turf is ready for the carts and the people who have more leisure time? How do we represent the homeowner in Washington so he has something besides crabgrass for the future lawn in Washington? How do we represent these users and represent them as a part of good environment?



## Special Discussion Period

(The following questions and answers were viewed following a tour of O. M. Scott & Sons research facilities. Host for the tour was David Green, Scotts Product Development.)

Dr. Daniel: How are you applying liquids in small plots? What type of sprayer and canister do you use? Many of us need better small plot application techniques.

Mr. Green: The small plot liquid applications are made through a modified spray system that we developed here at Scotts (Fig. 1). We use an air pressure tank that can be carried by the applicator or attached to a back-pack, as our source of pressure. This tank is charged with 120-150 lbs PSI and then, through the use of a regulator, this pressure is reduced to 30 lbs PSI.

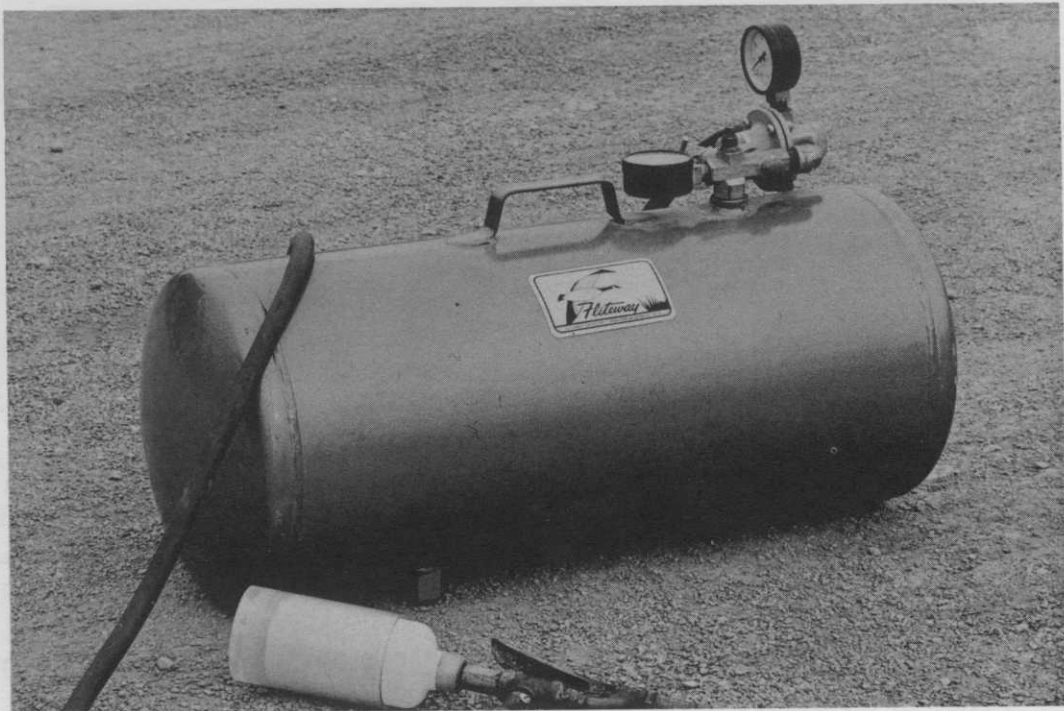


Figure 1. Modified spray system developed for making small plot liquid applications.

The actual spray unit consists of two valves; one turns the air pressure on and off, while the other regulates the spray (Fig. 2). The container for the spray consists of a plastic Nalgene bottle with a sleeve that slides over the bottle and provides additional support to the sides and bottom. The air pressure is turned on once to charge the container, then air pressure is turned off. The assembly is inverted so the liquid is in the discharge side of the container, then the liquid valve is opened to discharge the actual spray. We have adapters made to utilize 4 oz., 8 oz. and 1 liter Nalgene bottles.

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Figure 2. Close-up of spray unit and container (plastic Nalgene bottle with sleeve).

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After three years of use, we have found that this system is very effective, durable and completely portable. The Nalgene bottles used in application are discarded after the treatment. This greatly reduces the possibility of contamination in our plots. One problem we have encountered is that occasionally we get a Nalgene bottle that will not withstand the thirty pounds of air pressure, or is imperfect in its seal to the spray head.

