SURVEY OF CERTAIN WEED CONTROL PROBLEMS IN AFRICA SOUTH OF THE SAHARA

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Introduction

The object of this paper is to survey some of the tropical weed problems in Africa, south of the Sahara. The limits for equatorial, tropical and sub-tropical zones is accepted as 34°, which shows that practically the whole of the sub-continent, except for a small area in the Western Cape Province of South Africa, falls within this classification. Problems in the more temperate zones are similar to problems encountered in Europe, but observations are confined to the more important problems having a distinct tropical or sub-tropical bearing.

In order to review adequately the weed problems in this vast continent, it is necessary to survey the problem of agriculture as a whole in Africa, and to view the control of weeds from this aspect, in order to adopt a realistic approach to the problem.

It is recognised, especially in an undeveloped country, that the natural vegetation or ecological types of a region give a guide to the important factors of climate and soils, which again govern the suitability or potential of the land for agriculture. On the basis of the work of Shantz & Marbut[1] and Meredith & Hall[2] the region has been divided into eight distinct vegetation units or formations, the relative importance of which is indicated in Table I.

Table I

Vegetation type	Estimated area, square miles	Percentage
Tropical forest	1,191,800	13·8
Non-thorny woodland—tall grass	1,333,000	15·5
,, ,, ,, —short grass	858,100	10·0
Thorny woodland—tall grass	1,950,800	22·7
,, ,, —short grass	1,514,432	17·6
Grassland	433,000	5·1
Macchia	278,300	3·2
Desert and semi-desert	747,766	8·7
Others (temperate forest, swamps)	304,108	3·4
	8,621,300	100·0

These regions are indicated diagrammatically in Fig. 1 from which it is seen how the various formations are grouped in nearly concentric rings around the tropical rain forest. The change from one type to another is gradual, except where distinct topographical changes occur, and is primarily a result of diminishing water supply, as can be seen from an inspection of the rainfall distribution over this area. Within this great area, changes in altitude bring about changes in rainfall and temperature with corresponding reaction of the vegetation. For instance, increasing altitude accounts for regions of grassland or temperate forest and decreases for tracts of thorn thicket.

In general, tropical climates differ from temperate climates in the absence of large seasonal variations in temperature—the diurnal range generally exceeding the seasonal. Except in the equatorial zones, wet and dry seasons are sharply distinguished, and the hottest time of the year is just before the rains. The rain generally falls at great intensity in sharp thunderstorms. During the dry season, relative humidity is low and arid conditions unfavourable to plant growth prevail.

Tropical rain forest

This is the most luxuriant type, having developed under conditions of high rainfall and temperatures. The rainfall varies from 60 to 160 in. and the annual range of temperatures is 4°F. Although there are two rainfall peaks, there is no distinct dry season. The forest has a continuous canopy and has many layers.

The principal economic agricultural activities are growing of the oilpalm, cocoa, rubber, coffee, and to a lesser extent, bananas and rice. Apart from weeds in these crops, the principal weed problem is the control of water hyacinth.

sub-continent—that in Southern Africa—the need today is for an empirical approach to the problem of weed control, there being little to be gained for instance from attempting to measure slight differences between herbicides.

The paucity of research workers, not only in weed control, but in agriculture as a whole in Africa, and the widely different conditions even within a given type, demand that the experimental approach be simple and the investigations be conducted over as wide an area as possible. In this respect the author agrees entirely with Pfeiffer[3] who has expressed similar opinions.

Considering that the bulk of the population today consists of peasants, usually armed only with hoe, or a spear, and ekeing out an existence either on a tiny scrap of land or ranging over a wide area with cattle, it would appear that there will be no reasonable demand for herbicides for use by the African himself on his own account for 15–50 years. That there will be large outlets for herbicides in tropical Africa in the near future is undoubted—but this will come from independent white farmers as labour becomes scarcer; from estates growing plantation crops, which have special weed problems; and from authorities engaged in weed eradication on a national basis. This is in contrast to temperate European farming where the bulk of demand is from the individual farmer working his small farm intensively.

Specific weed control problems

Certain major problems only, will be selected for review here, viz.—

(1) Control of bush and trees, and other weeds in natural grazing.
(2) Control of weeds, principally grasses in plantation crops.
(3) Control of weeds in maize, chiefly by pre-emergence treatments.
(4) Control of aquatic weeds.

(1) Bush control in natural grazing

The control of undesirable woody species is a problem which occurs in the vegetation types described here as non-thorny woodland with short grass, thorny woodland with tall grass and that with shorter grass. Due to encroachment of bush the carrying capacity of the veld is drastically reduced, trampling occurs in the open areas and soil erosion soon begins. Bush encroachment is one of Africa's most serious weed problems.

Phillips[4] and West[5] find that absence of fire in conjunction with overgrazing leads to encroachment, and that the open woodland is really a pyroclimax. Fire may however, lead to coppicing of certain species,[6] and it is considered that the major effect of fire is to kill the seedlings and young trees and not the more mature constituents of the vegetation, which under certain circumstances may thicken up as a result of firing.

The aspect of grass protection during the summer months in order to allow maximum competition between grass and bush has probably not been sufficiently stressed in the past. It has been found recently in the bush veld of South Africa,[7] that three seasons of summer resting alone (without fire) has brought about a complete kill of certain bush species such as *Acacia arabica*, *A. permixta* and *Dichrostachys glomerata*. Other species such as *A. hebeclada* are not affected in a similar manner, and even should this finding be confirmed in other regions, the problem of controlling certain bush species still remains.

Control of woody growth in tsetse control.—The selective control of woody species in order to open the community and admit more light is one of the means of controlling fly. Burning has not always been successful and chemical control methods have been investigated as a possible means of liberating the vast areas under tsetse fly. A résumé of recent experiments using herbicides for the control of bush and trees will now be given.

Use of herbicides.—Experiments conducted by the writer[8] on *Acacia detinens* and *A. heteracantha* in the South African Bushveld showed that diesel oil alone, applied to the crown of the tree, resulted in complete kill. Basal bark treatments which were somewhat less effective, and the addition of a 4% w/v mixture of a 50 : 50 2,4-D/2,4,5-T low-volatile ester mixture did not improve the results.

Cleghorn *et al.*[9] also report a 67% kill of *Acacia subalata* by applying illuminating paraffin to the crown of the tree. Similar results have been obtained in Natal,[10] and although erratic results have been obtained in practical use, this method of control is employed in certain areas of the Union.

In the Eastern Cape Province of South Africa, work has led to a recommendation of 0·75 lb. of 2,4,5-T ester in 10 gal. of diesoline as a basal spray for *Acacia* species,[11] but the results with this mixture in other regions have not always been satisfactory.

Trials reported from Southern Rhodesia[9] using 2,4,5-T and 2,4-D on a number of Acacia and non-thorny species, show a considerable variation in reaction according to species, type of herbicide applied and method of application. In general, stem application has been more successful than over-all sprays, provided the herbicide is applied in a mineral oil carrier. Stump treatment appears to be more reliable than bark treatment, but the most promising results on five Acacia species were obtained using 1·5% w/v butyl ester of 2,4,5-T in diesel oil applied to slashed stems. An average kill of 76% was obtained using 2,4,5-T, 58% with diesel oil alone. A distinct species reaction was evident, diesel oil in the case of *A. karoo* and *A. subalata* giving 90% and 100% kill respectively, a better kill than where 2,4,5-T had been used in addition, and in other cases the results were reversed. Why the addition of 2,4,5-T to the diesel oil produced a lower kill than oil alone is a question for further study.

