1.

Setting the Scene

The issues that must be resolved by the chemical industry, registration authorities and advisers in their efforts to provide agriculture with effective and safe soil-applied pesticides.

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IS THERE A FUTURE FOR SOIL-ACTING PESTICIDES?

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ABSTRACT

Whilst the pesticide market is becoming more competitive and uncertain, there remain significant opportunities for new products. However, because of the cost of finding suitable products, manufacturers are being forced to be increasingly selective about the targets for their research. The search for soil acting pesticides will receive limited attention, and it is unlikely that there will be a large number of new products in this underexploited area in the near future.

INTRODUCTION

With the exception of herbicides, soil acting pesticides currently represent a small fraction of the total agrochemical market. This reflects the relatively small effort devoted to their discovery, and the fact that soil acting pesticides are more difficult to discover than foliar acting ones. This paper discusses the prospects of this situation changing.

THE FUTURE MARKET

The media devote about equal attention to the problems of oversupply of food in much of the developed world, and undersupply in much of the developing world. At present there is no technical constraint to nourishing the world, but there is no consensus of opinion about the likely balance between production and need by the end of the century. Certainly the need for crop production for food, fibre or fuel will grow and it follows that there will be a continuing need for the wider application of existing technology and the development and application of new technology.

For much of the developing world the application of available knowledge on mechanisation, irrigation and crop nutrition will greatly increase the yield potential of both cash and subsistence crops, thus increasing the incentive for pest control practices to protect the crop during growth or after harvest. It is in the developing world that the greatest benefits from crop protection are frequently to be found.

In the more developed world, the pressure for even more efficient production (usually achieved by higher yields) will ensure expanding use of crop protection techniques. Whilst advances in the genetic manipulation of crop plants, and in the better integration of available methods, will reduce the intensity of pesticide usage in some areas, there is no doubt that chemicals will remain in the front line of defence against pests, and the pesticide market is forecast to grow at a compound rate of over 4% a year for at least the next decade.

The pessimists in industry argue that most of the growth will be taken up by compounds already on the market, whose price could fall as they come out of patent: further, they argue, the market is quite well satisfied with available products, leaving few opportunities for innovation.

The optimists point out that we have not reached the limits of the technology, and that new types of products (eg growth regulators) will open up completely new markets. Still more potent pesticides will be found, and there will be value to be added by providing the means of delivering them to the pest more accurately.

Most companies take the optimistic view, and enticed by a larger share of this growing market, pour more and more money into the search for new products. The agrochemical industry is now spending some 1,000 million dollars per year on research and development, and standard discounted cash flow calculations show that, on any reasonable assumption of the future market, investment on this scale cannot possibly be rewarded adequately in the long term. Add to this the changing environment in which there is decreasing patent protection and increasing trade barriers in many countries, together with increasing popular pressure against the use of chemical aids for crop production, and it becomes clear that a Company should only stay in the race if its research is carefully targetted at the most worthwhile opportunities, and it believes the quality of its research gives it some competitive edge.

TARGET SELECTION

Having committed itself to a programme of research and development, a Company must then decide which are the most attractive targets against which to direct its research. Although screening of chemicals against pest targets is a relatively cheap process, the sheer logistics of handling a large number of screens, and more importantly, the efforts required by chemists to service the screens and follow active leads, limit the choice to about ten targets each for the major disciplines (insecticides, fungicides, plant growth regulators and herbicides).

Let us discuss an approach to assembling a screen for insecticides. The attractiveness of a target is governed by its commercial value and the probability of technical success. The commercial values can be ranked by weighting market size at the farmer level by such factors as mark-up between manufacturer and farmer (large in Japan, smaller in the UK), import taxes, time needed to register a new product (reduces attractiveness of US and Japan) etc. Making further assumptions about likely market share for a new product and possible profit margins enables one to not only rank targets, but also to discard those which look unlikely to be rewarding. Only those which are large enough to support the total cost of developing a new compound can be regarded as primary targets, though hopefully any compound developed for these major targets will find outlets on other less important ones.

