

ROOT FUNCTION AND THE SOIL

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Summary The performance of plant root systems is of interest from two viewpoints in relation to the use of herbicides - the absorption of materials which are applied to the soil and the manner in which reduced cultivation, made possible by herbicides, affects the growth of roots and hence crop yields.

A number of general aspects of root function and nutrient uptake are first reviewed to provide a background for discussing the absorption from soil of herbicides, especially simazine. Relationships between the uptake and translocation of these substances and of water are particularly considered.

Subsequently the response of roots to mechanical stress is examined in relation to the growth of crops in uncultivated soil. The need is indicated for interdisciplinary research if full advantage is to be taken of the new opportunities for reducing the efforts spent on cultivation.

INTRODUCTION

In a conference on the use of herbicides it is relevant to consider root function from two different viewpoints, namely, the absorption of herbicides which have been applied to the soil and the effects of new methods of cultivation on root growth and hence on the yield of crops. At first sight this latter question may seem outside the scope of this discussion but on a broader view it is of major relevance; one of the main contributions of herbicides to agriculture is the opportunity which they provide to reduce the labour spent on cultivation.

This paper attempts to provide some background - necessarily a superficial one - for considering both questions. No reference, however, will be made to movement of nutrients or herbicides through the bulk soil towards roots; this is considered in a later paper (Graham-Bryce, this conference).

ROOT FUNCTION

Interest in the function of roots centres largely on their ability to absorb nutrients and water but this is not their only contribution to plant growth. Substances synthesized in roots, for example kinins and giberellins move thence to shoots, playing an essential part in the complex processes which regulate plant growth. Indeed, the effects of some unfavourable conditions in the root environment, including waterlogging, appear to be due to changes in the synthesis of growth regulators rather than to the inadequate absorption of nutrients and water (Vaadia and Itai, 1969; Reid and Crozier, 1971). It would not be surprising if future research showed that some effects of sub-lethal levels of herbicides can be explained in a comparable way.

The recognition of the existence of these complex, but little understood control mechanisms, is equally important in considering root growth in less extreme soil environments. Under natural conditions the entire root system of any one plant is seldom exposed to a uniform environment - some parts are normally more favourably placed than others with respect to the supply of nutrients and water, temperature, oxygen supply, mechanical impedance, attack by predators or other factors. The response of root systems to such conditions can be so variable that at first sight no underlying pattern may be obvious. However, fuller enquiry reveals a widespread principle; if part of the root system is in a more favourable environment than the remainder, it usually absorbs more and grows more than if the entire root system experienced the same beneficial conditions; conversely the performance of the less favourably situated part of the root system is poorer. For example, nutrient uptake by a given part of an intact root system from a constant external supply may be greater by a considerable factor if nutrients are withheld from the remainder of the root system (Drew and Nye, 1969). Furthermore, as time passes the further development of laterals is largely confined to zones where the supply of nutrients, for example nitrate and phosphate, is more favourable (Fig. 1) (Drew *et al.*, 1971). Similarly, the restriction in the growth of root axes which can arise from many causes can frequently result in a considerable proliferation of laterals if they are not subject to the same constraint (Drew and Goss, 1971).

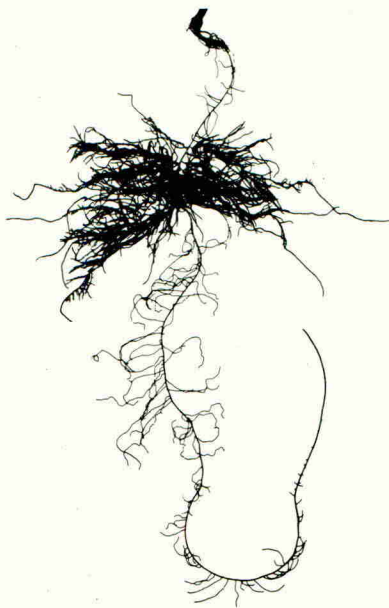


Fig. 1. Effect of localised supply of nitrate on growth of lateral roots of barley

The plant was grown for three weeks. The middle zone was supplied with a complete nutrient solution including 1.0 mM nitrate. The upper and lower zone received a similar concentration of nutrients except for nitrate which was 0.01 M. Only one seminal root is shown.

The existence of these compensating mechanisms is implicit in many classical observations (Weaver, 1926) but unfortunately they have received little detailed study. Present knowledge of growth control processes is inadequate to explain them but their existence has a number of important implications. The performance of a plant root system cannot be adequately understood unless it is considered as an integrated whole and in relation to the shoot wherein part of the control mechanism lies. Also it is to be expected that unfavourable conditions in an appreciable part of the potential rooting zone may have little effect on the performance of the plant if conditions elsewhere permit adequate compensatory growth; this is particularly relevant in interpreting root function in many field situations.

The compensatory response also complicates the study of many aspects of root function. Having in mind their intricate branching form and the considerable internal changes which occur with age, an obvious starting point in a detailed study of root function is to compare the potential ability of different zones - for example axes and laterals, young or old tissues - to provide the plant with nutrients. Unequivocal information on this subject can be obtained only if nutrients absorbed by selected parts of a root system are distinguished from those simultaneously absorbed elsewhere when the whole root system is exposed to a constant external supply - this requirement could scarcely be satisfied before tracer methods became available (Wiebe and Kramer, 1954; Russell and Sanderson, 1967). Contrary to earlier suggestions it is now evident that absorption is not confined to the young white apical parts of roots where the rate of respiration is highest and cells are thin walled. Provided part of the cortex remains intact, the conspicuous thickening of the endodermal walls is not a barrier to the radial movement of at least some of the major nutrient ions. Fine plasmodesmata provide passages from the endodermis to the pericycle and the entire living root system of cereal plants several weeks old possesses the capability of absorbing and translocating nutrients (Clarkson, Robards and Sanderson, 1971).

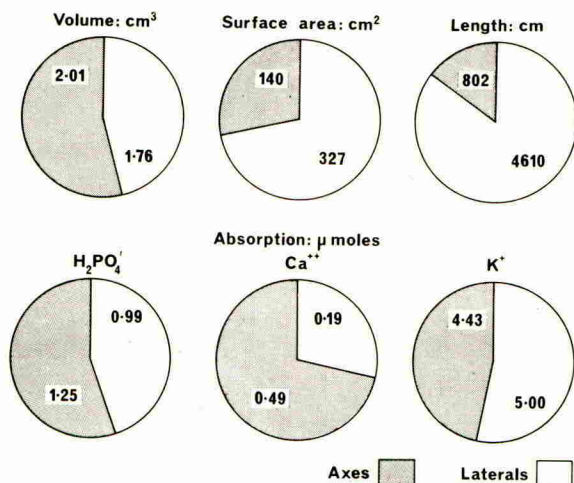


Fig. 2. The volume, surface area and length of root axes and laterals, and their contribution to the uptake of potassium, calcium and phosphate by barley plants, about 4 weeks old.

Indeed, if the external supply is constant the relative ability to absorb nutrients of different parts of such root systems, for example axes and laterals, is more closely related to the volume of living tissue than to any other parameter of root form which it is usually practicable to measure (Fig. 2) (Russell and Clarkson, 1972).

Detailed discussion of the mechanisms by which nutrients enter plants lies beyond the scope of this paper, but it is relevant to refer briefly to some aspects which may assist in comparing the factors which control the absorption of nutrients and of herbicides. From this viewpoint relationships between uptake of water and nutrients are of major interest. Both follow approximately the same route from the soil to the plant shoot but their uptake is controlled by different mechanisms. The rate at which water travels through the plant is determined primarily by evapo-transpiration from the leaves, whereas nutrient uptake is directly or indirectly under metabolic control. Some of the most obvious evidence that nutrients do not move initially by mass flow in water is provided by calculations of the Transpiration Stream Concentration Factor (TSCF) (Russell and Barber, 1960) defined as follows:-

$$\text{TSCF} = \frac{\text{quantity of solute/ml water transpired}}{\text{quantity of solute/ml external to root}}$$

If nutrients move passively in water the TSCF would not exceed 1 (and might be lower if any part of the system were less permeable to nutrients than to water). Depending on ambient conditions TSCFs for plant nutrients can vary widely (Table 1).

Table 1

TSCF for phosphate in barley and sunflower
in different environments

Concentration of phosphate	Transpiration	
	Low	High
Low P	50 - 156	11 - 34
High P	1 - 3	0.5 - 1

After Russell and Barber, (1960)

The influence of the nutrient requirement of the plant is evident from the fact that the highest values occur when the external supply is low; if in addition plants are transpiring slowly, the TSCF can exceed 100. The dependence of uptake on metabolism is thus clear. Other evidence of the relationship between metabolism and nutrient uptake comes from the well established effect of respiratory inhibitors but it does not necessarily follow that all ions are subject to active transport in the strict sense - that is to say that they are moved against an electrochemical potential gradient. The active transport of ion of one sign could lead to the passive movement of an ion of opposing sign against a concentration gradient to maintain the electrostatic balance. However, the salient features are that the entry of nutrients into plants is influenced directly or indirectly both by metabolic processes in roots and by utilization in the above ground parts. With many herbicides the situation is very different.

ABSORPTION OF HERBICIDES FROM SOIL

Many of the most important herbicides lie outside the scope of this discussion since they are normally applied to the leaves and stems of plants from which they may be translocated downwards, presumably in the phloem. Attention is confined to those compounds which are largely absorbed by roots, for example the substituted ureas and triazines, although entry through hypocotyls may also occur (Prendeville, 1968). Evidence from a number of workers (e.g. van Oorschot, 1970; Walker, 1972) indicates that these compounds move through plants with the water of transpiration.

Under a number of experimental conditions the TSCF for simazine in barley has been found less than unity (often about 0.8); it is little affected by the external concentration or by metabolic inhibitors. Wide variations in environmental factors influence it to only a small extent. This suggests strongly that simazine moves from the roots to the shoots of barley passively in the transpiration stream, though less rapidly than water (Shone and Wood, 1972a).

Even, however, if further work should show that other herbicides applied to soil also move passively to shoots in the transpiration stream, it cannot be inferred that the extent to which they reach their sites of action is determined solely by transpiration. Both the non-uniform distribution of herbicides in the soil and processes within the plants can greatly modify the situation.

The slow mobility of many herbicides causes them to be largely confined to the upper layers of soil, the highest concentration thus being experienced by the basal parts of roots and hypocotyls. There is some evidence that, as time passes, there is a decrease in the rate at which both water and simazine enter the older parts of roots (Shone and Wood, unpublished data) and that simazine may enter the hypocotyls of young radish seedlings, in contrast to roots, without the concomitant entry of water, provided that they are in contact with a solution containing the herbicide (Table 2). Accordingly as the root system elongates and increasingly absorbs water from deeper soil layers, the overall ratio in which herbicides and water enter the plant may generally be expected to decrease, especially if the surface soil dries.

Table 2

Translocation of simazine and water to
radish shoots from roots and hypocotyl

Simazine applied to:	Simazine ng	Water μ l	TSCF
Root system	9.8	60.0	0.6
Hypocotyl	6.6	1.5	16.0

Results per cm length of tissue

Many mechanisms within the plant can also affect the relative rate at which the herbicides and water move from the root surface to shoots. Relationships vary widely between species and between herbicides and are in the main little understood. In some species detoxification - conversion into non-toxic form - is of major importance. One of the best known examples is the detoxification of atrazine and simazine in maize (Shimabukuro *et al.*, 1970). Even, however, when the herbicide is not broken down, its movement to the shoot can be restricted by its retention in

specific organs, or by the existence of barriers to its movement. Strang and Rogers (1971a) have observed that diuron can be accumulated in lysigenous glands and trichomes of cotton. The same workers (1971b) have produced evidence that both the epidermis and endodermis in roots can be a partial barrier to the transfer of trifluralin in roots; the fact that the TSCF for simazine in barley is less than unity may perhaps be explained in these terms. There is considerable evidence also that in some species there is a restriction of the movement of herbicides from the veins of leaves into the mesophyll (Crafts and Yamaguchi, 1964). Sometimes the tolerance of plants to herbicides may be due to both types of mechanism. For example, in blackcurrant simazine is degraded to a marked degree during the process of translocation and in addition, only a small fraction of that which reaches leaves appears to pass out of the veins into the mesophyll where the phytotoxic inhibition of photosynthesis occurs (Shone and Wood, 1972b).

To sum up, there is at present no evidence that the uptake of many herbicides applied to the soil is metabolically mediated; upward movement appears compatible with passive transfer in the transpiration stream. None the less, numerous important and still partially understood factors, both external to the plant and within it, can profoundly modify the ratio in which herbicides and water are transferred from the soil to sites of herbicidal action.

REDUCED CULTIVATION AND ROOT GROWTH

When weed control by herbicides first made it possible to reduce the labour expended on cultivating arable land, it was natural to imagine that the more economical methods would at best give yields comparable to those after laborious seed bed preparation of the best traditional standard. It is timely now to review this opinion in the light of recent experience. The results of a number of field experiments on spring barley, both in this country and on the Continent, are summarised in Fig. 3; the situation of some other crops is broadly comparable (Cannell and Ellis, 1971).

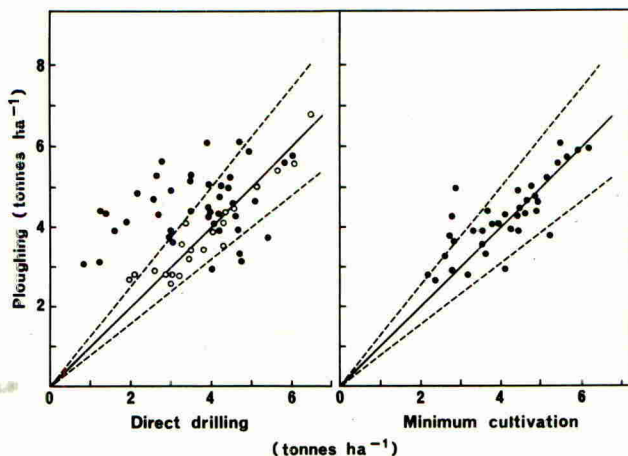


Fig. 3. The yield of grain of spring barley and winter wheat after direct drilling or minimum tillage compared with yield after ploughing.

Direct drilling or reduced cultivation has usually given appreciably lower yields than ploughing. This should not be regarded as a true measure of the basic unsuitability of the technique; difficulties have frequently been due to causes which it should be possible to overcome in the future, for example, inadequate experience and knowledge of fertilizer needs, the limitations of existing machinery and imperfect weed control. In some instances direct drilling has outyielded conventional cultivation - occasionally by over 20%. There are also hints that this difference can increase with time. Fig. 4 shows the results for the first year of an experiment conducted jointly by the ARC Weed Research Organization and the Letcombe Laboratory on an alluvial loam (Ellis and Elliott, personal communication). The more compacted soil conditions in the direct drilled plots led to an appreciable reduction in root penetration and the yield was significantly lower. However, when the same treatments were repeated for a second year, the difference was smaller and in the third year the yield on the direct drilled plot was significantly higher, 5150 kg ha⁻¹ as opposed to 4660 in the ploughed area.

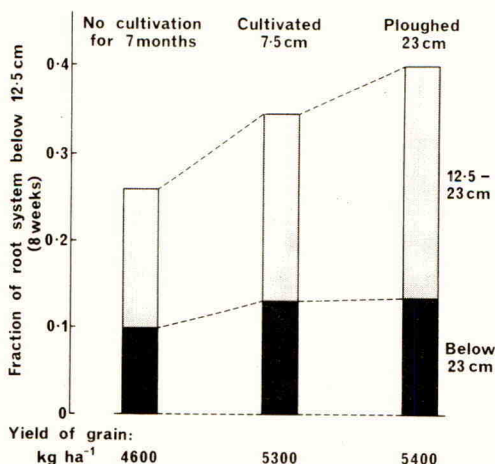


Fig. 4. Effect of cultivation on the penetration of roots of spring barley. Yield of grain for the three treatments is also shown.

Especially because of the considerable evidence that there are circumstances when cultivation is necessary to maintain good soil conditions, it would be easy to dismiss these indications to the contrary as due to random chance. But it would seem imprudent to do so without enquiring whether there are other reasons for considering that direct drilling or minimal cultivation sometimes have positive advantages in addition to the economy of labour. Since increased compaction is one of the most obvious characteristics of untilled soil it is relevant to consider the manner in which plant root systems respond to mechanical impedance. In the

laboratory the effects of this stress on root function can be studied independently of the other stresses, for example anaerobiosis, with which it can be associated in the field. The rate at which roots elongate can be considerably reduced if they have to resist pressures of more than about 0.2 bar (atmospheres) to enlarge pores in the solid media and 0.5 bar can bring about a five-fold reduction in their length; effects on emerging shoots are broadly comparable (Drew and Goss, 1971). Both root axes and laterals respond similarly to external pressure but, because of their smaller diameter laterals may enter freely the pores from which axes are excluded; in such situations an enhanced development of laterals may largely compensate for the reduced growth of root axes. The depth of the root system is thus considerably reduced but neither its total volume nor ability to absorb nutrients may be affected. This suggests that the restriction of root extension by mechanical impedance will not by itself reduce the productivity of crops provided that an adequate and continuing supply of nutrients and water is available in the restricted rooting zone. The observation in a number of field experiments that reduced root depth does not necessarily reduce crop yield may thus be explained.