By holding the spray unit upright, when the container is charged, any defects will be noted before the material is discharged, and the appropriate correction action can be taken.

Dr. Ward: After spraying a chemical, do you flush your line with water?

Mr. Green: We do not flush or purge the system with water. Concern by some of our people has been shown, but we have not encountered any problems in regard to compound contamination. In addition to discarding the container, the system is also purged with air after the liquid is dispensed.

Mr. Turgeon: We have a similar system at Michigan State. We use a one liter plastic Nalgene bottle and, rather than a sleeve arrangement, it is a canister. The plug is an integral part of the lid of this canister that operates in the upside down position off a CO<sub>2</sub> pressure source. All of this is carried on a belt around the individual that is spraying. As far as the discharge problem is concerned, we tested this system with 2,4-D ester and, using tomato plants as the target plant, we found that with normal discharge of CO<sub>2</sub> through the system, there was no subsequent carry over of the herbicide. So our system is quite well purged with the CO<sub>2</sub>.

Dr. Bingham: I was quite interested in the herbicides that get into the ground water using your sprinkling system. Are you studying the way the herbicides get into surface water?

Mr. Green: We have the capability to collect both surface and sub-surface water from these test plots. The plots are divided by cement dividers approximately 4 ft. in depth and the surface of the plot area was graded to a 4% slope. The surface collection is done by a tile which rises to the surface on the low side of each plot and drains into the collection basin. Sub-surface collection is done from a 4 in. clay tile centered in each of the plots. It also drains into the collection basin. No soil modification was performed in the area. The correct surface preparation was made, and the sod was placed on the surface of the native soil.

Dr. Kaufman: Are you looking for degradation products, parent material or both?

Mr. Green: We are looking primarily at the parent material. In some cases, we are looking for breakdown products as well. We are looking not only for pesticides, but we are also concerned about the movement of the phosphorus and nitrogen and how their availability or solubility is reflected on their movement in the surface and sub-surface waters.

Dr. Bingham: How do you sample the water that comes off? Do you sample at intervals, or according to volumes of water that you collect?

Mr. Green: Primarily, we collect samples from the water sample facility at specific intervals--not on a volume basis. Our collection facility is such that we can collect only up to a certain volume at any one time. The excess is permitted to overflow. We are operating strictly on time interval after treatment of the area after rainfall, or after irrigation has taken place on the turf. Two basic approaches are used to determine the content of these waters: bio-assays and chemical assays. In some cases we are running samples by both methods in an attempt to correlate results.

Dr. Appleby: How do you apply your granular formulations to these small plots?

Mr. Green: These applications are made through the use of modified Scotts spreaders. We cut the ends off a standard spreader, removed a section, then replaced the ends at a narrower width. The Scotts spreader sizes available commercially are 18 in., 24 in. and 36 in. Here we have cut them down to as narrow as an 8 in. width, and we have some other odd widths available. Other than this shortening operation of the spreader, we use exactly the same commercial spreader that a homeowner or professional person would utilize in application of a product.

Dr. Hemphill: Are you able to determine the content of the water from the drainage and mobility plots directly, or must you concentrate by activated carbon or some other method?



Mr. Green: At the present time we are running our analysis work on the straight collected sample. We are not concentrating it. This drainage and mobility facility is a relatively new system, and we are still in our infancy as far as developing testing procedures and all of our techniques.

Dr. Green: How do you come up with fertilizer recommendations for the homeowner, based on your fertility results here on the station? In other words, how do you extrapolate results to other soils and other environmental conditions?

Mr. Green: We have field stations located in other areas of the country, utilizing different soil types and climatic conditions. Our field station in Texas was moved recently in order to obtain a different soil type. The station was located on a heavy clay soil, and we have now moved it to an area that is almost completely sand. In addition to the work at our field stations, we also perform a considerable amount of testing on home lawns across the country. A separate division here at Scotts takes the proposed product from the product development group and disperses it across the country in virtually every state where the product would be considered for sale. By this stage in development, the product need no longer be applied by professionals, but is actually given to the homeowner who has a specific lawn problem that the product is designed to control. The homeowner makes the application of the product himself.