Against non-thorny species in Rhodesia,[9] stump treatments appear to have given the most consistent results. There are indications that the low-volatile esters of 2,4-D and 2,4,5-T are not as efficient as the butyl ester of 2,4,5-T on *Brachystegia spiciformis*, a 20% kill compared to a 75% kill respectively having been obtained. On *Pseudoberlinia globiflora*, only a 15% kill using low volatile ester was obtained.

These results are in sharp contrast to those obtained by Ivens[12] in East Africa where both of these last-mentioned species have been very successfully controlled using a 1% solution of 2,4-D or 2,4,5-T in diesel oil. Furthermore good results have been achieved on a number of Acacia species e.g. *A. hebecaloides*, *A. drepanolobium*; *A. nigrescens* and *A. tortilis* (*heteracantha*).

In East Africa Ivens[12] reports poor results on *Combretum*, *Euclea* and *Tarchonanthus*, species which tend to coppice if disturbed mechanically, and it appears that an important factor in determining whether a chemical treatment will be successful or not, may be the history of the tree itself, and its capability of producing coppice growth. This point is also made by Ivens[12] and may account for the variation in results being obtained in different areas. The practice of shifting cultivation practised by the native agriculturist has concerned many parts of these regions, and has probably resulted in the coppice type of growth widely encountered.

Results from over-all spraying of 2,4,5-T on thorn scrub have nowhere been very successful. This problem is of even greater importance than the need for a successful basal treatment, by virtue of the nature of the infestation in many areas.

A field for fundamental investigation is the relationship between the effects of mineral oils and 2,4-D/2,4,5-T mixtures; effect of method of application and volume of application on final effect; influence of coppice growth; formulation of herbicide employed; influence of climate on species reaction; are certain of the problems needing evaluation before much progress can be made in this field. Sporadic, unrelated experiments done at random are not likely to throw much light on this huge problem.

The question of the control of woody growth is an inter-territorial one, and of great importance in almost every country south of the Sahara, and a plea is made here for this subject to be placed in the hands of the Commission for Technical Co-operation in Africa South of the Sahara (C.C.T.A.*), who are at present engaged in handling another urgent weed control problem —that of *Echhornia crassipes*. By so doing it will be possible to arrange a definite programme of research covering all territories affected, designed in such a way as to allow direct comparisons of treatments and results and so lead to a speedier solution to this problem than would be otherwise possible. It is believed that Dr. West's plea[13] in relation to 'the need for a joint and positive approach to the problem of bush control in the federation of Rhodesia and Nyasaland and other African Territories', can only be answered by inter-territorial co-operation through C.C.T.A./C.S.A.

Other problems in grazing areas.—Various sub-shrubs and herbaceous plants constitute a problem in certain areas of woodland and grassland. These plants are unwanted because they reduce the amount of grass available, impede the movements of animals or are poisonous. In

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* An international body consisting of Britain, France, Belgium, Portugal, Central African Federation and the Union of South Africa.

the grassland areas, *Stoebe vulgaris* is an example of a non-poisonous sub-shrub. This species has invaded over a million acres on the Highveld of South Africa, principally on reverted fallows. It may be controlled by means of 2,4,5-T or by burning in early summer.

Senecio species, *Pachystigma pygmaeus* and *Geigeria Africana*, are examples of poisonous sub-shrubs. *Dichapettalum cymosum*, in reality a tree which has receded underground, is one of the most dangerous poisonous weeds in woodland areas.

Jointed cactus, *Opuntia aurantiaca*, a low growing, vile weed over about 3 million acres in the Eastern Cape Province, is a gigantic problem and is being controlled by State-subsidised 2,4,5-T butyl ester in illuminating paraffin. The upright prickly pear (*Opuntia* sp.) has been reduced in extent biologically and mechanically except in the coastal regions. 2,4,5-T is also effective against this species.

Solanum incanum is an example of the problem in trampled areas in East Africa.

In the moister regions of Natal, encroachment by woody species such as American bramble (*Rubus* sp.) in grassland and in wattle plantations, and *Lantana camara* in the coastal regions, are typical of the problem.

(2) Weed control in plantation crops

An important weed problem in plantation crops is the control of perennial grass species, chiefly *Digitaria scalarum*, although *Cynodon dactylon*, *Cynodon plectostachyus*, *Pennisetum clandestinum* and *Imperata cylindrica* may also be a problem.

In the Belgian Congo, *Paspalum conjugation* and *P. virgatum* are troublesome.[13] Fleming[14] has recently reviewed this subject and detailed observations on the problem may be obtained from this source.

It is clear that the control of perennial rhizomatous grasses such as couch, is a problem which cannot be satisfactorily concluded using mechanical methods, because of the virtual impossibility of removing minute portions of rhizomes, which rapidly give rise to a reinfestation. Furthermore, excessive cultivation of the soil, apart from the adverse effects on the soil itself, can lead to root injury in the crops concerned. Although cheap labour is available at present, the trend is for labour to become more scarce, which increases the interest in chemical control measures.

When dealing with the control of perennial grasses, it must be remembered that the natural phenomenon of plant succession is always at work, and that the removal of a sward of perennial grasses either mechanically or by a non-sterilising chemical, automatically opens the way for invasion by pioneers, usually broad-leaved weeds and *Cyperus* spp. This phenomenon is not always fully understood by planters and a treatment which may be successful in controlling the principal weed is very often condemned because of the subsequent weed invasion. It is desirable therefore that, in order to maintain a plantation free of weeds by chemical means, the initial application be a chemical designed to deal with the perennial grass, and that subsequent treatments be applied before the perennial weeds fully re-establish themselves, but after the germination of the annuals, in order to prevent seeding. This may call for a combination of herbicides for the second follow-up treatment.

Coffee.—Herbicides for use in coffee are restricted in that the slightest taint in the bean disqualifies the crop and it is important that absorption must be reduced to a minimum. TCA was first tried as a herbicide against couch in this crop, but it was found that phytotoxic symptoms in the crop developed[15] and this herbicide was dropped in subsequent trials.

Dalapon at 10–20 lb./acre was found to give satisfactory results, and a considerable amount of work using this herbicide alone and in combination with aminotriazole was undertaken at the Jacaranda Coffee Research Station in Kenya, and by Ivens of the Colonial Pesticides Research Unit, Arusha, Tanganyika[15]. Ivens has reported that dalapon or aminotriazole at 5–10 lb./acre has given a high degree of control for at least 12 weeks, but more work is required on the most effective time for spraying. Two applications of dalapon, at 2½ or 5 lb./acre, has also given effective control of couch. Coffee can generally withstand dosages of up to 10 lb./acre, but further work is also needed to clarify this point. It does appear that repeated low applications may be more effective and less injurious to the coffee than a single high application. The advantage of combining dalapon with aminotriazole does not appear to be clear, especially as final evaluation of results must be on a cost efficiency basis. However, should aminotriazole be capable of controlling the invading broad-leaved weeds, there may be a place for a mixture of dalapon and aminotriazole in a chemical weed control programme in coffee.

Tea.—The main weed problem in tea occurs during the first few years of establishment as at this time the young plant is particularly susceptible to weed competition. Once the crop achieves a canopy, the shade is sufficient to reduce weed competition to a minimum. However, during the pruning year when light is again allowed to enter, the problem may recur. The use of systemic grass herbicides appears to have possibilities in tea, but there is insufficient evidence regarding the tolerance of tea to applications of dalapon or other herbicides.