An important implication of studies of the response of root systems to mechanical stress is that the continuity of a sufficient number of pores down which roots can freely penetrate is the prime requirement for root development rather than the total extent of the pore space, though porosity must be adequate for gas exchange. When the soil is not disturbed the continuity of spaces which roots can penetrate can change in several ways. Channels left by the previous season's roots may be available to their successors and planes of mechanical weakness can develop between structural units. Moreover in untilled soil the soil microfauna may make a greater contribution. Both German (Baeumer, 1970) and British studies (Ellis and Elliott, personal communication) show that the earthworm population can be two or three times greater if the soil is not tilled and the ability of root axes to explore such channels is well established. The greater continuity of soil pores in untilled land is also suggested by German observations that despite the smaller total of pore space in untilled land the rate at which water infiltrates into the soil and the depth it reaches can be greater than after ploughing (Baeumer, 1970). There are also indications from the same source that untilled land can be less subject to compaction by traffic - its structure is more stable.

There thus seem plausible grounds for considering the possibility that the soil may on occasions become a more favourable medium for root growth if it is not disturbed by cultivation, assuming that weeds are otherwise controlled. No definite conclusion will, however, be justified until more extensive and prolonged investigations have been carried out on the effect of alternative tillage methods on soil physical conditions and on the detailed manner in which they influence root growth. It is also obvious that full advantage can be taken of opportunities to reduce or eliminate cultivation if attention is given equally to improved seeding equipment and developing herbicides to control those weeds which still create major problems. It would seem timely now to give thought to these matters in our joint planning of future work.

Finally, at a time when the effects of agricultural chemicals on our natural environment are so frequently discussed those who find pleasure in apparent paradoxes may be interested by indications that some agricultural chemicals may create a more favourable environment for soil fauna.

Acknowledgements

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HERBICIDE MOVEMENT AND AVAILABILITY IN SOILS

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Summary Factors influencing the movement and availability of herbicides in soil are discussed and the applicability of laboratory measurements to field conditions considered. Laboratory investigations have done much to characterise adsorption equilibria and behaviour under carefully controlled conditions. This has made it possible to predict and explain the broad patterns of behaviour in the field. However recent studies have emphasised the importance of considering not only equilibrium properties, but also non-equilibrium factors, such as rates of adsorption, accessibility of pores and surfaces in structured soils and the relative distributions of herbicides and plant roots, if more detailed understanding and prediction are to be achieved.

INTRODUCTION

The essential requirement for a successful soil-applied herbicide is that weeds should be able to accumulate it to a toxic concentration reasonably quickly from soil treated at an economic rate, without damage to any associated crop. The amounts accumulated by plants over a given period depend on the ability of the soil to supply the chemical and the ability of the plant to absorb it from this supply. Scott Russell and Shone (1972) consider absorption of herbicides by the plant; this paper is concerned with the factors which influence the supply of herbicide from the soil.

Many chemicals are very active when supplied to roots in nutrient solution, but soil modifies this intrinsic activity by decreasing the concentration freely available in the soil solution, by controlling movement from the point of application and therefore the distribution relative to plant roots and by affecting the rate of decomposition. This paper will concentrate on the first two factors. The well-known properties of the bipyridyl herbicides provide the extreme example of how soil can affect activity: these chemicals are freely available to roots and very active in nutrient solution but effectively immobile and unavailable in soil at normal rates of use.

The fundamental property governing the availability and mobility of herbicides in soil is the way they partition between the vapour, solution and solid phases in soil. This partition depends on the physical and chemical properties of the chemical and of the soil.

ADSORPTION

Adsorption, which represents partition between solid surfaces and solution, has been studied extensively in recent years, mainly by equilibrating portions of soil with solutions of herbicide in dilute aqueous suspensions (for a comprehensive

review, see Hamaker and Thompson (1972)). Generally the proportion of chemical adsorbed decreases as the amount present increases giving curved adsorption isotherms, but in many cases the curvature is small over the concentration range of interest so that a linear approximation may be used. In such cases it is convenient to characterise adsorption in terms of the distribution coefficient k_d , given by $k_d = \text{amount adsorbed per unit weight of soil } (\mu\text{g/g}) / \text{concentration in solution at equilibrium } (\mu\text{g/ml})$. Table 1 shows some typical average values for k_d in mineral soils and emphasises the wide range given by different herbicides.

Table 1
Distribution coefficients for adsorption by soil

Herbicide	k_d	Reference
Dicamba	0	1
Picloram	0.45	2
2,4-D	1.59	2
Simazine	1.93	2
Atrazine	2.94	2
Dichlobenil	4.19	3
Diuron	6.29	2
Linuron	18.1	2
References: 1 Burnside & Lavy (1966)		
2 Hamaker & Thompson (1972)		
3 Briggs & Dawson (1970)		

For involatile pesticides, partition into the vapour phase need not be considered and as adsorbed material can be assumed to be immobile and unavailable biologically, the extent of adsorption can be used to give a broad guide to the way chemicals will behave in soil and the uses to which they can be put. Thus weakly adsorbed chemicals which are not rapidly degraded, such as pyriclor, move relatively freely in soil and are easily leached. They are also freely available for uptake by plant roots. These properties make it difficult to obtain reliable selectivity by "depth protection" following pre-sowing or pre-emergence treatments so that these chemicals tend to be more suitable for weed control in non-crop situations. At the other extreme the bipyridyliums, which have immeasurably large distribution coefficients at normal rates of use, are so strongly adsorbed that they have no residual activity whatever in soil. Between these two extremes, chemicals which are moderately adsorbed are not easily leached, but have limited mobility in soil and are sufficiently available to be taken up by suitably placed plant roots. It is in this group, where distribution coefficients fall roughly in the range 2 to 30, that selectivity can be obtained by depth protection and herbicides such as the triazines and substituted ureas used for residual pre-emergence treatments are found.

These broad concepts have been known for many years, but surprisingly their implications have still not been fully incorporated into practical recommendations. For example, as pointed out by Briggs (1977), recommended rates for herbicides such as simazine are adjusted for different soils on the basis of texture, although it has been demonstrated repeatedly that the extent of adsorption is determined mainly by the organic matter content of the soil. Although organic matter content and clay content are generally fairly well correlated, soils which have been in arable cultivation for long periods may contain relatively low levels of organic matter so

that the recommended rates may be unduly large for such soils. Such factors may explain yield losses experienced after applying pre-emergent herbicides to field beans on plots from long-term arable sequences at Rothamsted and Woburn (Johnston and Briggs 1972) and could apply more widely as few farmers are in a position to detect small losses in yield.

In laboratory or greenhouse experiments where chemicals are uniformly incorporated in carefully prepared soil, it is possible to calculate the supply available to plants from a knowledge of adsorption and to account for the observed performance quantitatively and in reasonable detail (Graham-Bryce 1967, Graham-Bryce and Etheridge 1971). Other factors such as decomposition may be included in such calculations (Walker 1972). However, although it is clear that laboratory adsorption measurements also provide a broad guide to behaviour in the field as discussed earlier, it has long been recognised that in practice there is no simple quantitative relationship between distribution coefficient and performance. There are two main reasons for this which are considered in more detail later. First it is doubtful how far equilibrium laboratory measurements with dilute suspensions give a valid picture of adsorption under the conditions in the field. Second, the distribution coefficient measured in the laboratory is an equilibrium property whereas the toxic action of a herbicide depends on a series of rate processes by which the growing weed must accumulate the concentration required for kill. Although many of these rate processes are influenced by adsorption, the relationships may be complex. An obvious example of these processes is transport to the roots. Herbicides are usually applied in such a way that the initial distribution is localised and separated from the zone containing the roots. The pattern of redistribution in relation to the position of the roots therefore has a considerable influence on performance. Performance may be complicated further by decomposition.

Validity of laboratory adsorption measurements under field conditions

Laboratory measurements are usually made with dilute suspensions of dispersed soil which allow maximum contact between herbicide and soil surfaces and in which apparent equilibria are reached rapidly, usually within a few hours. The applicability of such results to soil in the field may be questioned on two related grounds: first whether the same surfaces are available in natural soils which are often aggregated and where the proportion of water is much less and secondly whether the kinetics of adsorption are comparable.

There is some evidence from experiments in which adsorption was compared at different soil:solution ratios that additional surfaces may be exposed for adsorption as suspensions become progressively more dilute. For example Grover and Hance (1970) found that distribution coefficients for linuron and atrazine increased as soil:solution ratios decreased. They attributed this to the disintegration of soil particles and exposure of fresh surfaces which occurs when suspensions are shaken to obtain equilibration and which they showed by sedimentation tests to be more extensive in dilute suspensions. Some recent experiments with the systemic fungicide ethirimol (Graham-Bryce and Coutts, unpublished results) take this point further. Adsorption by dilute suspensions of sieved (2 mm) soil was measured at soil:solution ratios of 1:2 and 1:20 after equilibrating for 48 h on a reciprocating shaker and compared with a further treatment in which a 1:2 suspension was first subjected to ultrasonic disintegration and then equilibrated on a gentle rotating shaker. Table 2 shows that, as in Grover and Hance's experiments, adsorption was less at larger soil:solution ratios, but this was affected relatively little by ultrasonic disintegration, although sedimentation tests showed that this increased dispersion of the soil particles. Further, when 1:2 suspensions were diluted to 1:20 a new equilibrium, lying on the original 1:20 isotherm was established without further shaking. Further detailed studies are required, and

other factors such as differences in the ionic composition of the soil solution in the different suspensions may be involved, but at their face value, these results suggest that additional adsorbing surfaces can be unmasked at smaller soil:solution ratios even without actual disintegration of aggregates. If this effect is widespread and the trend continues to the even larger soil:solution ratios in natural conditions, then laboratory measurements may substantially over-estimate the extent of adsorption.

Table 2

Average distribution coefficients (k_d) for ethirimol at various soil:solution ratios (solution concentrations 2-12 $\mu\text{g/ml}$ in M/100 CaCl_2)

Soil	Soil:solution ratio		
	1:20	1:2	1:2 after ultra-sonic disintegration
Whiskers	16.3	12.7	11.3
Steining	54.5	-	22.4

Whether or not a proportion of the adsorbing surface is completely unavailable in natural soils, kinetic studies leave little doubt that it is very much less accessible. Some recent results by Mercer (1972) with simazine illustrate this very effectively. When soils were equilibrated with solutions of radiolabelled simazine for 24 h, adsorption decreased as the soil:solution ratio increased as in the examples discussed above. For example in Letcombe soil, k_d decreased from 6.4 in a 1:20 suspension to 2.03 at field capacity (soil:solution ratio 1:0.4). However if the treated soil at field capacity was allowed to stand for periods up to 3 months, amounts adsorbed increased steadily. K_d values reached those in the 1:20 suspension after about 6 weeks and eventually exceeded them. These experiments demonstrate the long periods required to reach equilibrium and the inaccessibility of adsorption sites under natural conditions, and also the possibility that there may be slow adsorption processes which have gone largely undetected in short term laboratory experiments. Slow equilibration has also been observed in other studies (Hamaker *et al.*, 1966, Obien and Green (1969)).

In addition to these uncertainties about the validity of distribution coefficients measured in short term experiments with dilute suspensions, the significance of adsorption depends on the extent to which it is reversible, that is on whether the solid phase acts merely as a temporary reservoir from which the herbicide is released again as the concentration in the soil solution decreases because of decomposition, leaching or absorption by plants, or acts as a permanent sink from which the chemical is not subsequently released. Here again laboratory desorption experiments with dilute suspensions which allow rapid equilibration may give an oversimplified picture of behaviour in the field. With some exceptions, such experiments generally show that equilibrium is reached rather more slowly when approached by desorption than by adsorption, particularly with organic soils, but that provided sufficient time is allowed, adsorption is largely reversible. However in the field where herbicides are in contact with soils for prolonged periods under weathering conditions, reversibility is more questionable, particularly if the slow adsorption processes discussed above involve chemisorption and bond formation. Also, several experiments (Graham-Bryce 1967, Hilton and Yuen 1963) suggest that when treated soils are subjected to wetting and drying cycles, such as would occur under natural weathering, chemicals become more difficult to desorb.

In practice, therefore, predicting availability to plants from adsorption measurements is considerably more complicated than simple laboratory measurements would suggest, even without allowing for the effects of movement in soil. Before these effects are discussed, partition between vapour and solution will be considered briefly.

PARTITION BETWEEN VAPOUR AND SOLUTION

For a pesticide which obeys Henry's law (i.e. the concentration in solution is proportional to the vapour pressure) partition between solution and vapour may be calculated from the ratio of the concentration in the saturated vapour (which can be calculated from the saturated vapour pressure) to the concentration in saturated solution (i.e. the solubility). Table 3 shows values for some typical herbicides, from which it can be seen that in a soil containing equal volumes of water and air, even "highly volatile" herbicides such as EPTC and dichlobenil are present predominantly in the solution phase. However the proportion in the vapour phase is sufficient to affect behaviour of these herbicides considerably, as will be shown later.

Table 3

Partition coefficients between solution and vapour for various herbicides

Herbicide	Vapour pressure mm Hg	Solubility µg/ml	Partition coefficient (solution:vapour)
Trifluralin	1.0×10^{-4} (25°C)	0.58 (25°C)	3.22×10^2
EPTC	1.97×10^{-2} (24°C)	375 (25°C)	1.86×10^3
Dichlobenil	5.5×10^{-4} (20°C)	18 (20°C)	3.48×10^3
Monuron	5×10^{-7} (25°C)	230 (25°C)	2.36×10^5
Simazine	6.1×10^{-9} (20°C)	5 (20°C)	7.35×10^7

(Physical data from Hamaker (1972) and Martin (1971))

Most herbicides probably do not obey Henry's law strictly so that partition coefficients would not be independent of concentration. However there should be less likelihood that slow equilibration processes such as those discussed in relation to adsorption add further complications.

Combining the vapour:solution partition coefficient with the distribution coefficient for adsorption allows the complete distribution between the phases to be found.

MOVEMENT AND REDISTRIBUTION IN SOIL

Herbicides are transported in soil mainly by the physical processes of molecular diffusion and bulk transfer with moving water.

In free air, volatile herbicides can diffuse relatively rapidly. Diffusion coefficients are typically about 10^{-1} cm²/s, corresponding to an average displace-

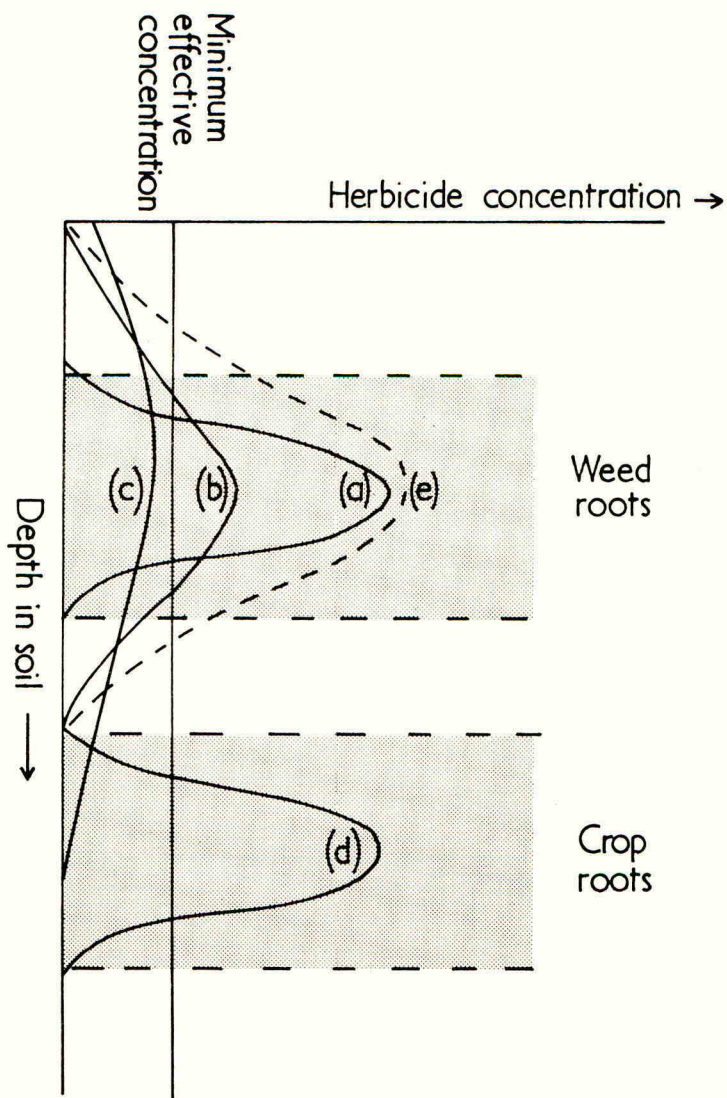
ment of 130 cm in a day. Diffusion coefficients in free solution are very much less (about 10^{-5} cm²/s, corresponding to average displacements of only 1.3 cm in a day). Involatile herbicides, or herbicides which partition extensively into water from air therefore diffuse slowly in moist soil, although the vapour pathway makes a significant contribution to diffusion even when the proportion in the vapour phase appears relatively small because vapour diffusion is so much faster than diffusion in solution. It is not until partition between solution and vapour exceeds about 50,000 to 1 that the vapour pathway can be neglected, and the properties of chemicals such as EPTC and dichlobenil must be seen in relation to such figures. Diffusion in soil is also retarded by adsorption onto solid surfaces and because the pathway through the pores is restricted and tortuous, giving diffusion coefficients typically of the order of 10^{-7} cm²/s. In suitable cases the effects of these different factors can be estimated (Graham-Bryce 1969) assuming partition between the phases is rapid compared with the changes in concentration produced by diffusion. While this may reasonably be assumed in short term laboratory experiments, the existence of slow adsorption and desorption processes such as those already considered suggests that diffusion is more complex in aggregated field soils. Whatever the detailed effects of the different factors, however, there can be no doubt that while diffusion must always be taken into account when considering transport over short distances such as in the micro-regions around granules or plant roots in soil, it is only for volatile herbicides that diffusion is likely to be effective for transport over long distances, particularly as displacements due to diffusion increase in proportion to the square root of time rather than directly with time.