In other words, homeowners tell us which product is most desirable to them. Normally, we will have two or three formulations that have shown considerable promise in the development stage and the homeowners are instrumental in making the final decision on the product in question. After the consumer division has obtained the homeowners' opinion of the products, we determine if (1) we can sell the product for a profit and (2) the market area is of sufficient size to warrant our investment in the product. In recent years, product variation and regionalization have been determining factors in the development of consumer products.

Dr. Sylvester: What pre-emergence crabgrass killers have given you the best results?

Mr. Green: We have two materials that we include in our tests here in Marysville as standards: bensulide and Dacthal (DCPA). They have been very good in the past as far as providing excellent pre-emergence crabgrass control. There are other materials on the market, of course, but I would have to point to these two as being the most outstanding in providing pre-emergence crabgrass control from a single application.

Mr. Bangs: There are several effective pre-emergence crabgrass controls that aren't used in our product line. Would you point out the reasons for this?

Mr. Green: Several factors are considered before we decide to incorporate a specific chemical into our product line. First, and most important, the chemical must be safe. Scotts has a commitment to not market any product which, in recommended usage, might be a health hazard to the user, his family or his pets.

Also, we look for chemicals that can be used on many types of turfgrass. For example, bensulide and Dacthal are both effective in controlling crabgrass when applied as pre-emergence herbicides. The important thing here is that one possesses considerably more tolerance to a broader range of turfgrasses. Bensulide is safe for use on bluegrasses, bentgrasses and both coarse and fine fescues. Dacthal, on the other hand, cannot be used on bentgrass without serious injury, nor can it be used with fine fescues without some thinning taking place.

If we can use one compound over a wide geographic area for many different types of turfgrasses, as compared to another which can be used in a smaller geographic area and maybe only on one or two desirable turfgrasses, we would most certainly give additional consideration to the herbicide which shows the greatest degree of turf tolerance. These are some of the factors we take into consideration before we make a final decision in regard to a product active ingredient that will be sold commercially to the homeowner.

## MIDWEST CURRENT TRENDS IN TURFGRASS WEED CONTROL

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### Introduction

The development of modern herbicides used for turf control has provided safe, efficient and effective turf management tools. These tools are good, but it is well established that a better understanding of the interaction of herbicides with environmental factors must be obtained.

Solving weed problems today requires total performance; selective control of unwanted vegetation without indiscriminately contaminating the environment.

America was not made great by a do-without attitude, and as turf researchers, we must not be hemmed in unduly in our research program. The current trend in turfgrass weed control demands an increased useage of herbicides. Thus, more knowledge on herbicidal action, ample educational programs and adequate, but fair, pesticide labeling is emminently needed.

The present trend in weed control in the Mid-West is based on continuous research and can be best illustrated by presenting the history of turf herbicidal development.

### Broadleaf Weeds

#### 2,4-D

2,4-D was used for the first time in Indiana in 1945 at the Elks Country Club near Lafayette. Since that time we have used

the sodium salts, the high volatile esters, the low volatile esters and the amine salts. The lithate form has not received wide attention. Within the 25 years of commercial use, 2,4-D has recorded a phenomenal record of tolerance, acceptance, use and success. The current trend for 2,4-D continues to be the adding of other materials to it in order to have broad selectivity, plus enhancement between chemicals.

### 2,4,5-T

2,4,5-T goes back to about 1950, or perhaps earlier. Its selectivity opened new avenues for controlling viney weeds, particularly clover, at rates that were quite acceptable. 2,4-D with 2,4,5-T gave a combination for bush killing which has been very useful, however, its current restriction for use around homes and streams is questioned by many. Replacement by MCPP and dicamba has reduced homeowner needs for 2,4,5-T. In most cases, 2,4,5-T did not kill chickweed or knotweed.

### MCPP

Although widely tested in Europe and Canada, MCPP has not received broad usage in the United States. It is very selective on clover and can be added to other materials. The use of MCPP and dicamba started about the same time in the Midwest. MCPP is presently used in some formulations.