Sugar cane.—Sugar cane is cultivated in Uganda, Tanganyika, Mozambique, Angola and the Union of South Africa. It is a high yielding crop and the economics are such that the use of herbicides is usually a practical undertaking. In Natal the sugar cane crop is the highest user of chemicals per unit area in agricultural practice at present. Except in certain restricted areas, as in Uganda for instance, the problem of perennial grasses is of secondary importance to the control of annual grasses and broadleaved weeds, and particularly *Cyperus* spp. In Natal, *Cyperus esculentus* is the most widespread member of this genus, while in Angola, Junca weed, *Cyperus longus*, is of particular importance. For the control of annual weeds and *Cyperus* spp., pre-emergence applications of 2,4-D or MCPA ranging between 2 and 4 lb. acid equivalent/acre are normally employed, which provides weed control for 4–6 weeks. Should grasses and *Cyperus* spp. have germinated before it has been possible to apply pre-emergence spray, however, a combination of 4–5 gal. of 5% pentachlorophenol with a growth-regulator may be applied. In this manner the control of emergent grasses is achieved together with the residual action of the growth regulator. In certain cases this combination spray may be applied up to the spike or flag stages of the cane, when minimum scorch occurs.

Where *Cyperus* spp. are severe it is common in Natal to apply a subsequent application of pentachlorophenol, which however, entails considerable scorching of the crop. The use of TCA at 15 lb./acre or dalapon at 5–10 lb./acre, has been found to give satisfactory control of *Cyperus* with minimum damage to the cane.

The use of substituted ureas has not been found satisfactory on a cost/efficiency basis. Simazin has also been investigated, but as yet satisfactory results have not been reported.

The principal weed problem is encountered from the time of planting until the cane canopies. In areas where the cane is thrashed before cutting subsequent weed control measures are reduced to a minimum. Where however it is necessary to burn before cutting it may be necessary to control weeds either mechanically or by means of chemicals.

In regions of flat terrain aerial application has possibilities for the post-emergence application of herbicides, but because of the limited acreage planted each day aerial pre-emergence application has only limited possibilities.

Sisal.—Labour engaged in sisal production in East Africa is demanding wage increases and this is causing increasing interest in chemical weed control. The use of herbicides in sisal must be considered as largely experimental and their rôle in the future will probably be that of assisting rather than replacing hand and mechanical methods of weed control. In general the present low prices being obtained for sisal rather limit the extensive use of herbicides.

Weed control is most important in the establishment period. It has been estimated that, at present, handweeding of nurseries may cost up to 250/- to 300/- per acre. Depending upon the weeds present, growth regulators up to 2 lb. acid equivalent/acre may be used. Hormone weedkillers used at these rates may sometimes cause distortion of the main spikes, but the set-back is usually only temporary. Where grass weeds prevail, TCA up to 40 lb./acre or dalapon at 10 lb./acre has given satisfactory results.

Mature sisal fields are normally only weeded once a year before cutting, with the result that heavy weed infection often occurs. It is unlikely that herbicides will prove economic in these situations.

(3) Weed control in field crops

Introduction

The control of annual weeds in field crops such as maize, beans, groundnuts, sorghum and potatoes, presents problems wherever they are grown. Here weed control in the principal field crop—maize—will be reviewed. The fact that weeds are depressing to the yield of maize is well known. In South Africa the problem has received a little attention and work recently completed by Marais[16] at the Reitvlei Experimental Station, near Pretoria, clearly emphasises the need for efficient weed control. This worker has shown that the more favourable the conditions are for maize growth, the greater is the reduction in the potential yield of the crop when in competition with weeds. This work shows that weed control operations should be aimed at securing a weed-free crop 30–50 days after planting. Because of the difficulty of eradicating weeds, particularly grass weeds, once they have become established, the only practical method of achieving this object is to begin weed control operations from the date of planting, and this is most feasible using a pre-emergence spray. The value of a pre-emergence treatment using either 2,4–D or MCPA in conjunction with either one or two subsequent cultivations, has been clearly demonstrated.[17] That this method of increasing yields, and thereby improving the economy of maize production in the Union, has not been more readily accepted, is an indication of the need for extension work amongst farmers.

Pre-emergence weed control in maize

The limitations of traditional and chemical methods where applicable has been recently reviewed for the Union of South Africa.[18] It is really only in South Africa and the Rhodesias that pre-emergence chemical weed control has developed to any extent and here maize will be used as an example to illustrate the general problems which are encountered in pre-emergence weed control.

Pre-emergence control is usually practised when the weed problem is such that post-emergence sprays do not adequately control the weed. This technique may also be used to control weeds susceptible to post-emergence spraying, but because of the higher cost of pre-emergence treatments, the complex nature of the operation and the variability of results, broad-leaved weed control is usually left to the easier post-emergence spraying. Pre-emergence spraying is practised, therefore, when it is necessary to control the annual grass weeds, such as *Eleusine indica* and *Panicum laevifolium.*

The success or failure of a pre-emergence treatment depends on the retention of the herbicide in the weed-seed soil layers. A successful treatment is one in which the herbicide is retained for a sufficiently long period to allow crop establishment without injuring that crop. Much depends therefore on the fate of the herbicide in the soil.

It is well known that the two principal factors affecting the fate of herbicides in the soil are microbical decomposition and leaching, which again are influenced by soil characteristics.[18] Because of the intensity of rainfall encountered and because of the damage which has occurred in Southern Rhodesia and South Africa from pre-emergence sprays in maize, it was decided to study the fact of leaching as related to several South African soils. The work was undertaken by Dr. P. M. Grant of our Research Department and it is hoped to publish the results in more detail elsewhere. Workers previously mentioned had already reported[19] the leaching of herbicides depends on the solubility of the agent, the amount and distribution of the rain and the character of the soil. Aldrich & Willard[20] found that the ester form of 2,4-D moved less than the salt forms and was the form most likely to give consistent results with less risk of injury.

The first step was to examine the relative movement of 2,4-D amine salt at the rate of 2 lb. acid equivalent/acre on seven soil types, using soil columns. The herbicide was applied to the surface and a given amount of 'rain' applied, the movement being measured biologically using cucumber seedlings. The study confirmed that the greatest movement occurs on the light sandy soils, but also showed that considerable movement was possible on a granulated type of clay soil. Here presumably, the percolation occurred between the granules.

Further studies were undertaken using three formulations of weedkiller on four sandy soils and one granular type. 2,4-D amine salt, 2,4-D *iso*propyl ester and a product developed by our Research Department designated F.6 were used. While the characteristic leaching pattern developed for 2,4-D amine salt and ester, there being virtually no differences between them, F.6 showed remarkable stability in the upper layers of the soil.

In the third step the work was confined to the Koppies soil—one on which rapid movement had occurred. 2,4-D ester, 2,4-D amine salt, 2,4-D acetamide, 2,4-D acid, MCPA potassium salt, MCPA acid and F.6 were compared at three levels of rainfall $\frac{1}{2}$, 1 and 2 in. Surprisingly, the acids and 2,4-D acetamide, although relatively insoluble, moved appreciably compared with F.6.

It was considered therefore that this particular product was worthy of field investigation. At our research station, near Bapsfontein in the Transvaal, 2,4-D *iso*propyl ester was compared with F.6 in a maize yield trial on a sandy loam soil the principal weed being the annual grass *Eleusine indica*. A comparison of the more important findings showed that over all rates, 2,4-D ester yielded 5·06 bags (200 lb.)/acre compared with 8·47 bags from F.6, the LSD being 0·27 bags. At the 2 lb./acre level of application, 2,4-D ester yielded 10·98 bags compared with 18·31 bags/acre from F.6.