Bulk transfer

Because of adsorption, bulk transfer of pesticides through soil by moving water can be regarded as analogous to a form of chromatography. The principles determining the pattern of movement can be illustrated by considering a common situation in practice: leaching of herbicide applied to the soil surface as a thin layer. According to simple chromatographic theory, such a layer would be leached downwards as an increasingly diffuse bell-shaped wave. The exact shape of this wave has important consequences for weed control which are illustrated schematically in fig. 1. This shows various possible distributions after a given amount of leaching. For illustration it is assumed that weed roots and crop roots are effectively confined to two separate zones of soil and also that there is a minimum concentration, the same for both weeds and crop, below which plants are undamaged. In reality lethal action depends on both concentration and time, but it is possible to think loosely in terms of a minimum effective concentration below which the rate of uptake by the growing plant can never be rapid enough to achieve a lethal concentration in the plant before the chemical is dissipated by processes such as degradation.

If the distribution after leaching is like that shown in (a) the herbicide is confined as a narrow band, well within the zone containing the weed roots and giving a concentration well above that required for kill. To ensure a more complete kill however there may be advantages in having a more diffuse distribution such as (b) in which the minimum effective concentration is exceeded throughout the required zone, although the peak maximum is less. When the distribution becomes as diffuse as that shown in (c) the concentration throughout the weed zone is too small for the plants to accumulate a toxic dose and also there is some chemical in the zone containing crop roots. However the concentration in this zone is small and there would be little risk compared with a chemical which was distributed as in (d). The amount of chemical in examples (a) - (d) is assumed the same. It is worth pointing out that increasing the amount of chemical would not only increase the peak concentration, but also considerably broaden the zone of effective action; for example (e) shows the distribution obtained by applying twice the dose of a chemical giving the distribution shown in (b).

Fig 1. Examples of possible distributions in soil after leaching from surface



Clearly many variations on these basic patterns of distribution are possible and the exact distribution given by a herbicide in a particular soil depends on factors such as the volume of water required to dissolve the chemical, the extent of adsorption, longitudinal diffusion in the soil pores and the rate at which adsorption equilibria are achieved in relation to the rate of water flow. The effects of these factors for the idealised situation in which the water flow is continuous have been analysed by Oddson *et al.* (1970) and Letey and Oddson (1972). As the importance of slow equilibration has been emphasised in this paper, the influence of the rate at which adsorption equilibria are established will be considered briefly.

As the effective rate of adsorption decreases, the depth of initial penetration by the chemical (during the period when it dissolves) increases. After this, the rate of adsorption has no effect on the position of the peak maximum, but the slower the rate of adsorption, the broader the wave and the smaller the maximum. Closely related to the effects of the rate of the adsorption process itself are effects due to hydrodynamic dispersion which is caused by the tendency of the leaching solution to move faster in large than in small pores and in the centres of pores than at the solid surfaces, and which results in variations on the micro-scale in the rates at which adsorbate reaches or leaves different parts of the porous system across the leaching front. The broadening effects of hydrodynamic dispersion are greater when soil is saturated and flow occurs mostly in large pores between aggregates in structured soils than under unsaturated conditions when the water tends to move much more slowly in smaller pores within the aggregates.

If, as the evidence discussed above indicates, slow adsorption/desorption processes (possibly involving chemisorption) occur in practice and part of the adsorbing surface is inaccessible in very fine pores, a considerable broadening of herbicide bands would be expected during leaching in the field.

Effects of water movements in practice

Under natural conditions water flow is obviously not continuous and the pattern of leaching also depends therefore on the extent and nature of water movement in the profile. For surface-applied chemicals, infiltration of rainfall or irrigation into the soil must be considered first. In Britain rates of rainfall are mostly smaller than the rate at which water can enter the soil so that the surface does not usually become flooded. Under such conditions the water content of the wetted soil and the rate at which the wetting front advances increase with the application rate, but the depth of penetration of a given quantity of rain is greater at smaller rainfall rates.

When rainfall stops, water within the profile is redistributed. The details of redistribution are very complicated and depend on the subsequent weather and the properties of the soil but the general features are described by Letey and Oddson (1972). In the surface layers, water in the larger pores drains away under gravity and as the soil becomes drier, hydraulic conductivity decreases rapidly and further downward movement is very slow. Evaporation at the surface may then start drawing water in the upper horizons upwards, transporting herbicide with it and partially reversing the earlier downward trend. Relatively immobile herbicides subjected to repeated wetting and drying cycles such as this may never be leached to drainage water during a growing season and merely be redistributed more and more thoroughly through the upper zones of the soil. However, lower in the profile the upward gradient due to evaporation between periods of rain may never be sufficient to overcome the downward gradient due to gravity and herbicide mobile enough to reach this level will be leached continuously to the drainage water.

When these complexities in the pattern of water movement are added to the uncertainties about adsorption discussed earlier, it will be clear that while it is possible to specify the factors which influence movement and to predict behaviour

in carefully packed columns of soil in the laboratory, prediction of behaviour in the field is much more difficult. This is well illustrated by results obtained by Riley (1972) with the herbicide haloxydine. This herbicide is not measurably adsorbed by mineral soils and in carefully prepared laboratory columns it is leached much as chromatographic theory would predict as a narrow band moving with the solvent front. After application to the soil surface in the field, however, the chemical became redistributed more or less uniformly throughout the 15-30 cm profiles sampled even after substantial amounts of rainfall. This is probably explained by fluctuating water movements associated with wetting and drying as described above, coupled with retention in fine pores in which water movement is very slow and from which the chemical is released only slowly to the larger pores where most of the water flow occurs.

The effect of movement on the availability of the herbicide to the plant depends on the position of the roots relative to the distributions produced, that is on the fraction of actively absorbing roots which is within the treated band. Within such a band, the rate of supply depends on movement to the root by molecular diffusion and bulk transfer with the water which moves directly to the root in response to transpiration, which are both influenced by the factors already discussed. Theoretical calculations for systemic organophosphorus insecticides (Graham-Bryce 1968) suggest that within the treated band these processes are unlikely to limit uptake and that amounts absorbed are more likely to depend on the rate at which the plant can absorb the chemical from the concentration presented in the soil solution.

CONCLUSIONS

Investigations into the interactions of herbicides with soil have so far done much to characterise adsorption mechanisms and equilibria, and behaviour under carefully controlled conditions. This has enabled the broad patterns of behaviour in the field to be explained and predicted. However it has become increasingly apparent that for more detailed understanding and prediction, it is necessary to consider not only equilibrium properties, but also non-equilibrium factors such as rates of adsorption, accessibility of pores and surfaces in structured soils and the relative distributions of herbicides and plant roots. New techniques, such as those involving direct autoradiography of soils treated with radiolabelled chemicals (Grossbard 1969; Graham-Bryce and Coutts 1971) are being developed and have already revealed how heterogeneous distributions of pesticides are on a micro-scale. It is from such non-equilibrium studies that the most significant advances in the understanding of herbicide behaviour in soil can be expected during the next few years.

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THE SOIL ORGANO-MINERAL COMPLEX IN RELATION TO HERBICIDE ACTIVITY AND
A POSSIBLE MEANS OF FORECASTING PERSISTENCE

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Summary It is probable that many of our ideas, concerning the control of organic herbicide decay in soil, are erroneously based on macroenvironment characteristics. Soil reaction, aeration and adsorptive phenomena are quoted as examples. It is now possible to separate, in a biologically stable form, the components of the organo-mineral complex. Consequently, it may prove rewarding to re-evaluate existing data concerned with herbicide residence times in soil. It is suggested that, after correlating soil physical and chemical characteristics with persistence, a simple numerical scoring system could be developed which would allow an accurate predictive approach to pesticide longevity.

For the most effective use of an agro-chemical its persistence, and that of any toxic byproducts, need to be known. With this information the optimum quantity of a chemical required to perform a specific function, over a predetermined period of time, can be assessed with some accuracy. At present herbicides are subjected to a range of tests to determine their persistence but due to the heterogenous nature of the soil environment, the results present only a very general guide to soil residence times. What is needed is an accurate predictive approach to pesticide longevity, eliminating the need for lengthy screening programmes and possibly based on a combination of soil physical, chemical and biological properties and the characteristics of the herbicide. These and other factors relating persistence to soil environmental conditions have been recently reviewed by the author (Burns 1972). It is the intention of this paper to outline some of the basic problems confronting workers in this field and to indicate some potentially rewarding approaches to their solution as suggested by research into the nature of the soil organo-mineral complex.

A. The Organo-Mineral Complex

In mineral soils most of the organic matter is colloidal in form and intimately associated with the inorganic fraction to form the organo-mineral complex (Kononova 1966). The humus-clay microenvironment is a site of high biological and non-biological activity and it is here that we need to look for the basic information concerning soil-herbicide interactions.

The nature of the relationship between the two colloidal components of the organo-mineral complex is poorly understood. It is suggested that polyvalent metals, such as Ca, Mg, Al and Fe, form cation bridges between the anionic clay and organic particles and that this association imparts resistance to the humic materials. Consequently, what appears as a readily accessible and ephemeral microbial substrate is, in fact, persistent for long periods of time. The study of the organo-mineral relationship has been partially hindered by an inability to separate the two components in an unaltered form. Traditional methods have involved the use of reagents which either destroy the clay minerals or degrade the organic matter.

However, in recent years it has been possible to separate the fractions by weakening the cation bridge with the use of Na-saturated exchange resins and by sonication (Edwards and Bremner, 1967). In the last three years we have developed techniques which allow the extraction of organic matter from soil in a pure (no colloidal clay) and unchanged (enzyme active) form (Burns et al, 1972 a & b). This procedure; involving sonication pretreatment followed by salt extraction, filtration and dialysis; affords material which may help to tell us about the complex nature of colloidal organic matter and its association with the organo-mineral complex.

It is well known that herbicide residence times in soil are closely related to their sorption characteristics at colloidal surfaces. Microorganisms, themselves, are adsorbed to a varying degree on soil particles and this phenomenon has been the subject of a recent review article by Marshall (1971). As both organic and clay particles carry an abundance of negative charges and microbes are also anionic, mutual adsorption may be through cation or water bridges, although it is fair to state that positive charges exist on colloid surfaces especially at acid pH's. As there is good evidence to suggest that reaction at both clay and organic colloid surfaces is two or more pH units below that measured by traditional means (McLaren 1960, Bailey et al 1968), adsorption of anionic particles by Coulombic forces or even ion exchange, should not be considered exceptional. The attachment of microorganisms to the soil components is poorly understood but it is evident that a variety of adsorptive mechanisms are involved together with the adhesive effect of extracellular exudates. As far as the microbe is concerned its association with the organo-mineral complex affords a supply of substrate augmented by adsorption from the soil water, either onto the colloid or the microbe itself, of additional organic substrates such as herbicides. Proliferation, high substrate turn-over rates and shorter times for pesticide persistence are all features of microbial activity in the adsorbed state.

Due to the variety of adsorptive reactions available to charged and uncharged particles it is not just the strongly cationic herbicides, such as the bipyridylium group, that are subject to the adsorptive influence of the organo-mineral complex. Consequently, the adsorption of herbicides may involve cationic, anionic and neutral compounds. Upon immobilization herbicide decay may either be accelerated, by being brought in contact with neighbouring microbes or extracellular enzyme molecules, or retarded if the substrate, enzyme and/or microorganism are adsorbed distant from each other. In the latter instance interaction may be delayed until sorption flux brings the potential reactants together.

Recent studies have shown that much of the persistent extracellular enzymatic activity in soil is associated with enzymes deeply situated in the organic material of the organo-mineral complex (Burns et al 1972 b). It is possible that herbicide molecules, with a varying ability related to charge and molecular size, are able to diffuse through a porous organic material and complex with a suitable enzyme. Eventually the products of this reaction would diffuse out of the organic colloid.

The non-biological loss of herbicides is also influenced by adsorption at surfaces which may retard both leaching and volatilization rates. If this adsorption occurs at the surface of the soil profile it may stimulate the photodecomposition of a wide range of herbicides, notably paraquat, diquat, monuron, atrazine and simazine. In addition adsorption onto clay and organic surfaces may catalyze the hydrolysis of triazines.

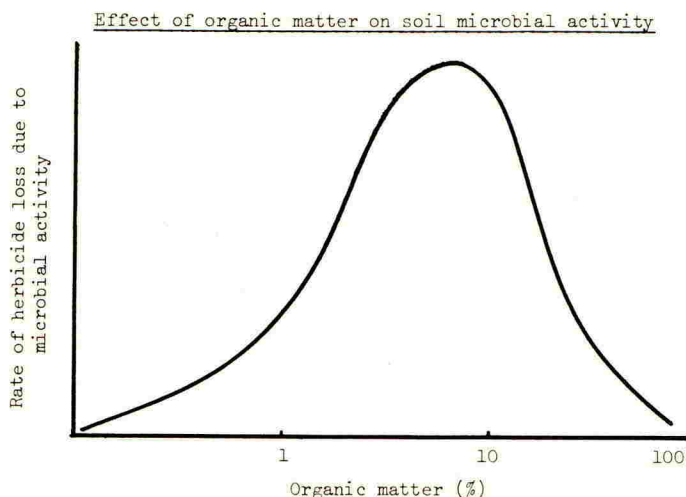
B. Characteristics of the separated components of the organo-mineral complex.

i) Clays: As a result of their structural (layering of silica and aluminium sheets) and physical (isomorphous substitution) properties, kaolinitic clays have

non-expanding lattices, an external adsorption area and low cation exchange capacities; whilst montmorillonite and vermiculite clays have expanding lattices, both internal and external adsorptive surfaces and a high exchange capacity. It is because the biological and non-biological reactivity of these inorganic particles is directly related to their surface areas, that soil clays, especially those of the expanding lattice type, assume an high degree of importance in soil-pesticide interactions. The differences in herbicide adsorption capacities between clay types are well known. For instance, the adsorption and immobilization of paraquat and diquat by interlamellar adsorption onto expanding lattice clays will retard or completely inhibit microbial decay and phytotoxicity. Kaolinitic clays, on the other hand, do not have such a dramatic effect (Weber and Coble 1968).

ii) Organic matter: There are many apparently contradictory reports describing both direct and inverse relationships between soil organic content and the persistence of a particular herbicide. As a result it appears that there are at least three ways in which organic matter can affect herbicide longevity. (Fig.1). In the first instance a minimum level of organic matter (probably > 1%) is necessary to support an active microbial population. In these situations the microbial diversity is such that the chances of there being an enzyme system present which will attack the herbicide molecule are considerable. In contrast, the quantitative and qualitative microbial population in a soil with less than 1% organic matter is such that extensive enrichment may be needed before any significant breakdown of the agro-chemical can occur. Thus microbial decay would be comparatively slow. In high organic matter soils (> 15%). The adsorptive capacity may serve to immobilize the herbicide, causing retardation of breakdown in much the same way as do the expanding lattice clays. This kind of relationship has been proposed for the thiocarbamate herbicides (Koren et al 1968) in which group inactivation may be due to strong adsorption in soils with high adsorptive capacities; volatilization in low adsorptive soils and microbial activity in soils of moderate adsorptive capacity. We are presently trying to evaluate this complex three-part relationship, with extracted organic matter fractions and a range of variably charged herbicides.

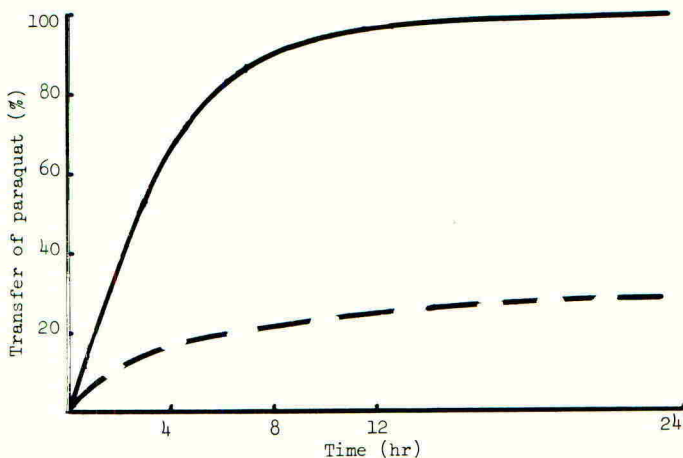
Fig.1.



It is also apparent that adsorption to organic surfaces may, in some instances, be of a more tenuous nature than that to clay surfaces. For example, our work with paraquat on separated clay and organic colloidal fractions (Burns and Audus 1970) has indicated that organic matter adsorption does not prevent microbial decay but that in an heterogeneous system desorption of paraquat from the organic matter and subsequent readsorption onto clay (probably within lattices) immobilises the herbicide and renders it biological inactive. (Fig.2). This phenomenon may account for any initial decay of paraquat immediately after application. Adsorption-desorption flux may be a common phenomenon among certain groups of herbicides and almost certainly occurs within the organo-mineral complex itself.