Using such strict criteria, certain pests remain clearly viable targets (eg *Heliothis* spp). Important pests which barely meet the criteria include rice hoppers (unless accompanied by rice borer activity) and tetranychid mites (unless accompanied by tortricidal activity). All of the soil inhabiting insect pests in the UK fail to qualify : indeed the only soil insect of sufficient importance to justify primary research is the corn rootworm (*Diabrotica* spp.), but even here the case is made marginal because the market is almost entirely within the United States, with its long and expensive registration requirements. The research on this target in the UK is also hampered by the fact that this pest is not endemic (no important beetle is) and so a proxy species has to be used for testing. The composition of a typical industrial screen aimed at discovering new insecticides is shown in Table 1.

Similar criteria are used to rank opportunities in other disciplines. There is certainly an attractive target for a good nematicide, and although the current market for soil fungicides is small, this is largely because of the absence of good candidates: there is, for example, no good chemical for the control of take-all of wheat (*Gaeumannomyces graminis*), a disease which reduces yield in all major wheat growing areas. Soil acting herbicides also represent attractive opportunities in spite of an increasing trend towards the use of post-emergence compounds which can be applied when the extent and composition of the weed problem is apparent.

There is, thus a sufficient number of financially attractive opportunities for new soil-acting pesticides to justify further research. In ranking these alongside other targets, however, it must be recognised that it is more difficult to discover soil-acting than foliar acting pesticides (herbicides are an exception because germinating seeds are much more sensitive than established plants).

Not only must the pesticide be inherently active against the pest but enable it to arrive at the required site, and remain active for long enough to exert its effect. The currently used pyrethroids are inherently active against most soil insect pests, but they have the wrong properties for exploitation as soil pesticides. (See below) it must have the right balance of physical and chemical characters to

TABLE 1

Composition of a typical industrial screen for insecticides

Diamond backed moth	-	Plutella xylostella
Old world bollworm	-	Heliothis armiger
Spider mite	-	Panonychus ulmi
Banded cucumber beetle	-	Diabrotica balteata
Potato peach aphid	-	Myzus persicae
Housefly	-	Musca domestica
Mosquito	-	Aedes spp
Grain weevil	-	Sitophilus granarius
Brown plant hopper	-	Nilaparvata lugens
Root knot nematode	-	Meloidogyne incognita

THE INVENTION STAKES

Having concluded that there are sufficiently attractive targets for its research, the Company must now implement a search for suitable compounds.

Most pesticides have been discovered by a process of random screening followed by analogue synthesis and optimisation. Breakthroughs have frequently come from chemicals synthesised for other disciplines or industries because they provide part of the pool of chemicals available for screening. The inventor applies for a patent when he judges the area to have been sufficiently well exemplified, recognising that any delay increases the chance of him being pipped at the post by another Company.

The information provided by publication of a patent on an important new toxophore acts as the starting signal for other companies to transfer chemists into this new area, and with few exceptions (eg paraquat, glyphosate) a whole family of more or less related analogues will enter development (eg triazole fungicides, pyrethroid insecticides, diphenyl ether herbicides). The inventor will, with luck, enter the markets first, but frequently with a bunch of competitors close on his heels, perhaps with superior molecules inspired by their own original discovery. Then follows a period in which competition increases sharply, and since the related chemicals are probably sufficiently similar in their properties to compete in the same market niches, prices are cut in order to gain market share or deter other competitors from entering the market. Since their introduction in 1975, the photostable pyrethroids have grown into a family with some $700m per year of sales - 15% of the total world insecticide market. During this period prices have fallen by over 50%, to the extent that many companies will be squeezed out of the field in the next few years. The farmer is the winner.

The only way out of this downward spiral for a company wishing to remain in the business in the long term is to invent, new, more cost-effective molecules. This requires commitment to a high level of expenditure over many years. Typically the industry returns a demanding 7-10% of sales on R & D, a level which can only be sustained if new molecules earning high gross margins can be produced at regular intervals. The result of failure to achieve this level of research productivity is a business with declining margins, and the need eventually to amalgamate or leave this highly competitive area.

Clearly the "me too" approach is too important and successful to be neglected by any company seeking to defend or increase its product range in the medium term: the proliferation of insecticides from the only four basic toxophores (pyrethroids, organophosphates, carbamates and chlorinated hydrocarbons) illustates this.