In an attempt to explain the stability of F.6 in the soil, the alkaline hydrolysis rates of 2,4-D *iso*propyl ester, 2,4-D-acetamide and F.6 were determined: 50% hydrolysis occurred in less than 10 min. with ester, in 40 min. with 2,4-D acetamide, and 260 min. with F.6. Assuming that alkaline hydrolysis is an important factor governing leaching in the soil, the relatively inert character of F.6 may be one of its important characteristics.

Post-emergence weed control in maize

The control of weeds in maize using chemicals, post-emergence, is fraught with difficulty and maize must be regarded as a sensitive crop. In South Africa, Rhodesia and East Africa damage has occurred when sprays were applied to maize having more than six leaves. Except when snapping occurs there is no evidence that damage will affect the final yield of the crop, but nevertheless it is a condition to be avoided. Present recommendations are to apply the weedkiller before the 5–6-leaf stage of the crop, and subsequent sprays should be applied using drop arms. Similar results have been obtained in East Africa, where most damage occurs when the maize is treated at heights between 5 and 12 in. Present recommendations in East Africa are to apply the weedkiller between the 2–4 in. stages.

The limitations which are imposed on post-emergence spraying restrict the aerial application of weedkiller to maize.

Other field crops

In South Africa potatoes, groundnuts and cowpeas are treated with pre-emergence sprays for the control of various weeds. The general principles applying to pre-emergence weed control in maize applies to these crops also.

(4) Aquatic weeds

Water hyacinth

Virtually the only aquatic weed of serious importance in Africa today is water hyacinth—*Eichhornia crassipes*; an infestation of *Salvinia* has, however, been noted in East Africa.[21] Information on hyacinth is obtainable from recent publications,[22] and from the work of these authors, the following is a brief résumé of the position. Water hyacinth was first reported in the Belgian Congo in 1952,[23] and by 1955 the situation was regarded seriously and it was decided in view of the potential danger that the matter would be best handled by C.C.T.A./C.S.A. By doing so, several territories endangered have been placed on their guard and effective measures for the control of the pest were initiated.

In 1955, a survey by Kirkpatrick indicated that 1000 miles of the Congo River, between Leopoldville and Stanleyville, were infested with the weed. The Navigable Waterways Service encountered serious difficulties in maintaining shipping because of the numerous islands of water hyacinth and the accumulation on the sides of the river which caused an extremely strong main current to flow in the open water. Moreover, delays in barge trains occurred because of the accumulation of masses of plants on the boats themselves. Not only has the Congo River itself been invaded but the weed has spread through several of the main tributaries. It has appeared in Angola and recently it has spread into the drainage system of the Nile, thus endangering a huge area.

Experimental work conducted in America showed that 2,4-D at the rate of 8 lb./acre successfully controlled the weed. A plan of action based on 2,4-D amine was drawn up for use in the Congo, consisting of three phases—initial application; follow-up spray; and patrol maintenance. The initial sprays were applied from boats using power pumps. The results were spectacular and after two years the weed had practically disappeared over 500 km. near Stanleyville. The cost of this treatment was fantastic, particularly in view of the difficulties entailed in the application of the weedkiller itself. Not only have the river banks to be sprayed, but also the fringes of numerous islands which occur in the river. In order to reduce the application costs, the use of helicopters has been investigated,[23] and this has been found satisfactory.

Infestations in other parts of Africa

Water hyacinth has been known for several years near Salisbury in Southern Rhodesia, in the Zwartkops River in Port Elizabeth, and is also present in Mozambique in the River Incomati. These infestations have not been serious and are being kept under control in a satisfactory manner.

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Discussion

Dr. E. Mez (S.I.A.P.A.).—Mr. Hattingh considers the use of mixtures of dalapon and aminotriazole as one of the most promising methods of controlling couch grass in coffee. Could he supply more details as to the ratios and application rates used by him in this connection.

Mr. Hattingh.—The work on the control of couch grass in coffee has been mainly carried out by Dr. Ivens of Arusha (see text p. 220). The proportions used were 5 and 5 lb. or 2·5 and 2·5 lb. of the two herbicides.

Dr. R. A. E. Galley (Tropical Products Institute).—Could Mr. Hattingh tell us how much of the quoted area under maize is in blocks of sufficient size to make aerial application of weedkillers a good proposition?

Mr. Hattingh.—60% of the maize is in blocks of sufficient size to make aerial spraying of weedkillers a good proposition.

Mr. W. Moore (Sutton & Sons Ltd.).—What varieties of grass are referred to under the general description 'couch' in the lecture?

Mr. Hattingh.—Many varieties come under this heading including *Cynodom, Pennisetum, Paspalum, Digitaria,* etc.

Mr. Moore.—When MCPA or 2,4-D is applied to *Cynodon* turf in South Africa, such as is used for sports such as on golf courses, for the control of broad-leaved weeds, what are safe dosages to employ to avoid injury to the legitimate plants?

Mr. Hattingh.—*Cynodon* turf is resistant to MCPA and 2,4-D. Of the former, the potassium salt should be used up to 4 lb/acre. In the case of 2,4-D, the amine salt is preferable to the esters as the latter are liable to damage the finer strains of grass.

Mr. J. D. Fryer (University of Oxford).—Mr. Hattingh has described to us some of the weed control problems that exist in Africa today. I believe that the conference would be interested to hear from him how research on weed control in Africa is organised, and how it is divided between Industry and the State. I would like to endorse Mr. Hattingh's remarks concerning the need for more work on the control of bush. This is a problem of increasing importance throughout many territories of Africa, and one that is only likely to be solved if the various Governments concerned co-operate in sponsoring research on all aspects of the problem, in particular on chemical control. Industry plays an important part in the development of herbicides in many parts of Africa, but this particular problem is far too large to be tackled successfully, either by Industry or by the existing official research workers in Africa. A long-term and extensive research programme carried out by a team of specialists in conjunction with Industry and with the existing official organisations concerned with bush eradication, is likely to be essential if a successful answer is to be found.

Mr. Hattingh.—Research work on chemical control of weeds in Africa is very limited. Industry carries out a certain amount, often in co-operation with the various departments of Agriculture, but there is obviously room for much more experimental work. The collaboration between the various organisations occurs when and as required. We agree with Mr. Fryer that establishment of co-operation for bush control between various Governments concerned is desirable and to this end we suggest that the problem of bush control be handled by C.C.T.A.

Mr. E. P. Whittaker (Fisons Pest Control Ltd.).—Mr. Hattingh stated that aerial application would be applicable if a good post-emergence herbicide could be found for the control of weeds in maize. If such a herbicide were found, would Mr. Hattingh indicate the area over which such a herbicide might be used?

Mr. Hattingh.—Approximately 8 million acres in South Africa and 4 million in East Africa. One would expect about one-third of the area to be treated.

ACTIVITY AND MODE OF ACTION OF TRIAZINE HERBICIDES

by

H. GYSIN and E. KNÜSLI

(*J. R. Geigy S.A., Basle*)

Introduction

In previous communications[1] the chemistry and the herbicidal properties of triazine derivatives were discussed, one of the major interests being if possible to find some relation between chemical structure and biological activity.

It is possible to replace the three chlorine atoms in cyanuric chloride by various substituents such as amino-, alkoxy-, alkylthio-groups, etc. The number of compounds in the triazine series showing some herbicidal activity in screening tests is considerable, and secondary and field tests are necessary to select the most interesting chemicals. This was done with two objects, (1) to find chemicals which can be used in crops, i.e., which show selective herbicidal properties, and (2) to find toxic materials suitable as total weedkillers for use on railroads, tank farms, etc.