### Dicamba

Dicamba has been a real boost to complete weed control. Its excellent control of knotweed (at any stage), clover and common chickweed has given us combinations, including 2,4-D and dicamba. There is a question, however, of how much dicamba should be used--1/8 to 1/4 lb. active per acre--to satisfactorily do the job.

Formulations carrying 4 to 10 parts 2,4-D to one part dicamba have been formulated and are on the market. Our research continues towards using the least dicamba possible in combinations for selective weed control.

## Weedy Grasses

### Phenyl mercury acetates

Phenyl mercury acetates, such as PMAS, Liquiphen and Dimet, were developed in the late 1940's. Their fungicidal value, plus their selective kill of some weedy grasses, made them extremely popular. The toxicity of the solution to hands (skin burns) was repeatedly experienced by careless operators. Nevertheless, PMA was the first bright spot in selective crabgrass control. Several golf greens became free of crabgrass for the first time in the early 1950's with 3 to 5 applications of PMA. Later, other materials negated it to minor usage. It still can serve, but the number of formulations on the market has decreased to very few.

### Di-sodium methyl arsonate

In the late summer of 1953, two plots at Purdue University were treated with methyl arsonate. Methyl arsonates were found to be successful in selectivity controlling crabgrass, then dallisgrass, and later johnsongrass, sedge, sandburs, foxtails and barnyardgrass from established turf areas. Its later usage for dallisgrass and johnsongrass control in southern areas adds to its success.

The methyl arsonates--di-sodium, monosodium, amine--soon replaced the phenyl mercuries for crabgrass prevention. In 1958, post-emergence was 99% of the crabgrass control market; today it is less than 5%. Meanwhile, entire golf courses and many lawns have been cleared of growing crabgrass. The philosophy of being able to have turf without crabgrass has permitted the homeowner to raise his sights, to increase his fertilizer, to upgrade his varieties, and to expect more performance and achievement.

Post-emergence has been largely replaced pre-emergence. Why fight the competition later when it can be prevented earlier? Nevertheless, the significant contribution of crabgrass killing chemicals has been immeasurable in lawn improvement in the last 20 years.

## Crabgrass Pre-emerge

Our pre-emerge research began at Purdue in 1954. That same year a one bag treatment of PAX at Kansas State University proved to be beneficial. By 1956, our Field Day featured crabgrass controls, including Alanap, calcium arsonate and lead arsenate. At that time, arsenic powders were dusty and difficult to apply uniformly. The principle, however, was proven in the greenhouse that phosphorus reduction and arsenic build-up gave selective toxicity to numerous plants, including crabgrass. By 1961, there were several pre-emergence crabgrass controls on the market.

Long-term residual from calcium arsonate applied eight years previously was observed in St. Louis; subsequently, in numerous places many formulations of arsenicals have been used. After thirteen years, one-half of my front lawn (5,000 sq ft) remains crabgrass-free, whereas the other one-half continues year after year to have some infestation.

## Poa annua

The black sheep of the turf family today is no longer crabgrass, but Poa annua, particularly for the sod grower, on the fairway and on the green. Our initial work to find a control for Poa annua began in 1950. We have continued to work through numerous cycles. Arsenic, although it fades away, does control Poa annua.

When the area is 95% Poa annua, it is going to be very noticeable when that much grass dies - whether it be a fairway, edge of a green, or parts of fairways. When the arsenic eliminates the Poa annua, there is going to be bare ground and the need for replacement. Therefore, if it is a golf course not yet treated with arsenicals, it appears to be a two year job involving reduction in phosphorus, accumulation of arsenic and the introduction and increase of desired species.

Occasionally there has been damage, usually delayed, on greens and fairways; even lawns. But this has been the exception rather than the rule. Meanwhile, timely application and uniform rates have greatly reduced the potential of competition.

At Maketawah County Club in Cincinnati, Ohio, the fairway was treated with arsenicals, and eventually it was perfect bluegrass. They changed superintendents and the new one added phosphorus and stopped the arsenic, and the fairway is again 95% Poa annua. The phosphorus additions overrode the arsenic.

It is estimated that over 500 golf courses in the Midwest and Northeast have fairway treatment programs with arsenicals, and over 100 of these have complete Poa annua restriction as an on-going fairway program. It is difficult and tedious. There should be an easier way.