"Me-too" chemistry seems to be necessary to stay in the race: but how can a company improve its chances of winning? Clearly it is necessary to invent new toxophores which should, at least, put the company on the front line of the starting grid for the next race, and might in very rare instances make him the sole starter (eg glyphosate)

The standard approach for discovering new toxophores has been the random empirical screening of as many diverse chemicals (synthetic or naturally occurring) as possible - typically 5-10,000 per year. This fruitful source has yielded most of the toxophores in current use. A reasonable success rate would be one in 10,000 chemicals entering development. The chances of discovering a soil acting pesticide would be significantly less - perhaps one in 50,000.

The new challenge is to use knowledge of biochemical or physiological processes to design new toxophores. This approach has achieved some success in the pharmaceutical field because of the great weight of background research in pharmacology, but in the field of crop protection there is much less background knowledge on which to build. Nevertheless recent advances in computergraphics enabling the three dimensional modelling of active sites or candidate inhibitors, are providing a significant boost to inventive thinking. Use of such techniques aided the discovery of the fungicides flutriafol (Marchington, 1983): the challenge is now to extend this process to the design of completely new toxophores.

The strategy for invention is thus dictated by the business need for a regular supply of new chemicals. Companies have maintained this by a process of random screening followed by analogue synthesis of their own, or anybody else's active leads. There are now signs that a more rational approach to pesticide design is beginning to yield results. However the problem of combining the requirements for inherent, pesticidal activity with the properties for exploiting this activity in the soil is particularly daunting.

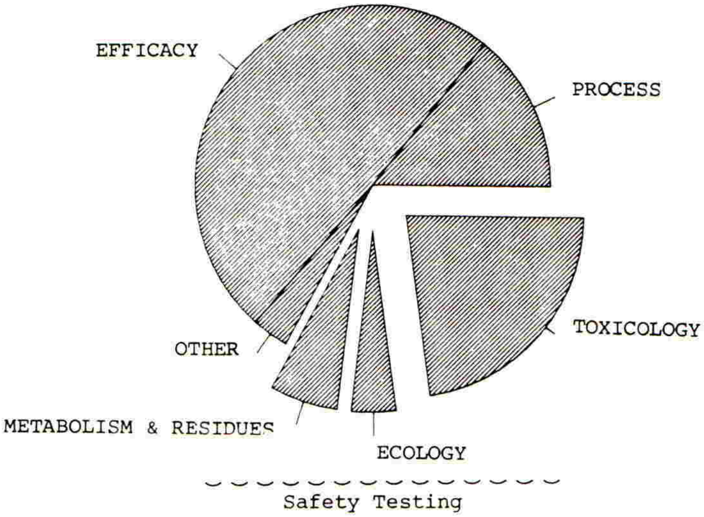
THE DEVELOPMENT SCRAMBLE

Whilst the invention or discovery of new pesticides offer the greatest technical challenge facing the industry, it is essential that the company has the ability to bring a new molecule speedily and efficiently to the market.

The process of developing a compound from initial characterisation to market is one which costs from £5-30 million depending on the number of crops and countries involved (se Fig 1) : it is not, therefore undertaken lightly. Already the chemical will have been tested in the field against its biological target for at least two seasons (possibly in the same year by utilising northern and southern hemisphere trial sites), initial toxicological studies will have been completed, and the commercial case made. The latter involves forecasting for at least 10 years ahead such parameters as market size, market share, prices in the market, manufacturing cost etc: and this for a molecule which may have only been synthesised in kilogram quantities at this stage. If it passes into full development, expenditure will rise to £2-5 million per year, depending on outlet, with no guarantee that the product will be technically (50% chance) or commercially successful.

Because of the high cost of failure during development, more and more emphasis is being placed on the quality of the decision to embark upon the process. Thus, for example, predictive tests of toxicology (eg mutagenicity, teratogenicity) or performance are increasingly used. For soil acting pesticides, early studies of such factors as adsorption/desorption, rate of degradation and leaching have successfully decreased the rate of drop-out during development. The balance between sufficient persistence to achieve the required biological effect, and excessive persistence leading to crop rotational or environmental problems is a delicate one, but one which can increasingly be predicted.