Fig.2

Transfer of paraquat adsorbed on a soil organic fraction through a dialysis membrane into water (---) and to the inorganic fraction of the same soil (—).



C. The Environment of the Colloid Surface.

As described previously the pH at clay and organic surfaces is considerably more acid than in the bulk suspension. Variations in acidity may affect both the adsorption process as a whole and the type of adsorptive mechanisms involved.

Reaction also has a more direct effect on herbicide decay by influencing the species of microorganism that can efficiently function at the colloid surface. For instance most soil bacteria are active in near neutral environments, whilst the acinomyces prefer alkaline conditions. Fungi, on the other hand, have an optimum pH somewhat on the acid side of neutral. As a result it has been suggested that, for instance the microbial decay of 2,4-D in acid soils is a function of the fungal population whilst the disappearance of dalapon and amitrole is very slow at acid pH's and presumably not readily metabolised by acidophilic fungi (Corbin and Upchurch 1967). Substrate preference of this nature by certain groups of micro-

organisms is not uncommon. Reaction may also affect microbial activities, in addition to species occurrence. For example the breakdown of DNOC by a Corynebacterium species only occurs at alkaline pH's. At neutral and alkaline pH's this bacterium utilises alternative nitrogen sources (Gundersen and Jensen 1956).

At the colloid surface water molecules compete with herbicides for adsorption sites. As a result persistence may be prolonged at low water levels as competition is less intense and more pesticide becomes adsorbed. Under dehydrating conditions it is suggested that the adsorption of herbicides is predominantly a feature of the clay particles; whereas at higher soil water levels, organic matter adsorption may be predominant. Water associated with colloid surfaces may also influence the activity of aerobic and anaerobic microorganisms. It is frequently reported that anaerobic decay is more rapid than that mediated by aerobic microbes, especially for organo-chlorine insecticides such as DDT and γ BHC.

D. Forecasting Herbicide Persistence.

Once the information regarding individual and combined effects of the components of the organo-mineral complex is at hand, we may be able to approach a predictive understanding of herbicide activity in soil. In the meantime there are a number of problems in using existing information referring to herbicide disappearance rates. For example, conditions of temperature, water and pH are frequently left unstated or vague and soil analyses are often incomplete or missing altogether. In addition an high number of reports use bioassays or the evolution of labelled CO₂ as a measure of pesticide persistence, although this type of experiment only measures the availability of the herbicide to the indicator plant or to the microbial population. As we have seen from the previous discussion adsorption may significantly effect the availability of a compound and this may be changed by a variation in microenvironment characteristics. For example it is possible for a bioassay to show a negative response to a herbicide at one period in time and yet a change in the pH of the soil may result in desorption and the subsequent reappearance of toxicity symptoms. In trying to assess the relative effects of the multitude of factors influencing persistence it is apparent that only direct extraction of the herbicide from soil affords a reliable estimate of herbicide loss. Even in this method there are problems concerned with consistent extraction rates and changes in the compound due to the method employed. However, with the now routine use of gas chromatography, accurate and rapid assessment of residue levels is readily available - at least for those compounds which lend themselves to this type of analysis.

What one would eventually like to see is a chart presenting easily understandable information relating soil chemical and physical characteristics to herbicide persistence. As far as the agriculturalist is concerned the system needs to provide him with figures for application rates and an accurate prediction of herbicide persistence under a given set of environmental conditions. One possible format for this information is a booklet presenting a scoring system based upon the comparative importance of the properties of the herbicide itself (chemical structure, solubility, vapour pressure, etc.), average soil temperature and water levels, pH and mineral and organic matter analyses (Table 1). Summation of scores for all these categories would then give an herbicide index which can be used to relate application rate to persistence in weeks (Table 2). With this type of information the farmer or horticulturalist will know exactly how much of a particular herbicide to apply to achieve a known effect over a predictable period. Valuable predictive methods of this type have been used in America for the last two or three years (Favre 1969). In these instances soil organic matter is used as the only criterion for predicting persistence and phytotoxicity and farmers and extension specialists have been using a chart relating colour to percent organic matter. From this information pesticide application rates are readily calculated. Our information should eventually allow for a more accurate and reliable method of estimating dose rates.

Table 1

Scoring organic and inorganic fractions for herbicide persistence
in a sandy clay loam soil

%	O.M.	Lattice clay	Non-lattice clay	Sand	Silt
1.0	9	1	4	6	5
1-5	4	2	5	5	5
6-10	2	3	5	5	6
11-15	3	5	5	4	5
16-20	6	6	6	2	6
21-30	8	8	6	2	5
31-40	9	10	8	4	4
41-50	10	10	8	6	4
51-75	10	10	8	7	4
76-100	10	10	8	9	4

High numbers are indicative of persistence

Table 2

Persistence index (in weeks)

lbs/acre

Total*	0.5	1	2	3	4	5
40	26	28	30	31	32	33
41	27	29	31	32	33	34
42	27	29	31	32	33	34
43	28	30	32	33	34	35
44	28	30	32	33	34	35
45	29	31	33	34	35	36
46	29	31	33	34	35	36
47	30	32	34	35	36	37
48	30	32	34	35	36	37

*Five categories in Table 1 in addition to numerical values for temperature, water, pH and the physical and chemical properties of the herbicide.

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SOIL-APPLIED HERBICIDES IN PRACTICE

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Summary Current recommendations for the use of soil-applied herbicides are considered in the light of the present state of knowledge of behaviour of herbicides in soil. Forecasts of future developments are made briefly.

The preceding papers in this Session have reported research and provided comment thereon which gives a conspectus of the way in which our detailed knowledge of the behaviour of herbicides in soil and our understanding of the factors which influence this have increased dramatically in recent years. My contribution is not a paper in the same category but is in the nature of a concluding comment on practical usage of soil-applied herbicides and on whether comparable strides have been made in recommendations for their use.

Modern soil-applied herbicides have featured in weed control recommendations in the UK for the past 15 years or more. One such early recommendation was for the use of monuron as a residual pre-emergence herbicide in asparagus beds which appeared tentatively in the 1956 paperback edition of the Weed Control Handbook. This particular recommendation is still present, with slight embellishment, in the 7th edition of the Weed Control Handbook the publication of which coincides with this Conference.

In the late nineteen-fifties many soil-applied herbicides came into established use and have stayed with us to the present time. Thus in 1960 a tentative recommendation for the use of simazine in field beans appeared in the Handbook and some of the wording of that recommendation is still readily recognisable in the corresponding recommendation in the new edition. In retrospect it seems remarkable how the early recommendations have stood the test of time. The present recommendation for the use of pyrazone in beet, for example, makes much the same reference to dose adjustment for soil type and to the advantages of incorporation in dry soil conditions, current or anticipated, as did the first tentative recommendation in 1965. However, in some other cases one may well question whether it is merely a matter of a recommendation based on limited trials and early field experience having become sanctified by time, with some of the ideas enshrined therein now overripe for questioning.

The main change that has occurred over the years is the proliferation in number of herbicides and situations in which they are utilised. Clearly it has been easier for industry to find good pre-emergence herbicides than good post-emergence herbicides. Clearly these have found acceptance with farmers and horticulturalists in spite of the restrictions and limitations which are applicable to them. In part their success lies in ability to give good and continuing weed control right from the time of germination of the crop, but it lies also in part from the absence of competitive post-emergence herbicides selective in the crops concerned.

What sort of guidance is provided for the user of these diverse herbicides in 1972? For the most part this guidance falls into a pattern. Let us first look at

that pattern and then see whether present research seems likely to help us to improve and extend this guidance.

The recommendation in the new edition of the Weed Control Handbook for the use of lenacil for weed control in sugar beet may be taken as a typical example. It starts with a series of maximum safe doses according to soil type with specific doses for very light soils, light soils, silts and warps, and medium loams, coupled with a restriction not to use at all on certain other soil types. There is then a restriction on timing in relation to drilling. There is also a recommendation specifically for use on high organic matter soils prior to sowing, involving incorporation to improve weed control performance on such soils. The main recommendation then indicates the part played by soil moisture in securing maximum weed control efficiency and the desirability of a moist seedbed and some rainfall after application. However it warns that exceptionally heavy rainfall can lead to leaching resulting in some damage to the crop. Finally a recommendation is made as to the time interval which must elapse following application before anything other than a crop tolerant to lenacil is sown.

This recommendation is reasonably representative of the type and extent of information provided for the user of a soil-applied herbicide. It exemplifies one problem for the ordinary user in that there is a great deal to learn and interpret in respect of each of the many soil-applied herbicides which he may be using.

Next I would like to draw your attention to some particular aspects of such recommendations, again taken from the Weed Control Handbook in its newest Edition. Firstly let us take the relation of soil characteristics to weed control performance and crop safety as reflected in dose used or absolute restriction to certain situations. Thus we encounter such phrases as 'should not be used on silt soils deficient in clay and organic matter' (mixtures containing chlorpropham for peas) or 'should not be used on soils of lighter texture than loamy very fine sand' (prometryne for peas) or 'not recommended on any very stony or gravelly soils' (lenacil for red beet) or the type of gradation of dose to soil description indicated previously in the recommendation for lenacil on sugar beet.

Does our wealth of knowledge on the adsorption and inactivation of herbicides by soils as exemplified in the paper by Graham-Bryce enable us to improve on such advice? The point has been emphasised that guidance in respect of dose is frequently based on texture, though the experimental evidence repeatedly demonstrates that organic matter content of soil is the main factor governing adsorption of most herbicides and hence presumably activity through control of availability and leaching. It can be argued that greater predictability of required dose could be obtained if this were based on whatever is known, precise or imprecise, on the organic matter situation in the surface layers of the field to be treated. However, practical experience both within UK as a whole and in Europe may well suggest that this represents an over-simplification. Research and experience also shows that other environmental factors can override soil composition factors.

The nature of the soil surface is sometimes specified, for example, 'seedbed should be left with a fine even tilth, preferably rolled' (cyanazine for peas) or 'should not be used on very cloddy soils' (prometryne for peas). Some doubt has been cast at times on the former type of recommendation because it may well give rise to a greater population of weeds requiring to be controlled, but the latter is aimed at preventing protection of portions of soil surface by clods, which thereby receive an inadequate dose of herbicide. Recommendations regarding drilling have become more precise and helpful as exemplified by 'should be drilled to give 12 to 25 mm of settled soil above the seed' (cyanazine for peas). This defines the requirement less ambiguously than in earlier times but still leaves the practical problem of securing this consistently with the available drills under the field conditions the farmer has to cope with.

Another aspect which is beginning to receive more careful consideration is incorporation. This is sometimes undesirable, leading to 'incorporation, whether mechanical or by irrigation, reduces the effectiveness' (nitrofen for kale) and at other times helpful e.g. 'shallow incorporation generally improves the activity under dry soil conditions' (atrazine for maize). In the latter type of situation discrimination is usually needed in order to enhance weed control without reducing the safety to the crop, for with many uses of soil-applied herbicides selectivity margins are comparatively small. This underlines the need for more information on how to achieve precise and reproducible patterns of incorporation under practical conditions in the field. This would enable exploitation of the information which is being acquired, as shown by papers in this Session, on the position of uptake of herbicides by both root systems and shoots as they make their way to the soil surface.

Comment on soil moisture in relation to weed control activity is now frequent. This may be in general terms along the lines 'good weed control depends upon sufficient rain falling after treatment to at least maintain soil moisture' (linuron for parsley) but with no suggestion as to how to secure this, or it may be tied to suggestions about timing, as for example 'most satisfactory results are likely to follow applications made in early spring when occurrence of rain soon after spraying is probable' (pyrazone for sugar beet), though this seems relatable more to a climate with a pattern more predictable than that of the UK. Sometimes advice is more specific as in 'under dry conditions the dose should be increased to 1.40 kg/ha' (pronamide for lettuce). Both the invited papers in the present Session have added considerably to the clarity of our thinking on soil moisture in relation to movement and availability of herbicides to plants in soil and in particular emphasise that in the field one is dealing generally with non-equilibrium conditions. In the past the tendency was to experiment with equilibrium conditions in the laboratory and to extrapolate therefrom, and with soil to solution ratios far removed from actual field situations. Now there is a greater variety in techniques used, as for example that reported by Grice and Hayes in this Session, and greater depth of thought as to what actually goes on in the soil. Thus we get nearer to understanding the complexities of what happens even if it is difficult to control these events.

Soil moisture relationships are also of importance insofar as some situations can arise which are conducive to damage to the crop, particularly where some element of depth protection is involved which is reduced by leaching to zones of maximum uptake by the crop plant. This leads to comments in recommendations such as 'heavy rainfall after spraying may lead to some crop damage' (nitrofen for oil-seed rape) or to injunctions such as 'watering after application should be avoided' (chlorpropham for lettuce). It is in the context of possible damage to crop that the research presented by Russell & Shone and by Walker in this Session is particularly relevant. The clear link between amount of uptake of herbicide by the root system with the extent of transpiration by the shoot of the plant should enable us to foresee conditions under which crop damage might occur through combinations of environmental circumstances favouring high transpiration rates by the vegetative part of an established plant and movement of herbicide from the soil surface to the principal zone of uptake by the plant. This link is probably of less consequence in respect of the weeds insofar as the lethal effect of most soil-acting herbicides is evident very shortly after emergence from the soil and before much transpiring surface has developed. However it is interesting to speculate that the spring sun and drying winds which favour effective mechanical weed control may also favour the weedkilling action of soil-applied herbicides as long as the soil itself does not become too dry.

Finally the user requires to know all he can about the duration of residual weed control and of possible risk to succeeding susceptible crops. Typical of the information which is provided is the recommendation 'at least 7 months should elapse after spraying before cereals or other susceptible crops are sown' (simazine for broad and field bean). Such recommendations do not recognise the diversity of factors governing the period of persistence though occasionally further guidance is

offered, such as 'on black fen soils the residual effect is shorter than on mineral soils' (propachlor for leeks). The need for the user of soil-applied herbicides to have more precise guidance on the likely persistence situation in his particular circumstances seems to be realised and the papers by Burns and by Osgerby in this Session represent two interesting approaches to this problem. This still leaves untouched one striking omission from recommendations, this being the absence of guidance on how to maximise the disappearance of unwanted residues of herbicide from soil. Even in our present state of knowledge more practical help could be given on this aspect than hitherto.

Turning now to the future of soil-applied herbicides in practice, how is all the accumulated research knowledge, of which we have been introduced to a microcosm in this Session, going to influence their use in the years ahead?

Firstly I think that we are dealing with situations in which a multiplicity of environmental factors have a great influence on the end result. We are now building up a considerable knowledge of the factors involved in controlling herbicide performance. The first stage is to use this knowledge to understand and explain what has already happened, whether this be in the typical commonplace circumstance, or in the unusual situation or result which occurs from time to time. The next stage is to foresee reliably what will happen, given a particular set of starting circumstances and a modest degree of foresight as to how these circumstances will develop and change; in some cases this may well allow the taking of action to avoid undesirable consequences or to achieve an optimal weed control outcome. This may also give rise to saving in time or cost involved in herbicide use. Another possible outcome is the simplification of complex recommendations and the reconsideration of time-honoured advice in the light of current knowledge. There is perhaps a further stage which we can usefully foresee. This is the development of more sophisticated methods of use of soil-applied herbicides based on this greater understanding. Such methods might not be applicable to the whole spectrum of users of such herbicides but might well be appropriate to more advanced farmers or to groups of farmers where the need for specialised equipment and expertise is involved. As an example one might suggest that there may be scope for precision incorporation in some circumstances but this may require purpose-designed implements not normally bought by the general farmer.

Secondly there may be repercussions on the design of herbicides. To be realistic, the pragmatic approach to herbicide discovery, development and use is still the usual and most rewarding one. This is the case with soil-applied as with other herbicides, and one is not going to forecast any imminent change to an era of designed herbicide molecules. However the increase in basic knowledge as exemplified in this Session, the increasing capability to predict behaviour in specific circumstances, and the relevance of specific properties of the molecule to this behaviour, will allow the pragmatic approach to be followed in a more sensible way with greater understanding, and some degree of tailoring of the molecule to give the required performance will be feasible.

Certainly one has no doubts that in spite of their imperfections soil-applied herbicides will continue to provide a valued part of the weed control armoury for the foreseeable future.

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Seventh edition (1972) Vol. II. Recommendations. ed. by J.D. Fryer & R.J. Makepeace.

The 1956 edition was published by the British Weed Control Council. The other editions were published by Blackwell Scientific Publications.

GLYPHOSINE - A PLANT GROWTH REGULATOR FOR
SUGARCANE AND SUGAR BEETS

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Summary Glyphosine has been extensively investigated as a chemical ripener for sugarcane during the past 3 years. Rates of 2-6 lb/ac formulated material applied to foliage 4-8 weeks prior to harvest has given positive results in many of the cane growing areas of the world. Increases in sugar yield have ranged from 3-30% with an average of 10%.

Evaluation of glyphosine on sugar beets grown in sand-nutrient culture in the greenhouse indicated a 25% increase in sucrose under high levels of nitrogen simulating non-ripening conditions. Little response occurred when glyphosine was applied to sugar beets under nitrogen deficient levels or ripening conditions. Field investigations with rates of 0.25-0.75 lb/ac applied at 3-5 weeks prior to harvest are in progress to fully evaluate field potential of this compound.