Simazin and its homologues

The group of 2-chloro-4,6-bis-alkylamino- and -4,6-bis-dialkylamino-*s*-triazines has been investigated thoroughly. The best-known chemical of this group is simazin, 2-chloro-4,6-bis-ethylamino-*s*-triazine, which was chosen for studies on the mode of action. We do not know for sure yet if the findings on simazin are applicable to all other herbicidally active 2-chloro-4,6-bis-alkylaminotriazines, but from the results available so far it appears that simazin can be safely used as a prototype. Because of its low solubility, simazin when used directly on plants or weeds is relatively inactive and its uptake through the leaves is negligible. When applied to the soil, however, it is taken up by the root system of crops and weeds. In order to bring simazin down to the roots, water is necessary, and it became evident that either the soils have to have a relatively high water content or that after the application of simazin appreciable amounts of rain fall.

So far the main use of simazin as a selective herbicide is as a *pre-emergence* herbicide on maize. In amounts of 1–3 lb./acre an excellent weed control is generally achieved. Under very dry conditions, as they existed in the Middle West of the United States during the 1958 season, the weed control by simazin was not always sufficient. In all other regions, however, where the rain conditions allowed simazin to penetrate into the soil, e.g., in Switzerland, France and in the Western United States, excellent results were obtained. In regions with large amounts of rainfall, simazin even applied as a *post-emergence* herbicide on maize gave very satisfactory results, although it was not taken up by the leaves of the weeds and its best activity is on the growing of young plants.

The most important use of simazin so far is its application as a general weedkiller on railroads, roadsides, tank farms, storage areas, garden pathways, etc. The quantities necessary for control depend on the weeds and soils but are normally between 5 and 15 lb./acre.

Atrazin

In regions, however, where rainfall is limited, another closely related chloro-bis-alkylamino-triazine gives much better results, viz., 2-chloro-4-ethylamino-6-*iso*propylamino-*s*-triazine, atrazin, which has a solubility in water of 70 p.p.m. compared with 5 p.p.m. for simazin. Because of its higher solubility, this compound is able to penetrate through the leaves, and it can therefore be applied as a pre- as well as a post-emergence herbicide on maize. Under dry conditions lower amounts of water are able to 'activate' atrazin so that even under these circumstances the compound is able to control practically all weeds present in maize. The higher solubility in water which is an advantage for application to maize is, however, a disadvantage when atrazin is applied to other crops. Brushes and trees which are highly tolerant to simazin are seriously affected when treated with atrazin, although crops like vine seem to be rather tolerant to it. It is not known yet if the vine plant, when treated over several years, is able to withstand atrazin treatment without showing phytotoxic symptoms, a quality which has already been proven for relatively high dosages of simazin.

There are differences between simazin and atrazin in their spectrum *vis-a-vis* weeds. Representatives of the *Panicum* varieties, especially *Panicum sanguinalis*, are much more resistant to atrazin than to simazin, while bindweed is controlled in a much better way by atrazin than by simazin.

Propazin

Of all the chloro-bis-alkylamino-triazines, simazin and propazin, 2-chloro-4,6-di*iso*propyl-amino-*s*-triazine, have the longest residual effect. Propazin has a solubility in water of 8·6 p.p.m. and is with simazin amongst the least soluble of the chlorobis-alkylaminotriazines. In some soil varieties propazin seems to have a still better residual effect than simazin, but its effectiveness in weed control is generally lower. Propazin resembles atrazin as regards tolerance to *Panicum* species. Atrazin and propazin are therefore not suited for a general weed control when *Panicum* varieties are present. *Propazin* can be used safely as a post-emergence herbicide on crops, such as fennel, celery, parsley and carrots. On artichokes further studies are necessary, as the younger plants seem to be more sensitive, and no definite conclusions can be drawn as yet.

Other simazin homologues

In addition to the three triazines mentioned above, a number of related chloro-substituted aminotriazines have been rested, chlorazin, ipazin and trietazin (the 4, 6-bis-diethylamino-, 4-diethylamino-6-*iso*propylamino- and 4-diethylamino-6-ethylamino- analogues of simazin).

Chlorazin and ipazin used in non-phytotoxic oil gave in amounts of 2–4 lb. good to excellent weed control in cotton. As ipazin seems to be significantly better than chlorazin, the investigations in the new season will be concentrated on isodiazin, especially as this chemical, when applied as an emulsion, showed practically the same weed control in cotton when compared with the oil formulation, so its application would be considerably cheaper.

Trietazin is a compound which can be used as a selective weedkiller on crops, such as peas, potatoes, tomatoes and soya-beans. When applied at pre-planting time in tobacco, some very good results were achieved, while in some cases, for unknown reasons, quite considerable damage was noticed. This problem needs further investigation.

Simazin analogues

If the chlorine atom in simazin or similar 2-chloro-4,6-substituted-amino-*s*-triazines is replaced by an alkoxy- or alkylmercapto-group, a number of very interesting triazine derivatives are obtained. These compounds, however, differ in one property which is common to all chlorobis-alkylaminotriazines investigated, namely in their pronounced toxicity to maize and similar plants; 2-methoxy- and 2-methylmercapto-4,6-bisethylamino-*s*-triazine are both able to kill maize and millet varieties in dosages which are perfectly safe for the respective chloro analogues. This is not only true for the direct methoxy- and methylmercapto-simazin analogues but the same general spectrum was found for all methoxy- and methylmercapto-bis-alkylaminotriazines which have been tested so far. In comparison with simazin and propazin, the respective methoxy-analogues have considerably higher solubilities in water, being 3200 p.p.m. for *methoxysimazin* and 750 p.p.m. for *methoxypropazin*, and for both compounds the lipoid solubilities are significantly higher also. This apparently enables the chemicals to be absorbed by the leaves as well as by the roots. The residual effect of methoxysimazin is considerably shorter than that of methoxypropazin, so that further investigations on the latter compound will be made.

The 2-methoxy-4,6-bis-alkylamino-*s*-triazines do not show sufficient selective properties and can be used therefore as general weedkillers only. Methoxypropazin, having a relatively low melting point, can be applied in emulsion as well as in wettable powder form. When used on existing weeds, the emulsifiable formulation gives an effect in a much shorter time. Within 2–4 weeks, in general, the performance of the wettable powder treatment equals that of the emulsifiable application. This difference may, however, be a definite advantage in favour of the emulsion, especially in the time of rapid growth. Use of a formulation of methoxypropazin as an emulsion and application in weed oil has a considerable effect on brushes. When grasses are present, these are controlled as well as the brushes, which may be an advantage over 2,4,5-T When deep-rooted perennial grasses, such as Johnson grass or Bermuda grass, are to be controlled, methoxypropazin is the best material tested so far, although the amounts required to control these grasses are considerably higher than for sensitive weeds—15–30 lb./acre, or even higher amounts, may be necessary to give satisfactory control. When atrazin is applied in these high dosages, it may give a similar control of perennial grasses.

If the methoxy-group in 2-methoxy-4,6-bis-alkylamino-*s*-triazines is replaced by a higher alkyloxy radical, such as ethoxy- or *iso*propoxy-group, the herbicidal properties of these chemicals are much inferior. Ethoxypropazin, e.g., can be applied to relatively sensitive crops, such as strawberries, without doing harm to the crop. The weed control is, however, rather poor. It is too early yet to decide if higher alkyloxy-4, 6-bisalkylaminotriazines are suitable for selective weed control.

In addition to methoxysimazin and methoxypropazin, the methoxy-analogues of atrazin and the 2-methoxy-4-methylamino-6-*iso*propylamino-*s*-triazine gave very promising results in the field. Further investigations will be necessary before definite conclusions can be drawn.

Of the methylmercapto-bis-alkylaminotriazines, e.g., *2-methylmercapto-4,6-bis-ethylamino-s-triazine* (*methylmercaptosimazin*), only preliminary field results are available yet and further investigations will be necessary in the forthcoming season.