Fig 1 : Development expenditure for a medium sized product - £12m



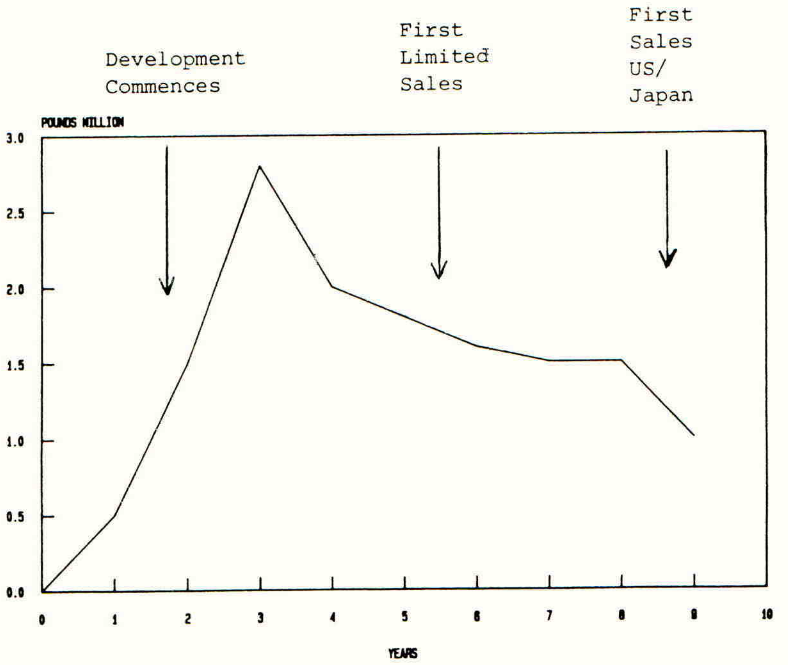
Once in development there are powerful arguments for proceeding to market as rapidly as possible. The race against competitors is already on. Further, the financial worth of a project is a function not only of the amount of cash generated by the product during its life cycle, but also the speed with which it generates it. Future products must pay interest on the risk money invested in their development.

The critical path of the development network is normally toxicological testing, which requires a minimum of four years for completion. To keep development time to a minimum one would start the toxicological programme as early as possible and run the other main studies - efficacy, manufacturing process, environmental safety etc. in parallel. The potential reward is early marketing: the risk is that of much greater abortive expense if the project fails for any reason. A lower risk approach is to carry out the main programmes in sequence, starting with the most risky (which might be efficacy, process chemistry or toxicology, depending on the molecule).

MARKET AT LAST

Assuming the various hurdles of development have been overcome, and the product can now be manufactured at a cost which enables it to be cost effective, is formulated to optimise its biological activity, and of proven safety and efficacy (to the manufacturer and regulatory authorities), the new product will now reach the market - which might well be very different from the one perceived when the compound first went into development. Unlike the heady days of the 1950's and 1960's when any good new compound 'sold itself', the launch and establishment of a new product now requires a very professional team effort by marketers, distributors and salesmen to establish a demand for the compound in the optimum market niche. This effort is demanding of resources, and, as in R & D, painful decisions have to be made about which products merit higher priority for promotion. In this fierce commercial climate, the new product must reward not only the heavy development costs incurred over many years (Fig 2), but also help fund research into the discovery of new candidates, and the cost of casualties in development.

Fig 2 : Cost profile for the development of a medium sized product



PROSPECTS FOR SOIL ACTING PESTICIDES

Thus whilst there is an undoubted market for new pesticides, the process of discovery, development and marketing is subject to increasing cost and competition, and the manufacturer is having to be more and more selective about areas of work. What emphasis should the search for soil acting pesticides have?

At present there are few clearly identified opportunities for major new soil pesticides (except herbicides), though there are probably many additional opportunities which are ill-defined at present because no chemicals are available to demonstrate the scale of the problem. Until the fungicides ethirimol and tridemorph were developed for the control of cereal powdery mildew, the extent of losses due to this disease were unsuspected. The newer broad-spectrum compounds such as triademinefon and propiconazole have demonstrated the importance of many other cereal foliar diseases. Unrecognised soil diseases could be an explanation for the large yield increases sometimes found following soil sterilisation. If there really is an untapped market here, why has industry been so unsuccessful in exploiting it, and will this improve in the future?