INTRODUCTION

The purpose of this paper is to review some of the early investigations on ripening sugarcane and sugar beets by chemical methods and to discuss glyphosine* as a chemical ripener in sugarcane and a potential ripener in sugar beets.

Ripening of Sugarcane and Sugar Beets

Sugarcane matures when active growth is slowed or terminated and reducing sugars are converted to sucrose and stored. Hartt (1963) studied the effect of defoliation on translocation of sugar and showed that removal of the upper leaves 8-12 days before harvest increased translocation of sugar into the stalk. Removal of lower leaves had little effect upon translocation. This suggested that the removal of young leaves would enhance ripening.

Sugarcane ripens naturally in some areas because of drought or cool temperatures slowing growth. In other areas where ripening conditions do not occur naturally, manipulation of nitrogen fertilizer, withdrawing irrigation water prior to harvest or topping have been used to ripen sugarcane but all have certain disadvantages according to Nickell and Tanimoto (1966).

* Early test work under Code No. CP-41845

Ripening as a problem has been more widely appreciated in sugarcane culture than it has in sugar beets since most sugar beets are grown in areas where cool night temperatures cause good ripening (Ulrich, 1955). However, the problem of delayed maturity due to excess nitrogen use has caused renewed interest in means of more effectively ripening sugar beets.

Beauchamp (1949) first reported use of 2,4-D as a chemical ripener in sugarcane. Others have tried this compound on sugar beets. Since that time many compounds have been tested for their potential as ripeners in both sugarcane and sugar beets, e.g. Nickell (1970), Nickell and Tanimoto (1966), Vlitos and Lawrie (1967), Singh and Wort (1970). Wort and Singh (1970). None of these compounds have yet come into regular commercial use because they lack consistent performance.

Glyphosine

A. Chemistry

Glyphosine [$\text{N,N-bis(phosphonomethyl)glycine}$] is a white highly water soluble (248,000 ppm at 20°C) powder with negligible volatility. It is formulated as an 85% soluble powder.

B. Toxicology

The oral LD₅₀ for rats is 3925 mg/kg indicating a low order of toxicity by oral ingestion. Classified as practically non-toxic, the minimum lethal dose by skin adsorption in rabbits is greater than 5010 mg/kg. Glyphosine is classed as a moderate skin irritant and a severe eye irritant without permanently affecting sight.

Ripening Sugarcane with Glyphosine

Trials with glyphosine have been conducted over three years in most of the major cane growing areas of the world under a variety of climatic and cultural conditions, e.g. Bieske (1970), Nickell et al (1971), Yates (1971), Julian and McIntyre (1970), Porter and Ahlrichs (1971), Tianco and Escobar (1970), and Mejia (1972). Table 1 shows representative results from trials in various countries.

Table 1

Sugarcane Ripening Studies with Glyphosine

	Percent Increase in sucrose
U.S. (Fla. & La.)	5-20
Hawaii	3-15
Philippines	15-30
Taiwan	0
India	5-10
Australia	0- 3
Fiji	15
Mauritius	10
South Africa	20
Mexico	10
Colombia	15
Puerto Rico	10
Dominican Republic	5-20

The chemical has been tested on both plant and ratoon cane with age of cane ranging from 6-24 months. There have been some differences in response noted with varieties but in general the best response is on varieties that are good ripening and good juice varieties.

The chemical hastens ripening prior to peak sugar levels and prevents deterioration of the sucrose after peak levels are reached. Under proper use conditions the chemical has given an average of 10% increase in sucrose with a range of 3-30%. The recommended use rate is 2-6 pounds of formulated material applied 4-8 weeks prior to harvest. Best use rate and time of application varies somewhat with the sugarcane growing area.

After application the sugarcane develops slight leaf flecking and tip burn. Yellowish or reddish leaf colorations may develop and new leaves may exhibit chlorosis. The terminal growth rate is decreased and the upper internodes are shortened but the stalk generally develops a greater diameter at the terminal end. Spindle death may occur followed by side shooting 3-5 weeks after application. The compound has slowed tassel emergence where the applications have coincided with flowering. Ratoon regrowth does not appear to be affected by application of glyphosine at the indicated use rates.

The effect of the chemical appears to be greatest when applied to sugarcane that is in an active physiological state. Condition of disease, limited moisture and other factors which may slow the metabolic rate of the plant appear to lower the response of the chemical.

Ripening Sugar Beets with Glyphosine

Glyphosine has potential as a chemical ripener for sugar beets as determined by greenhouse studies. Sugar beets were grown in sand-nutrient culture with high and low levels of nitrogen. High nitrogen levels were obtained using 0.005 M NO_3 in the nutrient throughout the experiment while low nitrogen was obtained by decreasing NO_3 levels 2 weeks prior to treatment with glyphosine so the beet petiole contained 2000 ppm NO_3 at the time of treatment. The low nitrogen was to approximate nitrogen depletion during ripening in the field and the high nitrogen to simulate non-ripening conditions of sugar beets. Beets were sprayed when 14 weeks old with 2 pounds glyphosine in 50 gallons water using Aerosol O.T. at 0.05%. Beets were harvested at 21 and 35 days after the chemical was applied. Table 2 gives the results of the sucrose analysis.

Table 2.

Glyphosine - Sugar Beet Greenhouse Studies - Sand-Nutrient Culture

<u>Treatment</u>	<u>Days after Glyphosine Treatment</u>	<u>Percent Sucrose (fresh weight)</u>	<u>Sucrose Yield (% of Low Nitrogen Control)</u>
High Nitrogen			
Control	21	10.1	89
Glyphosine	21	10.9	118
Control	35	11.8	87
Glyphosine	35	12.6	125
Low Nitrogen			
Control	21	13.2	100
Glyphosine	21	12.8	99
Control	35	14.1	100
Glyphosine	35	15.6	96

Under conditions of continued high levels of nitrogen, representing non-ripening conditions, glyphosine increased the sucrose 25% over low nitrogen control which represent ripening conditions. Superimposing glyphosine treatment on ripening conditions of low nitrogen did not enhance sucrose yield.

The utility of glyphosine to ripen sugar beets in the field is under intensive study in both Europe and the United States. Rates of 0.25 to 0.75 lb/ac applied at 3-5 weeks prior to harvest are being evaluated.

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SOME NEW HERBICIDES EFFECTIVE AGAINST WILD OATS

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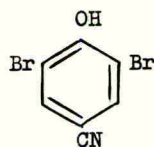
Summary

Research which led to the discovery of ioxynil has been continued and related substances which also possess useful selective herbicidal properties have been found. Two of these compounds, 3,5-dibromo- and 3,5-diiodo-4-hydroxy-phenyl methyl sulphone (bromoxynil and ioxynil) are amongst those which have been shown to destroy a number of weed species including wild oat.

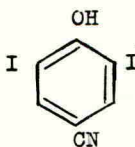
An important feature of their herbicidal action is the development of severe chlorosis which can lead to marked reduction in photosynthesis and death of the plant. The effect is produced by applying the chemicals to the soil as well as spraying them on to the leaves. A number of useful crops, including cotton, sugar beet, pea and various brassica species are not seriously affected when treated with herbicidal concentrations of these compounds.

INTRODUCTION

At the Seventh British Weed Control Conference I described research carried out in 1959 which led to the discovery of ioxynil and bromoxynil, two selective herbicides which are now widely used in agriculture (Wain 1964a, 1964b).



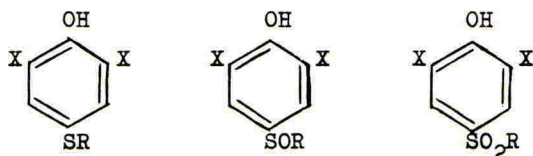
bromoxynil



ioxynil

This development arose from earlier research on influences exerted by the groupings $-NO_2$ and $-CN$ when substituted into an aromatic ring (Bennett & Wain 1936) and in the molecules of bromoxynil and ioxynil, the strong electron-attracting properties of

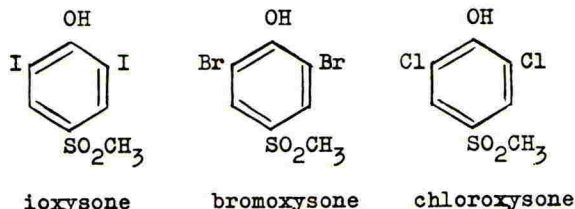
the -CN grouping were considered to be important in relation to the herbicidal activity shown. Further research was then initiated to determine whether replacing the -CN grouping in the above compounds with other electron-attracting groups would lead to the discovery of further new herbicides. From this investigation came the finding that compounds with the following general formulae possess an interesting type of herbicidal and selective herbicidal activity:



(X = halogen; R = alkyl)

Some of these compounds, when applied at rates of 2 lb per acre to seedling plants, destroy a number of species and especially certain grasses. An important feature of their phytotoxic action arises from a destruction of chlorophyll and inhibition of chlorophyll biosynthesis whereby the leaves and stems of susceptible plants become chlorotic and white. This leads to an almost complete cessation of photosynthesis and depletion of food reserves which may cause death of the plant.

Over the past few years Miss Rosemary Wain and the writer have synthesised a wide range of these compounds and their derivatives and they have been tested on a number of plant species. Amongst those which show the striking chlorotic and herbicidal effect referred to above are 3,5-diiodo-4-hydroxyphenyl methyl sulphone and the corresponding dibromo- and dichloro- derivatives. These sulphones, by analogy with ioxynil and bromoxynil, can conveniently be referred to as ioxysone, bromoxysone and chloroxysone respectively.



Although many of the compounds synthesised show this interesting type of herbicidal activity, the rest of this short paper will be concerned solely with the three sulphones mentioned above. These compounds, and more particularly bromoxysone and ioxysone, are amongst those which are effective against wild oat (*Avena fatua* and *A. ludoviciana*) and certain other grassy weed species which are responsible for considerable losses in yield of agricultural

crops in many parts of the world.

It has also been found that a number of plant species, including certain useful crop plants such as cotton, peas, sugar beet, cabbage and other brassica species are almost completely unharmed when they are treated at rates which are toxic to susceptible weeds. These compounds therefore possess useful selective herbicidal activity. Furthermore, such selective weed control can also readily be achieved by applying the chemicals directly to the soil as well as to the plants. Their movement into and within the plant has been shown to occur readily and treating only one leaf of dwarf bean plant, for example, can produce drastic effects over the whole plant.

EXPERIMENTAL

Some examples of the herbicidal effects of bromoxysone and ioxysone are given below:

Experiment 1.

Seedlings of a range of monocotyledonous plants growing in 4 inch pots were sprayed to run off with solutions of the sodium salts of bromoxysone and ioxysone at 1,000 ppm. active ingredient. A non-ionic wetting agent was present in each spray at 0.05 per cent. All plants became chlorotic. The mortality, recorded four weeks after treatment, was as follows:

<u>Species</u>	<u>Percentage mortality</u>	
	<u>Bromoxysone</u>	<u>Ioxysone</u>
Wild oat (<u>Avena fatua</u>)	95	80
(<u>A. ludoviciana</u>)	70	75
Wheat	80	85
Oat	75	70
Barley	70	90
Perennial ryegrass	20	30
Rice	80	90

Experiment 2.

Solutions of the sodium salts of bromoxysone and ioxysone were applied to the soil in which young seedlings were growing in 4 inch pots. The treatment rates were equivalent to 1, 2, and 4 lb of the compound per acre. The results were recorded after 32 days and are shown in the following table. The wild oat, rice and upright brome plants which survived all showed some degree of chlorosis.

Species	Rate per acre (lb)	Percentage mortality	
		Bromoxysone	Ioxysone
Wild oat (<u>A. fatua</u>)	1	20	10
	2	90	80
	4	100	100
" " (<u>A. ludoviciana</u>)	1	15	25
	2	75	80
	4	100	100
Rice	1	chlorosis	20
	2	40	70
	4	100	100
Upright brome (<u>Bromus erectus</u>)	1	chlorosis	chlorosis
	2	severe	75
	4	chlorosis	100
		75	

Pea, cabbage, cauliflower, brussels sprouts, kale, broccoli, cotton, sugar beet and couch grass (Agropyrens repens) were included in this experiment. Negligible damage was shown. There was some chlorosis and stunting in the sugar beet treated at the 2 and 4 lb rate with bromoxysone. The couch grass plants became chlorotic with all treatments and although all recovered, they remained stunted, compared with controls, until the end of the experiment.

Experiment 3.

Wild oat (A. fatua) was sown in 4 inch pots. Two days after sowing, the soil was treated with ioxysone and bromoxysone as aqueous solutions of their sodium salts, in both cases at a rate of 2 lb per acre active ingredient. Seedling emergence and early growth was similar to that of controls but the leaves of seedlings growing in the treated soils were bleached and white and all of them died within two weeks.

DISCUSSION

The important and likely use of these new herbicides would appear to be to kill certain grass weed seedlings which are growing with non-susceptible crops. As shown above, with wild oat it has been found that excellent control can be achieved with a single application of 2 lb per acre of bromoxysone or ioxysone when the seedlings are just emerging. When susceptible weeds are more well established, a single application of 2 lb per acre induces chlorosis but such plants have usually built up sufficient food reserves to survive until the chemical has been metabolised within their tissues. If this occurs and there is no further treatment, the plant eventually recovers and the chlorosis disappears. Its growth, however, has been checked, making it less

able to produce viable seed and to compete successfully with crop plants. An example of this is provided by the results obtained by Mr. A.C. Owers and his colleagues in a field experiment with sugar beet at the Norfolk Agricultural Station. Both bromoxysone and ioxysone were applied at 2 lb per acre as an aqueous solution of the sodium salt. A non-ionic wetting agent (Triton X100) was present at 0.05 per cent. The fairly high infestation of wild oat was at "Stage 4" (tillering just beginning) when the spray was applied. There was some yellowing in the beet plants but they soon recovered. The wild oat became very chlorotic and the plants were stunted but they survived and developed a sufficient area of green leaf to send up flowering spikelets. They remained reduced in size, however, compared with the controls, and the flowering heads were smaller. Ioxysone was slightly superior to bromoxysone in this experiment.

A further possible use of these selective herbicides is in grassland improvement. It has been found, for example, that undesirable coarser grass species, such as Yorkshire fog (Holcus lanatus) can be eliminated by bromoxysone or chloroxysone treatments which have little effect on more productive grasses such as Poa spp. and perennial ryegrass. The effect on the sward some months after such treatment can be spectacular.

These new herbicides can be used either as the free phenols or as their water soluble ammonium or alkali metal salts or as their salts with organic bases. It has also been found that certain of their esters can be equally effective.

Although a number of synthetic herbicides are now available for the control of wild oat (Holroyd and Bailey, 1970), this weed still causes serious losses of agricultural crops and is responsible for some of our most important weed problems at the present time. Unfortunately, the compounds here reported are phytotoxic towards wheat, oat and barley as well as to wild oat and to various other grass weed species.

In my most recent research I have sought means by which some degree of control of wild oat in cereal crops can be achieved with these compounds. One approach has involved a study of their esters, some of which might be preferentially hydrolysed in wild oat to the herbicidal phenol. It has been found that not only the nature of the ester but also the method by which it is formulated can give rise to different patterns of selectivity. This work, however, is incomplete and will not be further reported upon here.

Other research now proceeding with these compounds at Wye College includes studies on their metabolism and mode of action and their behaviour in the soil.

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PHYTICIDAL PROPERTIES OF SEVERAL
N-ARYLURONIUM AND S-ALKYLISOTHIURONIUM ARSONATES

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Summary Seedlings of several plant species were treated with some N-arylureas, several arylarsonic acids, their sodium, N-arylurionium and S-n-alkylisothiuronium salts. Arylarsonic acids were more phytotoxic than their sodium and N-arylurionium salts. Phytotoxicity of S-alkylisothiuronium salts depended upon the length of chain, the structure of the anion and the plant species. S-n-octylisothiuronium arylarsonates were the most toxic derivatives. They possessed the widest spectrum of phytotoxicity even at a concentration of $(6.25 \times 10^{-2} M)$. The compounds possessed different activities towards growth of main, secondary and adventitious roots. Some tissue disturbances were observed in cross sections of the cotton roots treated with phenylarsonic acid, sodium tolylurionium and S-n-octylisothiuronium phenylarsonates. Some of these compound induced several degrees of cytotoxicity ranging from slight to total mitotic inhibition. Sodium p-tolylarsonate and N-arylurionium p-tolylarsonate and N-arylurionium p-chlorophenylarsonates gave the highest rates of chromosomal aberrations.

INTRODUCTION

According to the "Principal of Covalent-Electrovalent Organic Molecule" (El-Nawawy and El-Kheshin 1960) the biological activities of many organic anions may be altered in the presence of certain organic cations and vice versa. (cf. El-Nawawy and Abou-Khatwa, 1967, El-Nawawy and Goma, 1968, and El-Nawawy and Kamel, 1969). Along the same line of studying structure/activity relationships, several organic and inorganic salts of arylarsonic acids were prepared and studied for their phytotoxic properties.

METHOD AND MATERIALS

I. Compounds:

The following compounds were prepared by the conventional methods.

Acids: Phenylarsonic (PA), p-tolylarsonic (TA) p-chlorophenylarsonic (CPA), p-nitrophenylarsonic (NPA) acids.