Among the group of the 2-alkyl-4,6-bis-alkylaminotriazines, no derivatives were tested thoroughly enough in the field for final conclusions to be drawn. The general spectrum of these 2-alkyl-bis-4,6-alkylaminotriazines, e.g., *2-methyl-4,6-bis-ethylamino-*s*-triazine* (*methylsimazin*) is, however, close to that of the respective alkoxy- or methyl-mercapto-bis-alkylaminotriazines.

Mode of action

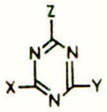
The response of the plants when treated with the triazine herbicides in comparison with the application of plant-growth regulators of the 2,4-D type made it unlikely that the two chemical groups have a similar mode of action. While 2,4-D acts directly on the germination of the seed, the triazines practically do not affect this stage of growth as described in earlier publications.[1] The first symptoms due to the use of triazine herbicides are necrosis and burning. Yellowing and drying of the leaves lead finally to a total kill of the plants. The time required for killing them depends on a variety of factors but takes place in one to several weeks normally. Gast[2] showed that with *Coleus blumei*, a plant which is especially active in starch formation, an application of simazin inhibits the accumulation of starch. When starch-free *Coleus* leaves were kept in the dark in a sucrose solution, the same author showed that these leaves were able to form starch in the presence of simazin, which proves that this herbicide inhibits the sugar formation. Moreland *et al.*[3] found that the phytotoxic activity of simazin is reduced when carbohydrates are fed to a plant through its leaves. All these findings make it highly probable that simazin interferes with phytosynthesis in a similar way to that of the urea herbicides of the CMU-type.

The Hill reaction

The urea herbicides show a typical reaction: it inhibits the so-called Hill reaction. Hill[4] showed that isolated chloroplasts of plants such as Angiosperms, *Stellaria media* or *Chenopodium bonus henricus* are able to form oxygen in the presence of light and ferric salts. Holt & French[5] later used redox dyes instead of ferric ions, and Horwitz[6] suggested the use of Janus Green as especially suitable for colorimetric determination. Exer[7] showed in our laboratories that simazin and related chloro-bis-substituted-aminotriazines inhibit the Hill reaction as shown earlier by Cooke[8] and Wessels & Van der Veen[9] for the aryl-alkyl-ureas. The concentrations which give 50% inhibition in the Hill reaction are summarised in Table I.

Table I

Comparison of inhibition of Hill reaction by substituted triazines



$$\left(\mathrm{V} = \frac{\text{concn. of simazin giving 50\% inhibition}}{\text{concn. of compound giving 50\% inhibition}}\right)$$

Z	X	Y	V	Z	X	Y	V
Cl	NH_2	NH_2	<0·0001	Cl	$NHBu^n$	$NHBu^n$	<0·0001
Cl	NHMe	NHMe	0·002–0·01	Cl	NH_2	NHEt	0·2
Cl	NHEt	NHEt (simazin)	1*	Cl	NHMe	$NHPr^i$	0·27 –0·44
Br	NHEt	NHEt	2 –2·4	Cl	NHEt	$NHPr^i$ (atrazin)	1·8 –2·1
Cl	$NHPr^i$	$NHPr^i$ (propazin)	1·03 –3	Cl	NHEt	$NHBu^n$	3·6 –3·8
Br	$NHPr^i$	$NHPr^i$	1·8	Cl	NHEt	NEt_2 (trietazin)	0·0025–0·008
Cl	$NHPr^n$	$NHPr^n$	0·4 –0·67	Cl	$NHPr^i$	NEt_2 (isodiazin)	0·013 –0·048
Br	$NHPr^n$	$NHPr^n$	1·7 –2	Cl	NEt_2	NEt_2 (chlorazin)	0·021 –0·04

Other herbicides	V
3-(3′-chlorophenyl)-1,1-dimethylurea (monuron)	0·7–1
2,4-dichlorophenoxyacetic acid (2,4-D)	<0·0001
Aminotriazole (AT)	<0·0001

* 1 for simazin = 50% inhibition at 7×10^{-7} M

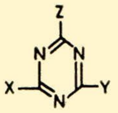
From this table it is obvious that simazin, propazin and their bromine analogues as well as atrazin show an inhibition of the Hill reaction in the same dilutions as for CMU. It is interesting to mention that out of all 2-chloro-4,6-bis-alkylamino-*s*-triazines tested in this reaction it is the 2-chloro-4-ethylamino-6-*n*-butylamino-*s*-triazine which gives 50% inhibition in the highest dilution. On the other hand this compound is relatively weak as a herbicide. Trietazin inhibits the Hill reaction only in concentrations 100–400 times higher than simazin, while the ratio of the herbicidal power of the two chemicals may be 1 : 2 to 1 : 4. This makes it likely that the concentration found to inhibit the Hill reaction is not directly proportional to the herbicidal properties of a chloro-bis-alkylamino-triazine. Adsorption by the soil, translocation of the herbicide in a plant, solubility of the chemicals, etc., may be potential factors for an explanation of the discrepancies between the degree of inhibition of the Hill reaction and the herbicidal activity. To take the Hill reaction as a general screening test for herbicides appears highly questionable, therefore, even in the limited group of the chloro-bis-alkylamino-triazines.

Among the known herbicides of other chemical classes, so far only the ureas give this typical inhibition of the Hill reaction. 2,4-D as well as aminotriazole are practically inactive in this test. We did not find, however, highly active chloro-substituted aminotriazine herbicides which did not at least cause some inhibition of the Hill reaction, so apparently the inhibition of the Hill reaction seems to be essential for the triazine herbicides, but an inhibition of the Hill reaction in high dilutions does not necessarily mean that this compound is a very active herbicide, at least when used on soil. A potential metabolite of simazin, 2-hydroxy-4,6-bis-ethylamino-*s*-triazine, does not inhibit the Hill reaction in concentrations of 10^{-4} and does not possess any herbicidal properties.

Among the group of the 2-alkoxy- and 2-alkyl-mercapto-bis-alkylamino-*s*-triazines some derivatives show in extremely low concentrations a 50% inhibition of the Hill reaction (see Table II). Some of the 2-methoxy-4,6-bis-alkylamino-*s*-triazines inhibit the Hill reaction in concentrations higher than simazin, others are less active inhibitors, but all the compounds of this type mentioned in the table are good herbicides. All 2-methylmercapto-4,6-bis-alkylamino-*s*-triazines investigated so far cause a 50% inhibition of the Hill reaction in a higher dilution than simazin and all are very active herbicides.

Table II

Inhibitory effect of 2-alkoxy- and 2-alkyl-mercapto-analogues of simazin in the Hill reaction



(V as in Table I)

Z	X	Y	V	Z	X	Y	V
OMe	NHEt	NHEt	1·3 –1·5	SMe	NHEt	NHEt	4·5–5·0
OMe	NHPr^i	NHPr^i	0·44–0·62	SMe	NHPr^i	NHPr^i	6·1–9·1
OMe	NHMe	NHPr^i	0·18–0·21	SMe	NHMe	NHPr^i	3·9–4·4
OMe	NHEt	NHPr^i	1·3 –1·5	SMe	NHEt	NHPr^i	6·1

Selectivity of herbicides

Attempts have been made and are still in progress to investigate which factors are responsible for the different sensitivities of various test plants to triazine herbicides. Theoretically there exist several possibilities why selectivity occurs: (1) Sensitive plants may be able to pick up the chemicals through their root systems and so accumulate a lethal dosage for the plant. In contrast, for physiological reasons, non-sensitive plants may not be able to take up the chemicals through the roots and so the plant would remain unaffected. (2) Non-sensitive plants may possess a mechanism to detoxify the chemical taken up to give non-phytotoxic materials, while a sensitive plant would not be able to metabolise the herbicide to harmless compounds. (3) A plant sensitive *per se* would be out of the sphere of the influence of a herbicide because of its special morphology, e.g., having its roots in deeper soil regions. There is as yet no experimental proof for the first theoretical possibility. Of the others, the detoxification is by far the more interesting and will therefore be discussed in detail.