The value of other pre-emergence materials, beyond arsenicals, offer certain convenience. In 1964, Tupersan was widely researched and it has served on new seedings very well. Balan at 3 lbs. active per acre has prevented crabgrass germination. So will Dacthal and Betasan at the proper rate. On established, uniform turf, one early fall application may be satisfactory for Poa annua control.

There is much potential in the use of growth regulators, such as Po-San, to produce short-term restriction in clippings, etc. There is also much potential in combinations which would permit selective restriction during introduction of special new varieties, such as elite type bluegrasses.

#### Summary

With the availability, selectivity and programs of herbicidal use, nearly every turf weed may now be controlled. Controls for bentgrass in bluegrass, for quackgrass in bluegrass, and tall fescue in bluegrass are still needed. These are difficult problems.

Today it is wise usage of chemicals that should be pushed. And it is careful planning and maximum utilization that should be encouraged.





## NORTHERN CURRENT TRENDS IN TURFGRASS WEED CONTROL

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### Introduction

Chemical weed control in turf became feasible when 2,4-D became available in 1946. Since that time, many other herbicides have been developed for use on lawns, golf courses and other areas of turfgrass. Some of these proved helpful for a time, but have been replaced by newer and better materials. The purpose of this paper is to consider our present turfgrass weed control methods and to discuss possible future changes that may occur as the result of research and/or government and public pressures.

At the outset, it might be useful to outline the turfgrass and weeds with which we in eastern Canada and the northeastern United States are concerned. Most lawns and golf courses in the area contain primarily bluegrasses and fescues. Merion and common Kentucky bluegrass are used most widely with Fylking and Windsor, coming in strongly in some areas. These latter two grasses are showing up on many golf courses, particularly on tees, aprons and approaches. Pennlawn creeping red fescue is widely distributed, both on lawns and on golf courses.

On golf course greens one finds Toronto, C-15 and Penn-cross bentgrass used most frequently. Northland and Cohansey look very good in research trials in Canada because of their early spring growth.

The broadleaf weeds found in turf in our area include dandelion (Taraxacum officinale Weber.), common plantain (Plantago major L.), ribgrass (Plantago lanceolata L.), heal-all (Prunella vulgaris L.), creeping charlie (Glechoma hederacea L.), black medick (Medicago lupulina L.), mouse-ear chickweed (Cerastium vulgatum L.), Veronica spp., creeping buttercup (Ranunculus repens L.), English daisy (Bellis perennis L.) plus several other less frequently occurring species.

Weedy grasses include crabgrass (Digitaria spp.), annual bluegrass (Poa annua L.), quackgrass (Agropyron repens L. Beauv.) and creeping bentgrass (Agrostis stolonifera L.). Of lesser importance are other annual grasses, such as foxtail and panicum, and perennials, such as orchardgrass and timothy.

#### Broadleaf Weed Control

The use of single herbicides, such as 2,4-D, 2,4,5-T or fenoprop (2,4,5-TP), has been almost completely replaced by mixtures of chemicals. Since each herbicide misses some of the weeds commonly found in turf, mixtures obviously would be expected to give a broader spectrum of control. Many mixtures are available, with the most commonly used ones being 2,4-D-fenoprop (2,4,5-TP), 2,4-D-mecoprop (MCP), 2,4-D-dicamba, and 2,4-D-mecoprop-dicamba. Even these mixtures will not control all broadleaf weeds found in lawns in our geographic area. Yarrow (Achillea millefolium L.), speedwell (Veronica filiformis Sm.) and mallow (Malva neglecta Wallr.) are among the most common resistant species found. However, control of such species may be obtained by using good maintenance procedures--fertilization, mowing and watering--in addition to the use of herbicides.

The question arises as to the long range effects of continued use of these herbicides on the desirable grasses. Remarkably, few studies of five years or longer have been carried out on specific turf species, even with 2,4-D. Our general observations would indicate that the phenoxy herbicides have had no harmful effects, either directly on the grass, or indirectly by affecting the soil microflora. The same seems to be true for dicamba.

Nevertheless, we need additional "hard" data in this area-- data on rate of shoot and root elongation, clipping weights and color changes.