Cations: Sodium (Na), 1-S-n-butylisothiuronium (BTBU), 1-S-n-amylisothiuronium (ATHU), 1-S-n-hexylisothiuronium (HXTHU), 1-S-n-heptylthiuronium (HPHTU), 1-S-n-octylisothiuronium (OTHU), phenylurionium (PU), p-tolylurionium, (TU), the three chlorophenylurionium (o-CPU, m-CPU, p-CPU) and the three nitrophenylurionium (o-NPU, m-NPU, p-NPU).

The compounds included in the tests were: the free acids, their monosodium or mono-organic cations, as well as free N-arylureas. Attempts to achieve disubstitution of the two hydrogen atoms were unsuccessful. This agreed with Freedman and Doka (1955).

II. Solution:

The compounds were dissolved in distilled water to give the following concentrations: ($2 \times 10^{-3}M$), ($5 \times 10^{-4}M$), ($2.5 \times 10^{-4}M$), ($6.25 \times 10^{-5}M$).

III. Test in Agar:

In this test agar solution (1.2%) was used containing the required concentration of the compound. While hot, the solution was poured in test tubes (20 X 1.5 cm) and left to solidify.

Materials and procedure: The seeds of cotton (Giza 45) (Gossypium barbadense) horse beans (Giza 1) (Vicia faba), purslane (Portulaca oleracea), common vetch (Vicia sativa), as well as grains of maize (amrecani badri) (Zea mays) and wheat (Giza 45) (Triticum vulgare) were used in the test. After soaking in water at 25°C for 24 hours, the seeds and the grains were left at about 25°C for another 24 hours. When the roots started to appear, uniform seedlings of all except purslane were selected and placed so that their roots grew into the agar. Each tube contained either one germinating seed (cotton, horse beans and maize), or two (wheat and common vetch). Purslane was added dry (several seeds/tube) on the disturbed surface of the agar followed by two drops of water. Five replicates of each treatment were made. The tubes were incubated at 27-28°C in a chamber illuminated for 12 hours daily.

IV. Test in soil:

Loamy soil (210 g) was placed in plastic pots (8 cm top diameter X 8 cm in depth). Each pot was stood on a plastic plate. The soil was inoculated with a spore suspension of Fusarium oxysporum var. vasinfectum, or crushed growth of Rhizoctonia solani. The soil was irrigated from below. After incubation for ten days under laboratory conditions each pot was sown with five seeds of cotton. The compound (15 ml of each concentration) was added to the soil from above. Five replicates were made for each treatment.

V. Histological studies:

Cross sections were made of the roots of treated cotton seedlings grown in agar and examined in the conventional way.

VI. Cytological studies:

These were made on the root tips of treated and untreated maize seedlings grown in agar. The methods and details of studies are reported by El-Sadek (1972).

RESULTS

I. Agar experiments: Structure/activity relationships:

(1) General phytotoxicity: Cotton and wheat: (tables 1 and 2)

Sodium, N-aryluonium and ETHU, arylarsonates were less toxic than the corresponding acids. Examples of toxicity decreased even further with dilution. Examples of extremely toxic compounds were found amongst the S-alkylisothiuronium

salts. OTHU and HPTHU of TA, CPA and NPA gave 100% mortality to cotton seedlings at $6.25 \times 10^{-5}M$. Apart from (HPTHU, NPA) the other compounds behaved similarly with wheat seedlings. (HXTHU, NPA) was fatal to cotton seedlings while (HXTHU, CPA) killed wheat seedlings at $6.25 \times 10^{-5}M$. None of the ATHU salts caused the death of wheat seedlings while (ATHU, CPA) and (ATHU, NPA), at $6.25 \times 10^{-5}M$, killed cotton seedlings. Thus the OTHU salts possessed a wider phytotoxic spectrum. The selectivity increased gradually with a decrease in the chain length of the S-alkylisothiuronium cation. The substituent on the benzene ring of the arylarsonate also contributed to the selective effect of the S-alkylisothiuronium salts. When N-arylureas were included in N-aryluronium N-arylarsonates the phytotoxicity to cotton seedlings disappeared completely at $6.25 \times 10^{-5}M$ with all salts and at $5.2 \times 10^{-4}M$ with most salts.

- (2) Relative toxicities of selected compounds to root and shoot systems. (table 3)

Different plant species were treated with $2.5 \times 10^{-4}M$ solutions of thirteen compounds. The results can be illustrated as follows:

Plant species	Compounds most toxic to root systems	Compounds most toxic to shoot systems
Maize	(TA, OTHU), (NPA, OTHU)	(CPA, Na), (CPA, TU) (NPA, Na)
Common vetch	(TA, H), (TA, Na) (NPA, H),	(TA, TU), (CPA, TU) (NPA, TU)
Horse beans		(CPA, H), (CPA, Na) (NPA, Na)
Wheat		(NPA, H)

Hence compounds containing CPA, or TU were more toxic to shoot systems. Death occurred after elongation of the root of horse bean seedlings treated with (NPA, H) and (NPA, Na).

- (3) Secondary roots:

Growth of secondary roots in cotton, maize, common vetch and horse beans was observed within 5-7 days after planting in untreated agar.

Complete prevention of secondary root-formation occurred in the following cases:

Table 1

Reduction, expressed as percent of control, in total length of cotton and wheat seedlings treated with sodium and S-alkylisothiuronium arylarsonates assessed after 7 days

COTTON																
Anions Cations	PA				TA				CPA				NPA			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
H	d	d	50	30	70	60	55	40	d	80	45	35	d	70	30	20
Na	d	70	40	0	55	45	45	35	70	55	30	15	50	30	10	0
BTHU	d	80	60	20	d	d	70	50	d	d	80	75	55	40	0	0
ATHU	d	80	75	10	d	d	d	60	d	d	d	d	d	d	d	d
HXTHU	d	d	60	20	d	75	65	50	d	45	45	35	d	d	d	d
HPTHU	d	d	70	70	d	d	d	d	d	d	d	d	d	d	d	d
OTHU	d	d	d	75	d	d	d	d	d	d	d	d	d	d	d	d

WHEAT																
H	d	75	70	45	70	50	50	40	d	d	d	d	75	50	45	0
Na	d	55	50	10	45	35	30	20	d	d	75	70	d	70	35	0
BTHU	d	65	65	45	d	d	60	50	d	d	80	65	d	85	65	0
ATHU	d	75	70	50	d	d	d	70	d	d	d	70	d	d	75	35
HXTHU	d	d	60	45	d	d	d	80	d	d	d	d	d	d	80	35
HPTHU	d	d	70	55	d	d	d	d	d	d	d	d	d	d	d	55
OTHU	d	d	d	65	d	d	d	d	d	d	d	d	d	d	d	d

d = dead, A = $2 \times 10^{-3}M$, B = $5 \times 10^{-4}M$, C = $2.5 \times 10^{-4}M$, D = $6.25 \times 10^{-5}M$.
 N.B. The figures in the table were obtained by calculating the actual reduction as a percent of control approximated to multiples of five.

Table 2

Reduction, expressed as percent of control, in total length of cotton seedlings treated with different N-arylureas and N-arylarsonates assessed after 7 days

Cations Concentrations	Anions															
	Free base				TA				CPA				NPA			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
H	-	-	-	-	75	50	50	25	100	75	25	25	100	75	25	0
Na	-	-	-	-	50	25	25	25	75	50	25	0	50	25	0	0
PU	50	25	25	25	25	25	25	0	25	25	0	0	50	25	0	0
<u>o</u> -TU	25	25	0	0	50	25	25	0	25	25	0	0	25	0	0	0
<u>m</u> -TU	100	75	75	50	50	25	25	0	25	25	0	0	25	0	0	0
<u>p</u> -TU	100	100	100	100	50	25	25	0	25	25	0	0	25	0	0	0
<u>o</u> -CPU	75	75	75	25	50	50	0	0	25	25	0	0	50	25	0	0
<u>m</u> -CPU	100	75	75	50	75	25	0	0	25	25	0	0	25	0	0	0
<u>p</u> -CPU	75	75	75	50	50	50	75	0	25	25	0	0	50	25	0	0

A = $2 \times 10^{-3}M$, B = $5 \times 10^{-4}M$, C = $2.5 \times 10^{-4}M$, D = $6.25 \times 10^{-5}M$.
 0 = No reduction in length, - = not done.

Table 3

Length (cm) of shoot and root systems of different
types of seedlings grown in agar containing
 $2.5 \times 10^{-4}M$ of the test compounds after 7 days

Compound	Length in cm					
	Cotton	Purslane	Maize	Common vetch	Wheat	Horse beans
Control	10/11	2.5/2.5	11/13	11/11	9/12	3/11
TA, H	4.5/6	2/2	8/7	8/2.5	4.5/6	3.5/3.5
TA, Na	6/5	2.5/2.5	9/9	11/3	7.5/9	3.5/7
TA, OTHU	0	0	2/1	0	0	0
TA, TU	8/7	0.5/1	8/7	3.5/8	7/0	2.5/7
CPA, H	6/6.5	0.5/1	1/2	0/0.5	0/0	0/3.5
CPA, Na	10.5/1	0.5/1	0.5/1	2.5/1	7/9	0/7
CPA, OTHU	0	0	0	0	0	0
CPA, TU	9.5/10	1/1	7/12	1/5	8/9	2/11
NPA, H	7/7	0	1/2	1/0.5	5/6	0
NPA, Na	9/9.5	0	2/7.5	1.5/0.5	6/8	0/2.5
NPA, OTHU	0	0	4/1	0	0	0
NPA, TU	9.5/10.5	1.5/10.5	8/12	1.5/4.5	8/10	2.5/8
TU	1/1.5	0	0	0	0	0

0 = Both root and shoot systems are zero in length.

- (a) Acids : NPA, : cotton, maize, common vetch, horse beans
CPA, : maize, common vetch, horse beans
TA : cotton
- (b) Sodium salts : NPA, Na: maize, common vetch, horse beans
CPA, Na: maize, common vetch
- (c) Tolyuronium salts: The three salts: common vetch
- (d) Tolyurea : cotton, maize, common vetch, horse beans
- (e) OTH salts of NPA, CPA and TA: Killed all the root systems.

(4) Adventitious roots

Inhibition of adventitious root formation in maize was observed with:

TA, H; CPA, Na; NPA,H and NPA, Na. Wheat seedlings were unaffected.

II. Growth of cotton seedlings in the presence of certain compounds and soil fungi: (table 4)

Table 4

Percent kill of 10 day old cotton seedlings as a result of combined effect of $2.5 \times 10^{-4}M$ solutions of certain compounds and soil fungi

Compound	Agar	Soil	Soil + R. solani	Soil + F. oxysporum
Control	0	10	70	25
TA, H	25	0	90	25
TA, Na	25	0	90	25
TA, OTHU	100	70	80	100
TA, TU	25	0	80	50
CPA, H	25	0	100	25
CPA, Na	25	0	80	25
CPA, OTHU	100	70	90	40
CPA, TU	0	0	60	25
NPA, H	25	0	80	25
NPA, Na	0	0	80	25
NPA, OTHU	100	70	85	50
NPA, TU	0	0	50	25
TU	100	75	90	75

The results of such an experiment were as follows:

- (a) TU + R. solani or F. oxysporum were more harmful to cotton seedlings than any of them on their own.
- (b) R. solani: Apart from (CPA, TU), the presence of all the compounds enhanced the harmful effects of the fungus.
- (c) F. oxysporum: (TA, OTHU), (TA, TU), (CPA, OTHU), (NPA, OTHU) and (TU) encouraged the toxic effects of the fungus.

III. Histological studies:

Cross sections were made in the zone of secondary roots of seven day old cotton seedlings grown in agar. In the untreated seedlings, cross-sections of the root showed four well differentiated vascular bundles. The xylem and phloem were well differentiated, the protoxylem was distinct, the endodermis was differentiated and pith was present.

In the presence of (TA, H) an increase in the diameter of the pith and vascular cylinder was observed. The xylem was not differentiated into four distinct groups and the xylem elements were randomly distributed, a process which involved the differentiation of procambial strands more than normal. Protoxylem elements were less differentiated. The phloem was not differentiated into four distinct groups, but rather it occupied a whole circle around the xylem; the protoxylem did not protrude through the phloem. The pericycle was divided into several layers in contrast to a single layer in the controls. Lateral root development was not hindered. This case represented an extreme anatomical disturbance.

Less severe anatomical disturbances were observed with (TA, Na) and (TA, TU). Lateral root formation was abnormally enhanced. (TA, OTHU) and (TU) hindered main and secondary root formation. Disturbances of the cylinder were similar to those recorded for (TA, H) above.

IV. Cytological studies:

These were done using the root tips of maize seedlings grown in treated agar. (TA, H), (CPA, H), their sodium and p-tolyuronium salts showed several degrees of cytotoxicity. (CPA, Na) and (CPA, TU) gave the highest rates of aberration. The latter was accompanied by mitotic disturbances (for further details cf. El-Sadek 1972).

DISCUSSION

The most toxic compounds were found amongst the S-alkylisothiuronium arylarsonates. Their effect depended mainly on the length of the alkyl chain and to some extent upon the substituent in the para position on the aromatic ring of the anion. However, toxicity was found to increase with chain length. This might be due to a gradual change of the (H/L) ratio towards the favourable value required for penetration into the root and movement inside its tissues. This physical property could not be the only factor since aryluronium salts of the same arylarsonic acids and of comparable molecular weights were inactive while the free bases and acids were active. Thus the activity might have depended upon both positive and negative ions of the S-alkylisothiuronium salts.

That arylureas, in the form of their uronium phenylarsonates, hydrochlorides or acetates, lose some or most of their activity towards cotton and wheat seedlings in agar, has been shown in our laboratory. This behaviour was observed at a certain concentration for each plant species. In unpublished experiments at this laboratory fluorometuron showed this behaviour clearly with cotton at $4 \times 10^{-3}M$ and even when a concentration of $6.25 \times 10^{-4}M$ was used, these differences could still be seen. These are salts of weak bases and should hydrolyse in aqueous medium (salt + water \rightleftharpoons acid + base). Phytotoxicity might be attributed to different entities in the solution: the salt, the free acid and the free base. Strong acidity e.g. $4 \times 10^{-3}M$ of hydrochloric or acetic acids were sufficient to kill cotton and wheat seedlings. The salts of fluorometuron and p-tolyurea were less phytotoxic at certain concentrations, while the free acids and free bases were toxic. Hence these salts did not give sufficiently toxic concentrations of base or acid upon hydrolysis. The pH of the solution may be taken as a function of the degree of hydrolysis. At a concentration of: $2.5 \times 10^{-4}M$: PA, H (4.1), PA, Na (8.7), TA, H, (4.55), TA, Na (6.8), TA, TU (6.4), TA, OTHU (6.3), TA, 1; 1-dimethyl 3-(3-trifluorophenyl)uronium (4.9), CPA, H (4.85), CPA, Na (6.8), CPA, TU (4.3), NPA, H (4.45) NPA, Na (7.5), NPA, TU (3.9). All these pH values are far from the two harmful extremes (0.1N acid or base) (Thomas, 1949). These data indicate that the pH of these compounds cannot be responsible for phytotoxicity and cannot be attributed to the hydrolysis of the salts.

In the soil fluorometuron was mixed with PA, H; PA, Na; acetic acid and sodium acetate. A definite decrease in the toxicity of fluorometuron was observed even at the rate of 3.6 kg a.i./feddan ($=4200 m^2$). The loss of toxicity of the urea derivatives might be due to cation formation which could lead to absorption in the soil in excess of its cation exchange capacity (Frissel, 1961), or, more likely, suffer an antagonistic effect from the anion.

Selectivity and relative toxicity depended upon the structure of each of the anions. There was an obvious selectivity in relative toxicity to each of the root and shoot systems of common vetch, horse beans, and maize. No such selectivity was observed with the very toxic OTHU derivatives.

Some compounds may have enhanced the effect of Rhizoctonia solani and Fusarium oxysporum.

CONCLUSION

- (1) Initial studies using certain l-S-n-alkylisothiuronium arylarsonates showed definite promising pre-emergence phytotoxic properties.
- (2) N-arylureas should not be formulated with acidic compounds as they lose their activity in the presence of acidic material. Hydrolysis of such salts appeared to be insufficient to liberate toxic concentrations of the corresponding acids.

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PHYTOTOXIC PROPERTIES OF SOME S-ALKYLISOTHIURONIUM
2:2-DICHLOROPROPIONATES AND TRICHLOROACETATES

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Summary The phytotoxicities of trichloroacetates and 2:2 dichloropropionates were increased in the presence of certain inorganic and organic cations. Amongst several inorganic trichloroacetates the sodium, potassium and calcium salts were the least toxic to cotton and wheat. $2.5 \times 10^{-3}M$ solutions of three N-arylammonium trichloroacetates killed wheat seedlings, calcium trichloroacetates did not. S-alkylisothiuronium salts of both acids (C₁-C₈) exhibited various degrees of phytotoxicity which depended upon the anion and structure of the S-alkyl chain. Several S-alkylisothiuronium salts were significantly superior to calcium salts of the two acids. Some interactions between certain mineral nutrients and some of these compounds were studied. Histological studies revealed anatomical disturbances and cytotoxic effects following treatment of seedlings with some derivatives.

INTRODUCTION

Studies of structure/activity relationships were made according to the principal of "Covalent-Electrovalent Organic Molecule" (El-Nawawy and El-Kheshin, 1960). Modifications of the activity of strongly biologically active anions (El-Nawawy and Ashry, 1965, and El-Nawawy and Khalifa, 1966) as well as biologically inactive anions (El-Nawawy and Kamel, 1969) were achieved. This paper described the modification by cations of the histological and cytological effects induced by two very active anions: trichloroacetate and 2:2-dichloropropionate.