Most pesticide screens are set up in such a way that the pest comes into direct contact with the candidate pesticide. For foliage applied pesticides, a similar position pertains in the field in that the pesticide can be sprayed directly on to the weed or infested crop. Even so influence of environmental factors and inefficient application methods mean that rates of application must be increased several fold in the field. In attempting to control soil pests one has the additional problem of delivering the pesticide to the site of action. If pest attack occurs on or near the seed, the seed itself can be applied in the seed furrow. For very high value crops, the incorporation of soil sterilants (such as methyl bromide) can be justified. But for most situations, the problem of delivering the chemical to the root zone, particularly in perennial crops, is the major constraint.

Two basic alternatives can be considered. The chemical could be applied to the foliage whence it would be translocated in the phloem to the root zone where protection could be provided: alternatively the chemical could be applied directly on or in the soil.

Both of the methods place major additional constraints on molecular structure. Whilst there are examples of pesticides which are active in the soil from foliar application (eg avermectin nematicides, acylaniline fungicides), the chemical/physical requirements for phloem translocation are incompletely understood (Price, 1983) and there seems little prospect that the rate of discovery of molecules which have the right properties for pesticidal activity and accumulation in the root zone will increase in the near future.

For a chemical applied directly to the soil, a critical balance of chemical and physical properties (in addition to those confining pesticidal activity) is needed for the chemical to redistribute to the required degree and retain activity. An application of 1 kg/ha leads to an initial concentration in the top 10 cm of soil of about 1 ppm, but this concentration is soon reduced by a variety of processes.

When placed in the soil, a pesticide enters an equilibrium between solid phase (absorbed or precipitated), liquid phase (solution) and vapour phase. Movement to the site of action is by diffusion or by movement of vapour or solution. Properties such as solubility and vapour activity are thus critical. Examples of compounds which move in the vapour phase are methyl bromide and trifluralin. On the other hand, many soil acting herbicides become activated by water movement (eg atrazine). Whilst the physical behaviour of a pesticide can be modified to some extent by formulation, this process can only be used to optimise properties which are already basically suitable.

In order to be cost effective, a chemical must persist for long enough in active form to prevent the necessity of frequent re-application where pest attack occurs over a period, or for too critical timing. The chemical must not, however, be so persistent as to lead to problems in the environment or on the next crop. Loss of activity can be caused by factors such as leaching, adsorption, absorption, volatisation or chemical or microbial degradation.

Whilst most of the properties required for good activity in the soil are understood it is much more difficult to predict the molecular configurations that will provide these properties, and obviously considerably more difficult to combine them with the exacting properties needed for activity per se. As discussed earlier, the science is only just entering the phase of being able to design active molecules from a knowledge of biochemical processes, it is unlikely that this technique will provide a significant boost to the discovery of soil acting pesticides in the near future. However, in the case of the pyrethroids, chemists have recently been able to modify the physical properties sufficiently to give molecules capable of redistribution in the vapour phase, whilst retaining full insecticidal potency. Such compounds show great promise as soil insecticides.

Recent research has yielded compounds of vastly increased potency, and there is no reason to believe that the limits of activity have been reached (Graham Bryce, 1981). A consequence of this is that more complex and inaccessible chemical structures become economically feasible because of the low application rates and consequent high bearable price per unit weight (over £100/kg for a recently launched herbicide). At the levels of potency now being reached, it is becoming feasible for products produced by fermentation to be cost competitive, and this opens up the prospect for the application of bio-technology to the production of pesticides. This will add stimulus to the search for pesticides derived from biological sources, and hopefully provide an additional source of soil acting pesticides.

The increasing trend for chemical companies to acquire interests in plant breeding and related sciences could lead to the development of new systems of propogation, such as encapsulated embryos, which could also open up new opportunities for pesticide use in the soil.

CONCLUSIONS

There is a need for new soil-acting pesticides, but the correct balance of chemical and physical properties required for activity in the soil, together with the very specific molecular confirmation needed for high levels of activity against the pest, make such compounds difficult to find. Advances in biotechnology and in the application of computers to aid invention, will change this situation but are unlikely to have a major impact in the near future.

ACKNOWLEDGEMENTS

Whilst the views expressed here are my own, they have been formulated using the data and ideas of many of my colleagues in ICI, whom I thank.

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PESTICIDES AND SOILS : A REGULATORY VIEW

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ABSTRACT

The role and development of studies to establish the behaviour of pesticides in soil are considered against the background of the overall data package necessary for the international registration of a new pesticide. The basic data requirements for the behaviour of pesticides in soil, which include metabolism, mobility and persistence are briefly described. The similarities and differences between the requirements of National Regulatory Authorities for soil data are considered and a number of current and future problem areas are discussed.