### Selective Control of Grasses

Although few problems currently exist relative to broad-leaf weed control in turf, the same cannot be said for the control of unwanted grasses. Methods to selectively remove perennial grasses, such as quackgrass, bentgrass, orchardgrass and timothy, without damage to the desirable species have not been found. However, the search continues, occasionally with some success (bromacil looks promising on orchardgrass).

Most annual grasses respond well to existing chemicals. Crabgrass in home lawns is still much discussed by lawn and garden editors but is readily controlled by several chemicals, including benefin, DCPA, bensulide, siduron, Azak and Bandane. These herbicides are applied as pre-emergence crabgrass controls and cause no discoloration to established turfgrasses. This condition is much more preferable than the temporary yellowing that usually occurred from the use of the older post-emergence crabgrass chemicals. In Ontario, fall application with bensulide or DCPA has been just as effective as early spring treatments. Azak has caused marked damage to the turf when applied in the fall, and benefin and siduron are ineffective the following spring.

Annual bluegrass (Poa annua L.) is considered a problem by many golf superintendents in the northern U. S. and Canada. It is found in golf greens, where it presents a different texture than bentgrass, and is particularly undesirable because it sometimes kills out rapidly, leaving bare areas. On the other hand, some superintendents feel they know how to "manage" annual bluegrass and find it useful because it grows rapidly in the spring, filling in areas that were killed by desiccation or snow mold.

The "crabgrass herbicides" may give good control of Poa annua under some conditions. At other times they do not.

Treatment with arsenicals is still used with good results by many golf courses, but it is slow and injury may result if even slightly excessive amounts are applied. In addition, the toxicity of the arsenicals has put them under somewhat of a cloud at the present time. Thus, it would appear that better methods are required to selectively remove annual bluegrass from bentgrass.

### Formulations

The first 2,4-D formulation commercially available was the oil-soluble ester. Widespread damage to susceptible crops from this volatile liquid soon led to its use being restricted to areas remote from such crops, and to the development of the low volatile sodium salt and amines of 2,4-D. This trend toward formulations that are less likely to vaporize has continued throughout the years as other herbicides useful on turf have been developed. There are very few, if any, ester formulations still sold today for use on turf.

Granular formulations of turf herbicides have been produced on a wide range of carriers. Currently, the most popular carrier is fertilizer. Such herbicide-fertilizer combinations make good sense as they not only reduce the effort of application, but the fertilizer helps control the weeds by stimulating the desirable grasses. Both "light-weight" and "heavy" granular formulations are on the market with little or no difference in effectiveness noticeable in research trials.

Mixtures of herbicides with other pesticides have been tested for use on turf, and are commercially available. There would seem to be merit in some of these mixtures, but with others the benefits are dubious. Additional research is required on possible interactions of the components of these mixtures, and whether they can be applied at a time that is satisfactory for obtaining good results from all components of the mixture. For example, a mixture of a pre-emergence crabgrass herbicide and a post-emergence broadleaf herbicide cannot be applied in our geographic region at a time that will give control of both types of plants.

## Growth Regulators

Several chemicals are currently being tested, and two are being used by golf course for grass growth retardation. An ideal chemical would inhibit the growth of grass at a desirable height, maintain a suitable green color and control weeds at the same time. No such chemical has been found to date, but the morphactin materials show some promise, particularly for use on roughs and hard-to-mow areas of the golf course. In addition, fairly good dandelion control is given by this chemical.

## Application Equipment

Most turf weed control chemicals of the 2,4-D type were originally applied by an air-pressure sprayer. This is still true when these herbicides are used on golf courses, turf farms, parks and roadsides. However, the trend has been away from spray applications, as far as home lawns are concerned. The difficulty of maintaining a sprayer from year to year, coupled with the fact that a separate sprayer had to be kept for herbicide use, made a homeowner very receptive to other types of application equipment. Thus, granular herbicide-fertilizer combinations that could be applied with a relatively inexpensive, long-lasting spreader have become popular. Also, particularly for urban dwellers, aerosol herbicide applicators have found ready acceptance.