METHOD AND MATERIALS

I Compounds:

Anions: Trichloroacetate (TCA). 2:2-dichloropropionate (DCP)

Cations: Na, K, Ca, Ni, Pb, N-o-chlorophenylammonium (o-CPA), N-p-chlorophenylammonium (p-CPA), the S-alkylisothiuronium cations: 1-S-methyl (MeTHU), 1-S-ethyl (EtTHU), 1-S-propyl (PrTHU) 1-S-n-butyl (1-BTHU), 2-S-n-butyl (s-BTHU), 1-S-(2-methyl) propyl (1-iso-BTHU), 2-S-(2-methyl) -propyl (2-iso-BTHU), 1-S-n-amyl (1-ATHU), 2-S-n-amyl (2-ATHU), 1-S-(3-methyl n-butyl) (1-iso-ATHU), 1-S-n-heptyl (HPTHU), 1-S-n-octyl (1-OTHU) 2-S-n-octyl (2-OTHU).

Mineral nutrients: NaNO₃, (NH₄)₂ SO₄, K₂SO₄, Na₂HPO₄. These were used at the concentrations of 0.1M, 0.01M and 0.001M.

II Solutions:

The compounds were dissolved in distilled water to give the following concentrations: ($5 \times 10^{-3}M$), ($3.3 \times 10^{-3}M$), ($2.5 \times 10^{-3}M$), ($1.25 \times 10^{-3}M$), ($6.25 \times 10^{-4}M$), ($3.125 \times 10^{-4}M$), ($1.5625 \times 10^{-4}M$).

III Test Materials:

The seeds of cotton (Giza 45) (Gossypium barbadense), purslane (Portulaca oleracea), common vetch (Vicia culcarata) and horse beans (Giza 1) (Vicia faba) as well as the grains of wheat (Giza 45) (Triticum vulgare) and jungle rice (Echinochloa colonum) were used in this test.

IV Procedure:

All the compounds were tested by the method described by (El-Nawawy et al 1972). In certain experiments the required concentration of nitrate was added as sodium nitrate, ammonium as ammonium sulphate, and phosphate as sodium monohydrogen phosphate. The test materials were cotton seeds and wheat grains. Three replicates were made for each treatment.

V Histological Studies:

The effects of these compounds on the root tissues of cotton seedlings were studied in the conventional way.

VI Cytological Tests:

These were carried out with horse bean seedlings as described by El-Sadek (1972).

RESULTS

A-Cotton and wheat seedlings

I-Trichloroacetic acid and its derivatives. (Tables 1 & 2)
From Table 1 the following points were observed.

- (a) The following trichloroacetates were the most effect against cotton and wheat seedlings: H, PA, o-CPA, p-CPA, Pb, Zn, Mn and Ni. The Ba salt was also very active against cotton seedlings. At $5 \times 10^{-3}M$ all these compounds either killed the seedlings or gave 90% reduction in their length.

With respect to cotton seedlings the amine, Ba, Pb, Ni and Zn salts effected 100% mortality of the seedlings at the three concentrations used. Na, K and Ca salts were the least active metal salts, while the manganese salt lost 40% of its activity at the lowest concentration.

Wheat seedlings were, in general, more tolerant than cotton seedlings. TCA, PA was the only one which gave 100% mortality at 2.5×10^{-3} ; TCA, o-CPA and TCA, p-CPA gave 85 and 90% reduction in total length respectively. TCA, Pb; TCA, Zn, and TCA, Ni affected 90, 85 and 85% reduction in total length respectively at the lowest concentration.

- (b) Toxicity of the S-alkylisothiuronium trichloroactates: (Table 2). At $3.125 \times 10^{-4}M$ 1-OTHU and 2-OTHU salts gave 100% mortality of cotton and wheat

seedlings. At the same concentration all the other S-alkylisothiuronium salts did not kill the seedlings. Their overall toxicity to cotton seedlings was rather low and to wheat shoot was zero although with most of the compounds their activity against the roots of wheat seedlings was very high. At $1.25 \times 10^{-3} \text{M}$ HPTHU salt was able to kill cotton seedlings. TCA, 2-ATHU was more toxic to cotton roots than the other two C₅ compounds, while analogous 1-ATHU and 1-iso-ATHU salts were more toxic to the shoot system. With respect to wheat seedlings the 1-ATHU derivative was far more toxic to the roots than the other two C₅ analogues. TCA, 2-BTHU was more toxic to the wheat root than the other two C₄ derivatives.

Table 1

Reduction, expressed as percent of control, in total length of cotton and wheat seedlings treated with several trichloroacetates assessed after eight days

Cations	TCA 5×10^{-3}		TCA 3.3×10^{-3}		TCA 2.5×10^{-3}	
	Cotton	Wheat	Cotton	Wheat	Cotton	Wheat
H	d	d	d	95	d	80
PA	d	d	d	d	d	d
<u>o</u> -CPA	d	d	d	d	d	85
<u>p</u> -CPA	d	d	d	d	d	90
Na	65	60	45	60	20	50
K	35	60	35	50	20	45
Ca	35	80	40	70	20	65
Ba	d	65	d	60	d	55
Pb	d	d	d	95	d	90
Zn	d	d	d	95	d	85
Mn	d	90	d	67.5	60	55
Ni	d	95	d	95	d	85

II - 2:2-Dichloropropionic acid and its derivatives (Table 3)
 $3.125 \times 10^{-4} \text{M}$ solutions of the HPTHU, and 1-OTHU, and 2-OTHU, salt killed cotton seedlings while the minimum concentration which killed wheat seedlings was $1.25 \times 10^{-3} \text{M}$. Solutions of 2-ATHU, and HPTHU salts gave 100% kill of cotton seedlings at $2.5 \times 10^{-3} \text{M}$. The other S-alkylisothiuronium and inorganic salts did not kill any of the seedlings. The roots of wheat seedlings recovered in most cases at the lowest concentrations of the compounds containing C₁ to C₆ chains.

B-Effects of certain compounds on weeds:

- (1) $3.125 \times 10^{-4} \text{M}$ solutions of HPTHU, 1-OTHU and 2-OTHU of DCP, and OTHU, TCA gave 100% kill of common vetch seedlings. The other isothiuronium derivatives were of low toxicity and did not prevent secondary root formation. 1-OTHU, DCP was fatal to the seedlings even at $1.5625 \times 10^{-4} \text{M}$. Its toxicity to the main root was 50% at $7.8 \times 10^{-3} \text{M}$, but it prevented secondary formation. Calcium and sodium TCA and DCP were slightly toxic at $3.125 \times 10^{-4} \text{M}$.
- (2) $6.25 \times 10^{-4} \text{M}$ solutions of Ca and the C₅, C₇ and C₈ isothiuronium salts of DCP as well as the two C₈ derivatives of TCA were fatal to jungle rice seedlings. The toxicity of all the compounds decreased appreciably with further dilution.

- (3) $6.25 \times 10^{-4} \text{M}$ solutions of HPTHU and 1-OTHU salts of both acids killed purslane seedlings. HPTHU, 1-OTHU, 2-OTHU, salts of DCP remained fatal even at 7.8×10^{-5} to purslane seedlings. Calcium and sodium salts of both acids lost their activity at $1.5625 \times 10^{-4} \text{M}$.

C-Combined phytotoxic properties of mineral nutrients and two herbicides in agar (Table 4 & 5)

The four nutrient salts showed different types of behaviour with TCA, Ca and TCA, 1-OTHU salts. From these tables the following can be concluded:

- (1) Death of cotton and wheat seedlings occurred in the presence of: 0.1M ammonium sulphate, potassium sulphate and sodium monohydrogen phosphate in the presence or absence of either of the two 'herbicides'.
- (2) 0.01M solution of sodium monohydrogen phosphate + $1.5625 \times 10^{-4} \text{M}$ solution of TCA, 1-OTHU and 0.001M of the former compound + $1.5625 \times 10^{-4} \text{M}$ TCA, Ca were fatal to cotton seedlings.
- (3) 6.25×10^{-4} solutions of TCA, 1-OTHU + 0.1, 0.01, 0.001M of sodium nitrate, or 0.001M of sodium monohydrogen phosphate were fatal to wheat seedlings.
- (4) 0.01M solutions of all nutrients were non-toxic to cotton seedlings. 0.01M solutions of sodium nitrate and potassium sulphate behaved similarly with wheat seedlings. 0.01M solution of sodium dihydrogen phosphate was toxic to the roots, but not to the shoots of wheat seedlings.
- (5) When one of the constituents of the mixture was very toxic, the mixture behaved similarly, e.g. any solution of TCA, 1-OTHU + any nutrient solution; two exceptions of this inference were recorded for the roots of wheat treated with a $3.125 \times 10^{-4} \text{M}$ solution of potassium or ammonium sulphate.
- (6) With respect to cotton seedlings 0.01M and 0.001M solutions of all the nutrients, especially sodium monohydrogen phosphate partially alleviated the toxic properties of $6.25 \times 10^{-4} \text{M}$ solution of TCA, Ca. Complete alleviation of the toxic effect to the roots of the latter solution was achieved by 0.1M of sodium nitrate and 0.001M of all nutrients except ammonium sulphate.

D-Histological Studies:

Transverse sections of the roots of cotton seedlings grown in agar containing TCA, H: DCP,H; Na, Ca and 1-OTHU salts of both acids showed general inhibition of growth and somewhat excessive development of lateral roots near the transition zone near surface of agar. The roots averaged up to 12 roots per 0.5 cm. length of root. As well as this, there was a general collapse of parenchymatous tissues. No other abnormalities were observed.

E-Cytological Studies:(horse bean seedlings)

The incidence of mitotic divisions and of chromosomal aberrations in primary roots showed that trichloroacetic and 2:2 dichloropropionic acids and their sodium salts possessed comparable rates of mitotic division to the controls. The trichloroacetates and dichloropropionates produced 1-2% chromosomal aberrations while 1-S-n-octylisothiuronium trichloroacetate and 2:2-dichloropropionate showed high cytotoxicity and stopped mitotic division completely. This was accompanied by nuclei disintegration in the primary roots treated with 1-S-n-octylisothiuronium 2:2 dichloropropionate. The roots appearing above the surface of the medium showed normal rates of mitosis and only 1% aberrant cells. This might indicate that translocation through the parenchymatous tissue was limited. There was an

Table 2

Reduction, expressed as percent of control, in length of root and shoot of cotton and wheat seedlings treated with different trichloroacetates assessed after 7 days

Compounds	$2.5 \times 10^{-3} M$		$1.25 \times 10^{-3} M$				$3.125 \times 10^{-4} M$					
	Cotton		Wheat		Cotton		Wheat		Cotton		Wheat	
	R	S	R	S	R	S	R	S	R	S	R	S
TCA, H	87	65	88	87	55	48	25	80	20	20	0	75
TCA, Na	20	28	15	80	20	15	0	78	10	15	0	75
TCA, Ca	50	50	28	81	35	45	25	80	25	15	0	82
TCA, MeTHU	65	50	45	80	50	35	10	78	40	18	0	75
TCA, EtTHU	60	40	7	80	25	20	0	80	25	15	0	75
TCA, PrTHU	45	45	5	75	40	15	0	80	20	18	0	80
TCA, 1-BTHU	55	37	10	80	35	15	0	80	20	18	0	75
TCA, 2-BTHU	67	38	65	80	60	17	25	80	40	18	0	80
TCA, 1-iso-BTHU	60	33	0	80	42	25	0	78	30	22	0	75
TCA, 2-iso-BTHU	52	36	10	80	48	35	0	85	50	10	0	82
TCA, 1-ATHU	47	50	90	78	30	20	0	80	15	10	0	75
TCA, 2-ATHU	75	80	53	83	55	53	15	85	25	40	0	78
TCA, 1-iso-ATHU	70	60	25	85	53	44	10	80	47	10	10	75
TCA, HTHU	75	75	68	80	74	27	35	78	50	22	20	75
TCA, HPTHU	d	d	d	d	d	d	d	d	d	d	55	65
TCA, 1-OTHU	d	d	d	d	d	d	d	d	d	d	d	d
TCA, 2-OTHU	d	d	d	d	d	d	d	d	d	d	d	d

d = dead

R = root

S = shoot

Table 3

Reduction, as a percent of control, in length of root and shoot of cotton and wheat seedlings treated with different 2:2 dichloropropionates assessed after 7 days

Compounds	$2.5 \times 10^{-3} M$		$1.25 \times 10^{-3} M$				$3.125 \times 10^{-4} M$					
	Cotton		Wheat		Cotton		Wheat		Cotton		Wheat	
	R	S	R	S	R	S	R	S	R	S	R	S
DCP, H	85	75	d	d	75	45	d	d	70	45	65	75
DCP, Na	60	52	75	83	40	42	45	81	45	27	0	65
DCP, Ca	75	60	85	88	68	42	45	85	54	41	45	80
DCP, MeTHU	70	60	80	87	65	40	48	80	35	35	35	75
DCP, EtTHU	60	60	83	82	58	30	28	84	43	25	25	75
DCP, PrTHU	70	60	55	92	58	40	30	81	43	14	0	75
DCP, 1-BTHU	68	45	60	85	45	25	10	80	50	21	0	75
DCP, 2-BTHU	68	45	55	82	55	25	8	82	58	20	0	75
DCP, 1-iso-BTHU	70	52	55	89	60	45	35	87	50	35	0	83
DCP, 2-iso-BTHU	70	45	55	81	68	22	10	80	53	20	0	75
DCP, 1-ATHU	68	43	95	81	60	42	28	78	43	20	0	75
DCP, 2-ATHU	d	d	87	87	65	65	55	85	60	30	30	65
DCP, 1-iso-ATHU	68	52	45	82	60	30	15	80	58	28	0	68
DCP, HPTHU	d	d	d	d	d	d	d	d	d	d	80	70
DCP, 1-OTHU	d	d	d	d	d	d	d	d	d	d	96	82
DCP, 2-OTHU	d	d	d	d	d	d	d	d	d	d	90	85

d = dead

R = root

S = shoot

important difference between 1-S-n-octylisothiuronium trichloroacetate and 1-S-n-octylisothiuronium 2:2 dichloropropionate. The former compound stopped mitotic division in the peripheral layer of the meristematic region of the primary root (2mm in diameter) while the region of the middle layer showed mitotic division with 3.2% aberrant cells. The latter compound gave complete inhibition of mitotic division and the disintegration of nuclei in the primary roots. This might be due to a quicker diffusion of the second compound. Thus the two compounds can be described as cytotoxic compounds with the ability to inhibit mitosis and cause disintegration of nuclei. Their translocation through parenchymatous tissue appears to be limited, but the upwards translocation through the xylem appears to be rapid.

Table 4

Effect of calcium and 1-S-n-octylisothiuronium trichloroacetates, alone and with some nutrients on length (cm.) of root (R) and shoot (S) of cotton seedlings assessed after 5 days

Nutrient Compound	Conc. (M)	Plant System	Alone	With TCA, Ca			With TCA, 1-OTHU		
				A	C	C	A	B	C
Water		R	9.50	4.5	7.4	8.0	d	d	2.5
		S	7.20	3.6	6.3	7.0	d	d	3.2
NaNO ₃	0.1	R	3.0**	4.50	3.80*	3.80**	d	1.3	1.80
		S	3.50**	4.0	4.20**	4.0**	d	1.0*	1.0**
	0.01	R	10.0	6.0	9.0	9.0	d	1.4	3.0
		S	8.0	6.0**	6.0	7.30	d	1.3*	3.0
	0.001	R	10.50	8.20*	7.50	8.50	d	1.0	2.20
		S	8.20	6.20**	6.30	7.50	d	1.0*	3.30
(NH ₄) ₂ SO ₄	0.1	R	d**	d**	d**	d**	d	d	d*
		S	d**	d**	d**	d**	d	d	d**
	0.01	R	5.50**	5.80	6.0	6.0	d	0.8	2.50
		S	4.50**	4.50	5.0	5.30*	d	0.8	3.0
	0.001	R	9.0	6.20	8.0	9.0	d	1.0	2.50
		S	7.20	5.50*	5.60	5.30*	d	1.0	2.50
K ₂ SO ₄	0.1	R	d**	d**	d**	d**	d	d	d*
		S	d**	d**	d**	d**	d	d	d**
	0.01	R	8.80	6.50*	5.80	6.50	d	d	2.0
		S	6.50	5.30	6.30	6.0	d	d	1.70
	0.001	R	9.0	6.0	6.50	7.50	d	d	2.0
		S	7.50	5.30	6.50	7.0	d	d	2.50
Na ₂ HPO ₄	0.1	R	d**	d**	d**	d**	d	d	d
		S	d**	d**	d**	d**	d	d	d*
	0.01	R	7.20	6.0	6.20	6.50	d	d	d
		S	5.30	5.0	5.30	6.0	d	d	d*
	0.001	R	10.0	8.80**	10.0	d**	d	d	2.0
		S	8.0	7.20**	7.0	d**	d	d	2.0

d = dead, A = $6.25 \times 10^{-4} M$, B = $3.125 \times 10^{-4} M$, C = $1.5625 \times 10^{-4} M$

Length of root and shoot sign. diff. from herbicide:

* at P = 0.05

** at P = 0.01

Table 5

Effect of calcium and l-S-n-octylisothiuronium trichloroacetates, alone and with some nutrients on length (cm.) of wheat seedlings assessed after 6 days