Roth[10a] analysed wheat seedlings as representatives of triazine-sensitive plants. Wheat seedlings when kept in a nutrient solution containing 2 p.p.m. of simazin are able to pick up appreciable amounts of simazin, which is found in both roots and leaves. The amounts found in the leaves after 6 days are in the neighbourhood of 5 p.p.m. calculated on the fresh weight. If, however, a simazin-sensitive plant is grown in soil instead of in a nutrient solution, the uptake is by far smaller.

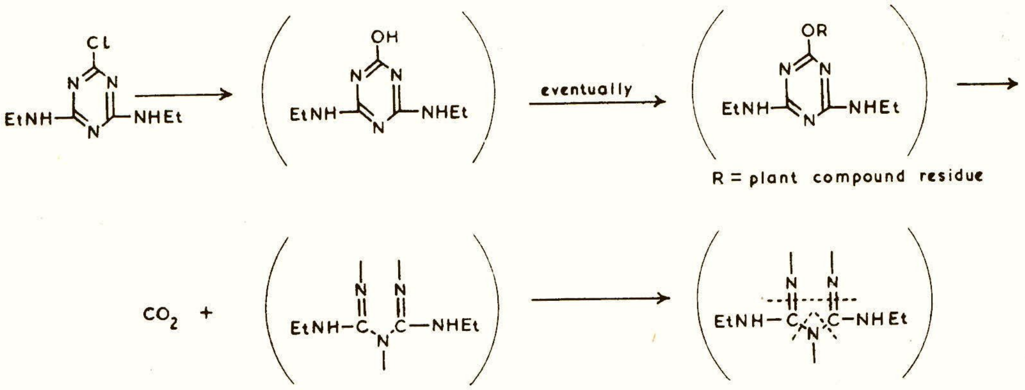
When maize seedlings are kept in nutrient solutions, only a fraction of a p.p.m. of simazin can be found in the leaves, while the amounts in the roots decreased from 7 p.p.m. on the first day to values lower than 2 p.p.m. after 4 days. This indicates that simazin taken up by the roots is transformed into another compound or compounds. In young maize plants grown in soil we were never able to find any significant amounts of unchanged simazin, the analytical sensitivity of the u.v.-method used being 0·1 p.p.m. This indicates that in young maize plants grown in soil the uptake of simazin is slow enough for a system present to metabolise the chemical. Roth could show when using a freshly pressed juice from maize plants to which simazin was added that it practically disappeared over a period of 100 hours, while from freshly pressed wheat juice a recovery of over 90% of unchanged simazin was obtained. It is likely that one or more systems are responsible for different rates of metabolism of simazin and may be the critical factors between sensitive and non-sensitive plants.

Although a considerable effort was made for the identification of the system responsible for the breakdown of non-tagged simazin, we have not yet been able to elucidate its chemical nature. We also failed to prove if the metabolite or metabolites were still triazine compounds or if the decomposition of the triazine ring had taken place during detoxification. Work with tagged simazin was indicated and radioactive cyanuric chloride was prepared from radioactive cyanogen chloride, tagged at the carbon atom. By substitution of two chlorine atoms by ethylamino-groups radioactive simazin (=simazin*) was obtained. Freed[11] grew maize seeds in soil which was thoroughly mixed with the product. The young plants were harvested periodically over the growing period of maize. In these experiments Freed confirmed our earlier findings with non-labelled material. The uptake of simazin* applied at the rate of 2–8 lb./acre was less than 1% of the total quantity of radioactivity available for the plant even under the best possible conditions in soil. Freed extracted the plant material thoroughly with chloroform and after a purification procedure chromatographed the extract on paper. While the original simazin* has in this system an R_F value of 0·85–0·92, over 60% of the extract showed radioactivity at an R_F value below 0·80. This suggests the absence of free simazin in the chloroform extract.

Rogers[12] grew maize and soya-beans in nutrient solutions containing labelled simazin and demonstrated the uptake of radioactivity by both plants in similar amounts. In paper chromatograms of maize extracts, no spot appeared at the original position, while in extracts from soya-beans a sharp peak was found where simazin was expected, indicating that this plant does not metabolise simazin. Both Freed and Rogers are of the opinion that the first metabolite, the compound which gives in the paper chromatograms the spots with an R_F value lower than that of simazin, may be 2-hydroxy-4,6-bis-ethylamino-*s*-triazine (=hydroxysimazin).

Davis[13] found that radio-autograms of maize, cucumber and cotton treated with simazin are distinctly different. While radioactivity is uniformly spread in the maize plant, in cotton and in cucumbers spots of various intensities can be detected. This indicates that there is in the maize plant a uniform distribution of the breakdown fragments which makes it likely that they are used by the plant, while the other two plants show isolated spots of unchanged simazin which cannot be metabolised by these plants. From these experiments it appeared likely that the decomposition of simazin went further than hydroxysimazin, and there was a breakdown of the triazine ring.

Determination of radioactive CO_2 would be therefore the crucial experiment. The formation of CO_2 would prove the ring-opening and the total breakdown of simazin to harmless metabolites. Freed[11] carried out this experiment with maize plants which were grown in sand and then transferred to a saturated solution of simazin* in a closed system through which air was blown. The gas was passed through barium hydroxide solution, where radioactive barium carbonate was obtained. When the maize plants were kept in total darkness during the whole experiment, within three days 63% of the total radioactive simazin taken up was metabolised to radioactive CO_2. When kept under normal light exposure for 48 hours, only about 10% of the radioactive simazin was metabolised to CO_2. Bearing in mind that the uptake of simazin was favoured in Freed's experiments by keeping the plants in nutrient solutions, the chances that intermediates of the metabolism in appreciable amounts can ever be found seem to be rather low. The stability of the remaining skeleton of the original triazine ring when one carbon is broken off seems to be rather limited. Because of the chemical reactivity of fragments such as amines, ureas, guanidines, etc., it is very likely that they are able to give reactions with chemical substances present in the maize plant. The fact that the CO_2 appears as an end-product of simazin metabolism in the maize plant (which proves that the triazine ring is broken), the reactivity of the fragments formed from the original triazine ring and the uniform distribution of the whole plant as found by Davis,[13] make it likely that the metabolites of simazin are utilised by the plant for further growth. A suggested scheme for simazin metabolism in maize is as follows:



Addendum

The Hill reaction and its inhibition

Some details on the mode of action of the newer herbicides, such as the ureas and the halogen fatty acid amides, are known. The urea herbicides of the CMU type interfere with photosynthesis and they inhibit the so-called Hill reaction. Until recently it was generally agreed that the Hill reaction is based on the photolysis of water. In a recent publication, however, Warburg & Krippahl[14] disagree with the historical theory and postulate that the action of light in the Hill reaction is due to the splitting of carbon dioxide. Their explanation of the Hill reaction is that ferric salts oxidise carbon in a dark reaction to CO_2 and that in the light CO_2 is split into $C+O_2$. In a series of experiments Warburg & Krippahl showed that, when ferric salts are replaced by quinones using *Chlorella* as test plant, carbon is oxidised in the dark to CO_2. When CO_2+quinones are added simultaneously only quinone is used, while CO_2 disappears as shown in the following equations:

$$\begin{aligned} 2\ \text{quinone}+2\ H_2O+C &= 2\ \text{hydroquinone}+CO_2+60{,}000\ \text{cal.}\\ CO_2 &= C^*O_2-60{,}000\ \text{cal.}\\ C^*O_2 &= C+O_2\\ \text{Balance: } 2\ \text{quinone}+2\ H_2O &= 2\ \text{hydroquinone}+O_2\\ (C^*O_2 &= \text{photolyte}) \end{aligned}$$

If, however, higher CO_2 pressures, such as 100 g./sq. m., are used, CO_2 is utilised as found by the aforementioned authors more recently.