A similar picture has developed with respect to the application of pre-emergence chemicals for crabgrass and Poa annua control. Here, essentially all homeowner use is restricted to granular materials applied with a fertilizer spreader. Golf courses and parks apply a greater proportion of these herbicides as granulars than they do the 2,4-D-like chemicals, primarily because of the formulations available and the fact that smaller areas are usually involved.

In the future, the use of air-pressure sprayers will further diminish. Gravity flow machines or other devices that will reduce drift hazards will be used by more golf courses and others

for treatment of large turf areas. Aerosol containers, for all their ease of use, will not increase in favor among homeowners because of their limited potential for other than "touch-up" control. Thus, the current trend toward the application of more herbicide-fertilizer mixtures on lawns will undoubtedly continue.

### Legislation

We have seen the effects of pressures exerted by a sometimes misinformed public on several pesticides in the past few months. These pressures will continue and we can expect that some of the herbicides used for turfgrass weed control will come under fire. Already we have seen 2,4,5-T banned for several uses in both the U. S. and Canada. Even 2,4-D has come under a cloud as a "potentially dangerous" teratogenic agent. Any chemical that has any appreciable persistence in the soil is suspect, which would include dicamba. Thus, our research on turfgrass herbicides must be oriented more and more toward obtaining "hard" data on such things as long-term effects and possible toxicity to soil organisms in order to counteract the scare stories so prevalent today.

## WESTERN CURRENT TRENDS IN TURFGRASS WEED CONTROL

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The current trends in turfgrass weed control in my section of the country, and perhaps a reflection of the western area, have not changed much in the last few years. We are using practically the same pre and post-emergence herbicides that we did four or five years ago, and our methods of application are about the same. We have changed the time of application in a few instances; e.g., mid-August instead of a September application of most pre-emergence herbicides for Poa annua control. We still use DCPA, bensulide, benefin and diphenamid on our bermudagrass turf for annual grass control, and 2,4-D, silvex, and dicamba for the broadleaved plants. The organic arsonates are used for the post-emergence control of crabgrass (Digitaria spp.), sandbur (Cenchrus pauciflorus), johnsongrass (Sorghum halepense), dallisgrass (Paspalum dilatatum) and nutgrass (Cyperus rotundus). The contact herbicide, paraquat, is more widely used now for the control of winter annual plants, particularly in dormant bermudagrass turf.

### Consumer Use of Herbicides

There is little doubt that the homeowners of today are generally interested in the production of good turf and are willing to spend time and money to achieve this goal. I think this is a reflection of the economy and the free time people have to spend working in their lawns. Too, this is a very important form of relaxation for many people. Dr. Dayton L. Klingman, Weed Investigations, USDA, at a recent meeting in Virginia, commented that there is a limit to how much money people will spend on weed

control. Although homeowners are willing to spend time and energy in the production of a rather high quality turf, I believe they would prefer to combine as many operations as possible, such as the application of herbicides and fertilizer, and minimize the number of operations required per year.

There is still a need for herbicides with lower concentrations of active ingredients for a greater margin of safety in home lawn use. Even among turf research workers, there is some reluctance to use translocated herbicides for broadleaf weed control in mid-summer that are highly concentrated, or present a drift hazard for other plants. This would be true of dicamba and 2,4-D in some formulations. Herbicides such as these exhibit maximum activity when absorbed by plant leaves, but they also have considerable activity in the soil. Dicamba used alone at recommended rates for broadleaf weed control is causing, in my opinion, some second thoughts by the average homeowner on its use.

#### Ecological Concern

Concern by the general public over the environment and pollution problems seems to have reduced the use of some arsenic compounds on home lawns. Herbicides that accumulate to toxic proportions in the soil profile are, in general, probably declining in popularity for regular use in weed control programs. The use of foam as a carrier and a marker for herbicides used by the homeowner, as well as industrial concerns, perhaps will provide adequate safety for the mid-summer application of translocated herbicides that are now used with some reluctance, or not at all. Perhaps we will see a greater number of combinations of herbicides with synergistic activity being used. A combination of such herbicides could, perhaps, be used at much lower rates with equal or greater effectiveness than either of the materials used alone.