Nutrient Compound	Conc. (M)	Plant System	Alone	With TCA, Ca			With TCA, l-OTHU		
				A	B	C	A	B	C
Water		R	12.0	6.6	11.5	12.0	1.0	2.0	8.0
		S	17.0	3.5	5.0	5.0	2.3	4.0	8.5
NaNO ₃	0.1	R	4.0**	6.0	5.5**	6.0**	d	0.3	2.0**
		S	8.5**	4.0	5.0	4.5	d	1.5	3.0**
	0.01	R	11.5	11.0**	11.0	11.0	d	2.0	5.0**
		S	17.5	4.0	5.0	4.5	3.0	3.5	8.5
(NH ₄) ₂ SO ₄	0.001	R	12.0	11.0**	11.0	11.2	d	1.8	5.5*
		S	15.0	9.0**	4.5	4.2	0.5	4.5	5.0
	0.1	R	d**	d**	d**	d**	d	d	d*
		S	d**	d**	d**	d**	d	d**	d**
K ₂ SO ₄	0.01	R	10.0	7.5	8.5*	8.5**	2.8	6.2**	8.0**
		S	13.5**	4.0	4.5	5.3	4.2	4.0	5.2*
	0.001	R	11.5	9.0**	9.5	10.5	1.0	4.5*	8.8
		S	16.0	5.0	5.0	5.3	3.0	5.0	5.0**
Na ₂ HPO ₄	0.1	R	d**	d**	d**	d**	d	1.2	2.0**
		S	d**	d*	d**	d**	d	2.0	3.0**
	0.01	R	11.5	9.5*	8.5*	11.0	1.0	7.0	8.0
		S	18.0	4.0	3.0	4.8	4.0	5.0	5.0*
0.001	R	12.0	11.0**	11.5	12.5	0.5	4.0	9.0	
	S	19.5	4.5	5.0	5.0	3.0	4.5	5.0*	
	0.1	R	d**	d**	d**	d**	d	d	d**
		S	d**	d	d*	d*	d	d	d**
0.01	R	7.5**	8.0	8.5*	7.0**	0.7	0.8	0.7**	
	S	17.0	4.0	4.5	6.5	3.0	2.5	4.0	
	0.001	R	12.0	11.0**	11.0	11.0	d	0.6	3.0
		S	18.0	4.0	4.0	4.0	d	3.0	6.0

d = dead, A = $6.25 \times 10^{-4} M$, B = $3.125 \times 10^{-4} M$, C = $1.5625 \times 10^{-4} M$

Length of root and shoot sign. diff. from herbicide:

* at P = 0.05

** at P = 0.01

DISCUSSION

Several inorganic and arylammonium trichloroacetates and certain S-alkylisothiuronium trichloroacetates and 2:2-dichloropropionates were far more toxic than their corresponding sodium or calcium salts. At certain concentrations they were fatal to cotton, wheat, common vetch, purslane and jungle rice seedlings in agar medium, Ca, Na, or K salts were only slightly toxic.

That certain inorganic and arylammonium trichloroacetates were more phytotoxic than Na⁺, K⁺, or Ca trichloroacetates might be due either to differences in the ratio (pK_b/pK_a) or to the action of the cations themselves. It is expected that this ratio is higher for Na, K and Ca salts than that of the other salts.

Concerning the S-alkylisothiuronium salts (alkyl = C₁ - C₈), toxicity was more appreciable with a chain length of C₆, C₇ and C₈. Within this group of compounds the toxicity was in the following descending order C₈ > C₇ > C₆. The joining of the atom of the isothiuronium group to the first or the second carbon atom of the C₈ chain did not lead to an appreciable difference in activity. With C₄ and C₅ chain derivatives there was some relation between the activity of the compound and the structure of the chain or the position of the sulphur atom. TCA, 2-BTHU was more toxic than the other three analogues to cotton and wheat. The corresponding derivatives of DCP were equally active. DCP, 2-ATHU was, however, more phytotoxic than the other two isomers to cotton seedlings. DCP, 1-iso-ATHU was less toxic than the other two analogues to wheat roots. In general no simple rule for describing the relationship between the structure of the cation and its activity could be drawn. The net effect depended upon the anion and plant species.

The reason for the stronger activity of the S-alkylisothiuronium salts of TCA and DCP might be due to the toxicity of the cation or to a modification of the hydrophilic/lipophilic ratio of the salt towards the optimum value required for physical penetration of biological membranes. This was clear when the cytotoxic properties of Ca and 1-OTHU salts of both acids were compared.

Similar organic salts of TCA has been reported : 1-dimethyl-3 phenyluronium trichloroacetate (Martin 1971a), and 3-(4-chlorophenyl) 1,1-dimethyluronium trichloroacetate (Martin 1971b). These two were described as general herbicides effective in total weed control of uncropped areas when used at high rates. It may be worth while trying some of the long chain S-alkylisothiuronium trichloroacetates or dichloropropionates for the same purpose.

The interaction between mineral fertilizer and soil pesticides has been studied by several authors in soils and nutrient solutions. In this work emphasis was placed on the interaction between a single nutrient and a single herbicide in agar medium. Several instances of partial alleviation of the toxic effects of the herbicide were observed. This might be explained by the possible competition between similarly charged ions in the nutrient solution and the "herbicide" for uptake by the plant. With respect to wheat seedlings this alleviation was confined to the effect on the root system. This may indicate that the interaction may have caused the rapid upward movement of toxic constituents of the mixture.

The results of the cytological studies showed that the penetrability was appreciably improved by replacing Ca by 1-OTHU cations. This effect could be attributed to both the anion and the 1-OTHU cation. DCP, 1-OTHU had a more pronounced effect. Its H/L ration may be more suitable for penetration in the systems used in the present work.

CONCLUSION

By working according to the "Principle of Covalent-Electrovalent Organic Molecule" it was possible to achieve a considerable increase in the phytotoxicity of strongly active compounds. The cytological studies gave some explanation for this change which may be due to an increase in the lateral translocation through the parenchymatous tissues and subsequent upward translocation through the xylem.

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CHEMICAL REPRESSION OF AGROPYRON REPENS CLONES WITHOUT SOIL CULTIVATION

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Summary: Experience with cropping experiments using no-tillage systems had indicated that Agropyron repens will cause problems. In a pot experiment the shoots of two clones of A. repens were treated with several herbicides with or without pre-treatment by paraquat. Half of the pots prior to herbicide treatment had the aerial growth removed once by cutting, the other half twice. Only small differences in reaction to the chemicals were noted between the two clones, and the frequency of defoliation did not affect this reaction. Plants treated with paraquat prior to treatment with TCA or TFP were generally more susceptible to these latter materials. TFP (alone) was relatively ineffective. Plants treated with paraquat after treatment with dalapon produced a more rapid effect than dalapon alone, but this duplex application showed no increase in efficiency over straight paraquat. Paraquat applied late in the day was more effective than that applied early in the day. The assessed bud activity generally stressed the vitality of the rhizomes. However, paraquat followed by TCA and paraquat followed by TFP demonstrated a very promising reduction. In this treatments clone K2 was more adversely affected than clone K1.

INTRODUCTION

Agropyron repens (couch) can be controlled by cropping systems employing competitive crops, or more directly by mechanical means (Fail 1956). Herbicides can assist control measures based on burying shoots, deep-burying rhizomes and/or fragmenting rhizomes (Håkansson 1969 and 1971). The current and ever-increasing interest in minimum cultivation and no-tillage systems poses the problem of controlling this weed without soil disturbance. In such cases the only possible mechanical control measure is that of cutting the aerial parts of the weed, a measure which can not be employed in the growing crop. Experience in commercial practice suggested that regular repeated spraying of the shoots with paraquat is ineffective as a long-term measure. Residues of grass-controlling herbicides in soil restricts their usefulness in the majority of no-tillage systems which are based on continuous cereals. The introduction of 2,2,3,3-tetrafluoropropionate (TFP) (Aelberse et al. 1969) suggested that this material could be utilised in no-tillage systems, and the results of a pilot trial carried out in 1970 with A. repens in pots are summarized in Table 1.

The TFP caused a repression of growth when the plants had been defoliated or sprayed with paraquat previously. Following TFP treatment many of the ends of rhizomes were rotting and bud proliferation was observed.

There is increasing evidence that clones or varieties of crops (Van Hiele et al. 1970) and weeds may react variably to herbicides. Haddad and Sagar (1968) discovered such a variation between 4 clones of A. repens when treated with relatively low doses of aminotriazole and dalapon.

Table 1
Total dry weight of shoots + stubble + rhizomes (TDM)
and number of green shoots per pot of A. repens

	No TFP treatment			TFP applied 29/7		
	TDM 1/12	28/9	1/12	TDM 1/12	28/9	1/12
	g	green shoots		g	green shoots	
Untreated	30	60	94	38	47	104
Cut 24/7	30	58	115	13	3	0
Paraquat 24/7	26	33	89	20	2	3
	rhizomes planted		5/3	cut	28/9	
	spray treatments		29/7	harvested	1/12	

METHODS AND MATERIALS

Clones K1 and K2 of couch were used in this trial. Clone K1 was from arable sandy soil containing 15% o.m.; the rhizomes of this clone are thicker and less branched than K2. Clone K2 was obtained from grassland on a peat soil. Rhizome growth of K1 starts earlier than K2, and K2 produces abundant fine shoots. The distribution of dry matter is characteristic (Table 2). Utilising a method similar to that of Turner (1969),

Table 2
Percentage of total plant weight

	Clone K1		Clone K2	
	roots	rhizomes	roots	rhizomes
Sampled	26	17	45	4
Sampled	21	18	42	8

Mitscherlich pots containing sandy soil were planted on 8 March with 5 rhizome pieces each approximately 1.5 cm long bearing one bud. Seventy pots were prepared from each clone. The pots were placed out-of-doors and after one month 100 ml of a nutrient solution (5 ml N MgSO₄ + 10 ml N CaNO₃ + 10 ml N KH₂PO₄ + 5 ml A-Z trace element solution + 60 ml water) was added to each pot.

When the rhizomes started to branch (5 June) the shoots in 35 of the pots of each clone were cut off. After this defoliation the pots again received 100 ml nutrient solution. At the beginning of August the shoots in all of the pots were removed.

Table 3
Treatments and dates of spraying 5 month old plants (at 2-3 leaf stage)

	19/8 (1800 hr)	20/8	23/8	26/8
control	-	-	-	-
par. ev	paraquat	-	-	-
paraquat	-	paraquat	-	-
TFP	-	-	TFP	-
par. + TFP	-	paraquat	TFP	-
dalapon	-	dalapon	-	-
dal. + par.	-	dalapon	-	paraquat
TCA	-	-	TCA	-
par. + TCA	-	paraquat	TCA	-

Dose rates per ha were:

paraquat 1 kg a.i. TFP 5 l 90 w/v% with 16 l 11 E oil added
TCA 75 kg dalapon 20 kg

About 3 weeks later regrowth of 2 to 3 leaves had occurred. According to Hakansson (1967) the d.m. content of the underground parts would then be at a minimum. The spraying treatments (Table 3) were commenced at this stage.

The evening treatment of paraquat was applied at 1800 hours on 19 August. Then the pots were kept in dark for 14 hours till 800 hours next morning. All other paraquat treatments were applied in the morning. This evening treatment was motivated by the work of Akhavein and Linscott (1970) who found that paraquat had an increased and longer-lasting effect on *A. repens* when applied just before a period of darkness, possibly due to a greater degree of translocation.

The TFP, paraquat and combination treatments were already motivated above. For TCA the combination with paraquat was also tried. Combinations as given in table 3: TFP or TCA preceded by paraquat. Bakermans and Ten Holte (1972) applied paraquat one day after TFP or TCA. They obtained a quicker killing of the leaves and a better growth of direct drilled *Raphanus sativus* but the final result of the extra paraquat treatment on the control of *A. repens* was negligible. In the combination with paraquat dalapon had to precede paraquat because of the necessary uptake of dalapon by the leaves.

Eight weeks after spraying the plants were removed and the soil washed away. Samples of rhizomes which were generally in good condition were laid out on foam plastic under moist conditions in the dark for 5 weeks. From all treatments of the K1 clone there were approximately 600 buds when laid out, and from the K2 clone about 350; each rhizome was approximately 5 cm in length. After the 5 weeks, when the number of shoots was more or less constant, a count was made of the new shoots. The water supply was then replaced by 2% KNO_3 solution to break dormancy and the light was turned on. Four weeks later, bud activity was assessed by counting shoots.

RESULTS

Paraquat applied in the morning affected K2 less rapidly than K1; paraquat applied before darkness was more effective on both clones than that applied in the morning. Ten days after treatment there were still green portions of the shoots, and further new shoots had emerged.

Paraquat followed by TCA or TFP killed the plants at the same speed as paraquat alone as a morning treatment, but no regrowth occurred (Table 4).

Table 4
Total number of active shoots (old and new) per pot on 11 October after treatment in August

Cutting treatments	Clone K1		Clone K2	
	1 x	2 x	1 x	2 x
control	187	171	216	266
par. ev.	9	23	28	4
paraquat	31	29	40	70
TFP	53	56	207	236
par. + TFP	1	0	1	0
dalapon	53(46)	31(29)	73(46)	97(65)
dal. + par.	1	4	26	47
TCA	26	20	17(2)	40(9)
par. + TCA	0	0	0	0

(the figures in brackets indicate definite new shoots where these were distinguishable)

When dalapon was followed in 6 days by paraquat, dying-off was slower than from paraquat alone and no true new shoots appeared. Paraquat produced scorch on the shoots, but growth continued and tillers were formed out of old sheaths. Dalapon by itself resulted in a very slow effect; there were living shoots 7 weeks after treatment and many new shoots were then present under the older ones.

TFP by itself caused a 75% reduction in living shoots of the K1 clone; on the K2 clone some growth inhibition was observed but no shoots died. TCA killed 90% of the shoots; K1 demonstrated no regrowth, K2 gave an average of 5 new shoots per pot.

In the case of the untreated controls, K2 was more effective in the production of rhizomes, and this difference also occurred following early defoliation.

Table 5
Percentage of rhizome buds which developed shoots

Clone	(a) after 5 weeks in dark				(b) 4 weeks after (a) plus KNO ₃ in light			
	K1		K2		K1		K2	
	1x	2x	1x	2x	1x	2x	1x	2x
control	50	50	57	53	50	55	59	62
par. ev.	39	30	21	20	43	33	26	23
paraquat	33	34	27	25	35	41	34	31
TFP	40	40	57	62	49	52	65	69
par. + TFP	14	5	4	4	31	19	5	11
dalapon	20	29	45	39	43	46	63	45
dal. + par.	29	26	32	15	45	41	39	31
TCA	6	1	5	4	27	13	28	13
par. + TCA	+	+	0	0	11	6	1	2

Table 5 records the numbers of shoots developed after 5 weeks on foam plastic and subsequently 4 weeks following treatment with KNO₃. The untreated controls demonstrate that without the influence of herbicides bud activity is limited even after the longer period. Of the chemical treatments, paraquat + TCA is promising, being more effective than TCA alone or than paraquat + TFP. The treatment with KNO₃ stimulated bud activity in all but the control and the paraquat and TFP treatments. The additional defoliation (2 x), which would reduce the carbohydrate reserves in the rhizomes, did not produce a significant reduction in bud activity. In treatments involving paraquat, clone K2 was more adversely affected than clone K1.

DISCUSSION

The preliminary trial cited in the introduction demonstrated positive results from TFP applied after treatment with paraquat. Bakermans (1972) has recorded several similar positive results in no-tillage field experiments although he has detected some seasonal variations. Very strongly infested fields could be freed nearly completely. For maize crops atrazine doses are very effective as a complement. However, the use of TFP in the pot experiment described above was rather disappointing, particularly if not preceded by paraquat. Some pots which demonstrated no regrowth were put outside from December 1971 onwards. In June 1972 there was no difference in the quantity of regrowth compared with the untreated controls, neither was there difference in bud activity. Because of the bud proliferation by TFP, this material sometimes produced more shoots.

The dying-off after application of dalapon followed after six days by paraquat was slower than that from paraquat only; the reason for this may be that the barrier in the nodes to the transport of dalapon (Lund-Hoelie 1969) may have some influence on the systemic effect of paraquat. Jeater and McIlvenny (1960) found quicker top-kill from mixtures of dipyridyl herbicides with dalapon or amitrol than from the latter ones alone. But these mixtures did not appear to have any greater effect on the regrowth of *A. repens* than did dalapon alone. Schmitlin and Pigot (1969) achieved more control of *A. repens* by paraquat after amitrol only when paraquat was applied at least 14 days after amitrol.

The positive results of paraquat followed by TCA suggested that the technique be tested in the field, and treatments were made in an attempt to eradicate *A. repens* clones resulting from a 4-year old experiment. The treatment was carried out in December 1971 during a period of night frosts. At the beginning of May 1972, when the field had to be ploughed-up, the repression of growth by the paraquat + TCA was

greater than that from TCA alone, but there was no obvious eradication. Samples of rhizomes were taken for analysis of bud activity according to the method described above; the results were disappointing although a large number of the counted shoots was very small and weak.

The conclusions from the work reported here may be valuable in understanding the fundamental response of couch to such treatments, but other factors could affect the usefulness in the field. TFP has been withdrawn for official approval in the Netherlands, however the first impressions of glyphosate suggest it could be a very suitable alternative (Evans 1972).

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