As shown in Table I above the herbicidally active phenylureas such as CMU and the most active 2-chloro-4,6-bis-alkylamino-*s*-triazines such as simazin inhibit the Hill reaction in about the same dilutions, showing a 50% inhibition at concentrations of 7×10^{-7}. As regards the inhibition of the Hill reaction there is apparently a good parallel between the phenylurea derivatives such as CMU and the 2-chloro-4,6-bis-alkylamino-*s*-triazines such as simazin, but as regards the behaviour to plants there are considerable differences between the two groups.

When CMU is applied to the foliage of plants such as beans, it is quickly absorbed and translocated through the leaves, but translocation to the other parts of the bean plants is much slower. Simazin when applied to leaves of plants is taken up very little, while other 2-chloro-4,6-bis-alkylamino-*s*-triazines such as atrazin are absorbed from the foliage and from the roots. Atrazin is, therefore, much more related to CMU than to simazin in its behaviour as a herbicide with the exception of maize and millets, to which atrazin behaves just like simazin and completely differently from CMU.

Metabolism of simazin and its analogues

In order to show what happens to CMU in the plant, Freed[15] made studies with radioactive CMU and found that the amount of CMU taken up by a plant during growth decreases while the concentration of another radioactive compound is increased. When hydrolysed with 2N-HCl acid this complex could be split; over 90% of unchanged CMU was found, which indicates that no final breakdown of CMU takes place in the plant. Such a breakdown could be expected because *in vitro* *p*-chloroaniline, dimethylamine and carbon dioxide can be obtained rather easily with dilute mineral acids. According to our knowledge this metabolism has not yet been shown in the plant. In relation to another newly introduced herbicide, Randox, which is, chemically, chloroacetic acid diallylamide, a metabolism was suggested[16] to occur in maize involving the hydrolysis of the chlorine atom to a hydroxyl group and then scission to glycollic acid and diallylamine. These fragments may react with plant constituents. Randox, being rather tolerant to maize, served therefore as an example for metabolism studies. The reactivity of the chlorine atom in chloro-fatty acid amides is similar to that in a 2-chloro-4,6-bis-alkylamino-*s*-triazine such as simazin. Systems present in the maize plant could hydrolyse the chlorine atoms in both molecules to hydroxy-groups. This would mean that, in the case of simazin, hydroxy-simazin, which is chemically 2-hydroxy-4,6-bis-ethylamino-*s*-triazine, would be the first product of metabolism in a plant such as maize. The possible metabolism pathway of simazin has been indicated above.

In all our studies on the metabolism of 2-chloro-triazines, simazin has been used as an example hitherto. In the past few weeks Roth[17] made analogous tests with atrazin in order to prove if these two compounds behave similarly or differently when added to maize sap. With fresh juice from maize at different pH, practically identical amounts of simazin and atrazin were metabolised within 72 hours. At pH 2·1, 31% of simazin is metabolised while 32% of atrazin disappears from the solution. At all other pH the respective amounts of simazin and atrazin which were metabolised were practically identical. In an analogous experiment with wheat juice instead of maize, from originally 41 μg. of atrazin Roth found after 6 days 39 μg. If, instead of wheat juice, maize juice is used, the original value 50 μg. decreases after one day to 37 μg. and after 6 days to 21 μg. The figures for simazin are very similar. It is apparent, therefore, that atrazin undergoes the same metabolism in maize as occurs with simazin. The assumption that simazin can be used as an example for the metabolism of all 2-chloro-4,6-bis-alkylamino-*s*-triazines is very likely to be true. At present Freed[11] is working with several further tagged 2-chloro-4,6-bis-alkylamino-*s*-triazines so that within a few weeks it should be known if for these compounds also C^*O_2 is the end-product as shown already by the same author for simazin.

Roth[10b] investigated different systems present in various simazin-sensitive and -non-sensitive plants and obtained the results shown in Table III.

Table III

Classification of plants grown in aqueous solutions of simazin

Resistant:	*Zea mays, Coix lacryma, Imperata cilindrica*
More or less resistant:	(*a*) Millets (5 varieties), *Sorghum halepense*
	(*b*) *Vitis vinifera* (5 varieties)
Sensitive:	*Triticum* (4 varieties); *Lolium italicum* (2 varieties)

From the plants studied so far maize was found to have a unique position as it is able to break down simazin directly. Roth extracted from maize plants a phenol—or more likely a polyphenol—fraction which is able to metabolise simazin *in vitro*. By paper chromatography Roth located it as a definite spot, which suggests that the fraction is likely to be a well-defined chemical. Phenols and polyphenols from other relatively simazin-resistant plants like millets or *Imperata cilindrica,* however, break down simazin *in vitro* only when horseradish peroxidase is added. Furthermore, unaltered simazin was isolated in considerable amounts from *Imperata cylindrica,* which remained unaffected when grown in a simazin solution. Thus it is evident that these plants neutralise the phytotoxicity of simazin in different ways. To gain further knowledge Roth paid special attention to the oxidative diastases, namely to catalase and peroxidase, and also to the presence of the polyphenols in the plants mentioned above, and obtained the results in Table IV. He found a high catalase activity in all simazin-sensitive plants. On the other hand, plants with various degrees of resistance showed a significant content of polyphenols, often accompanied by a high peroxidase activity. Very high resistance was met where a high polyphenol content was coupled with a high peroxidase activity. Roth postulates that the triazines interfere with the redox-potential level appropriate for the normal function which chlorophyll has to fulfil in the plant. If this level is maintained by catalase, simazin seems to be able to destroy the equilibrium, but if peroxidase+polyphenols predominate, simazin would be or become ineffective.

Table IV

Oxidative enzymes and polyphenols in plants resistant and non-resistant to simazin

	Measured activity of		Content of
Type of plant	catalase	peroxydase	polyphenols
Resistant	poor	***	***
More or less resistant	(*a*) poor	***	*
	(*b*) poor	poor	***
Sensitive	***	***	poor to *

The fact that by substitution of the chlorine atom in simazin by alkoxy- or alkylmercapto-groups the phytotoxic spectrum of the 2-chloro-4,6-alkylamino-*s*-triazines is altered, seems to be an indication that the nature of the group in the 2-position is of special importance for the biological behaviour of the compounds of this series. In the metabolism of simazin and similar 2-chloro-4,6-bis-alkylamino-*s*-triazines the chlorine atom seems to be the first site of attack. Studies are in progress to find out if the 2-position in the alkoxy- and alkylmercapto-analogues of simazin plays the same important rôle also and how the metabolism of neutralisation of the phytotoxic properties takes place in these triazine derivatives. That we have not been able to find any unaltered simazin in maize plants and that Freed isolated radioactive C^*O_2 from maize treated with tagged simazin, seem to be sufficient evidence that this herbicide is completely broken down to fragments which are used by the plant. This is already more than could be found for most other herbicides actually used, although the exact pathway of simazin metabolism is not yet elucidated.

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