#### Summary

The current trends in turfgrass weed control in the western part of the United States, in my opinion, have not changed much in the last few years. We are using the same pre- and post-emer-



gence herbicides, plus maybe one or two new ones, that we did four or five years ago. Our methods of application are about the same, but we have changed the time of application in a few instances. In general, the herbicides DCPA, bensulide, benefin and diphenamid are used for the pre-emergence control of annual grasses, with 2,4-D, silvex and dicamba used for the post-emergence control of broadleaved plants. The contact herbicide, paraquat, is widely used for the control of winter annual plants in dormant bermudagrass turf. A need still exists for herbicides with lower concentrations of active ingredients for greater margins of safety for use by homeowners. There will probably be more combinations of herbicides with synergistic activity made available for general use. These will provide equal or greater effectiveness than either material used alone, and at much lower rates.



## SOUTHERN CURRENT TRENDS IN TURFGRASS WEED CONTROL

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The development of herbicides for use in warm season turfgrasses has been distinctly different from that in cool season grasses because of differences in the susceptibility to some of the more common turf herbicides. For example, centipedegrass, bahiagrass and St. Augustinegrass are not tolerant to the organic arsenicals. The most common turfgrass along the Gulf Coast region, St. Augustinegrass, is susceptible to the phenoxy herbicides as well. On the other hand, the triazines can be safely used on St. Augustinegrass, centipedegrass and zoysiagrass.

Effective and safe herbicides for weed control in St. Augustinegrass was not developed until the early 1960's. The first experiment to demonstrate the tolerance of St. Augustinegrass to triazine herbicides was conducted by Ralph W. White, Jr., in 1958. At that time, much of the St. Augustinegrass sod was heavily infested with water sedge (Kyllingia spp.). White tried five herbicides and found simazine gave outstanding control of water sedge and other weeds, with no injury to St. Augustinegrass. Later, tests indicated that atrazine gave better post-emergence control of dicotyledenous weeds than did simazine. O. M. Scott & Sons employed Mr. White and, during 1960 and 1961, extensive turf weed control experiments were conducted throughout the South. In 1962, a combination fertilizer-herbicide (containing atrazine) was marketed under the name of Bonus for St. Augustinegrass. The rapid and widespread acceptance of Bonus for St. Augustinegrass and a companion product, Bonus for

Dichondra, added much impetus to the development of products containing plant nutrients and pesticides. Thus, Scotts was a pioneer in the development of a safe, effective and easy to apply herbicide for control of weeds in St. Augustinegrass and dichondra.

In addition to the differences in tolerance of warmseason and coolseason turfgrasses, the prolonged growing season in the South presents other problems. Annuals do not adhere to the "prescribed" life cycle for annuals. For example, in south Florida, crabgrass germinates 12 months of the year. For pre-emergence herbicides to be effective under these conditions, it is usually necessary to make three or four applications annually. Also, crabgrass and other annuals do not die a natural death after producing seed, but continue to be a problem for two or more years.

The numerous species of weeds present in southern turfgrasses makes control difficult. Many of the weeds present in the North are also found in the South. In addition, several species indigenous only in the South are common problems. Nematodes, insects and fungi frequently weaken turf, allowing weeds to become established. Sandy soils, high temperatures, and winds causing severe moisture stress weaken turfgrasses and permit invasion of drought tolerant weeds.

The condition outlined above explain why turf weed control is necessarily "big business" in south Florida. While no one chemical is a panacea, effective herbicides are now available for most situations.

The pre-emergence herbicides, except siduron, that are used on coolseason turfgrasses can also be used on the warmseason turfgrasses. The organic arsenicals and the phenoxy's can be used for post-emergence control of weeds in bermudagrass and zoysiagrass. Phenoxy's also can be used on centipedegrass and bahiagrass.

Atrazine is the primary herbicide for use in St. Augustinegrass. This herbicide also can be used for control of weeds in zoysiagrass and centipedegrass. It provides effective pre-emer-

gence control of most annual weeds. In addition, it will give post-emergence control of the common broadleaf weeds, except creeping beggarweed (Meibomia or Desmodium spp.).

Recent tests indicate that Kerb and Herban give effective and safe control of Poa annua in bermudagrass. These two herbicides gave both pre- and post-emergence weed control. Presently, however, neither is labeled for use on bermudagrass.





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