INTRODUCTION

Before any new pesticide can be marketed, the company responsible for its invention or development must first assemble a comprehensive data package which fully elucidates the chemical, biological and environmental properties of the chemical. It is this data package which forms the basis for the assessment by official Regulatory Authorities of the potential risks which the use of the pesticide may pose to man or his environment, both in the short and long term. One very often hears this data package referred to in rather facile terms and it is worth making the point at the very outset that the package represents a considerable financial commitment by the manufacturer. It is currently estimated that the cost of obtaining data necessary to secure international registrations for a new pesticide is in the region of £2.5 million. Considerably more expense is involved in actually marketing the pesticide as one must also account for development costs, investment in manufacturing facilities and many other cost incurring factors.

Before considering the specific requirements for data on the behaviour of pesticides in soil it is relevant to consider the nature and development of the overall data package needed for the registration of a new pesticide.

THE REGISTRATION DATA PACKAGE

In hindsight, when one considers the nature and extent of the data package that was deemed necessary as little as twenty five years ago, one might conclude, perhaps rather harshly, that the risk assessment process was extremely limited. It is, however, pertinent to point out that the data package and subsequent assessment merely reflected the contemporary 'state of the art' and the degree of public concern prevailing at that time. In both cases considerable changes have occurred over the past 10 to 15 years.

Thus 25 years ago the major hazard arising from the use of pesticides was seen as an acute risk and the minimal requirements for toxicological data reflected this assessment. With an increasing awareness of potential longer term hazards, which were associated with the use of chemicals in general and not confined to pesticides, there came demands for more data. Thus tests involving long-term feeding studies in experimental animals became standard requirements for the assessment of chronic toxicity and carcinogenicity. Specific incidents, such as the unfortunate and tragic outcome of the thalidomide issue, focused attention on other areas of toxicology and in turn led to more stringent demands for data in the areas of teratogenicity and reproductive toxicity. At about the same time new tests were being developed in other fields and, in particular, tests for mutagenic potential have since become a well established part of the data package. It may be tempting providence but I would suggest that toxicological requirements have now reached something of a plateau.

The concern with long-term exposure to a pesticide has also been reflected in the extent of residues data which are required to support registrations. Pesticide residues data also assume an international importance in fora such as the Codex Committee on Pesticide Residues and through European Commission Directives. Even the most cursory review of the scientific literature indicate the vast amounts of data which have been generated on pesticide residues in a very wide range of human and animal foodstuffs. As with toxicological data, the availability of suitable techniques have played a crucial role in the acquisition of residues data and the use of Gas Chromatography and more recently High Performance Liquid Chromatography is intimately linked with residues data. In passing it is worthwhile noting that this large amount of information on pesticide residues indicates that the correct use of pesticides does not lead to residues of toxicological significance. Thus the position in 1984 confirms the view expressed some ten years ago (Barnes 1973) that 'there is not one iota of evidence that any environmental contamination that has been identified as having been due to the use of pesticides in air, food or water has been followed by any detectable change in the incidence of human disease or disability'.

Perhaps not surprisingly, as man looks firstly towards his own safety, concern regarding the effects of pesticides on the environment gained real momentum at a later stage than the concern with direct effects on humans. Initially this area of data requirements focused on potential hazards to wildlife i.e. birds, bees and fish, but has subsequently expanded to include data on the effects on other beneficial insects, soil organisms and a wider range of avian and aquatic species. As has already been mentioned specific incidences or growing experience lead to additional requirements and the realisation that organochlorine insecticide persisted in the environment for some significant period of time resulted in increasing demands for data on the behaviour of pesticides in soil, data which will be discussed below, have subsequently extended beyond the specific area of persistence.

Before considering the 'soil data package' in more detail it is worth reflecting on the above summary of the total data package and noting the inter-relationships between the various categories of data. This is represented diagrammatically in Figure 1 from which it can be seen that the toxicological and animal metabolism data are closely related to the residues and plant metabolism data and are also linked with the wildlife data. These in turn are associated with the data on the behaviour of the pesticide in soil and water. All these areas combine to comprise a comprehensive dossier of information which provides a data base on which to predict the potential effects of the proposed uses of the pesticide on man and his environment.

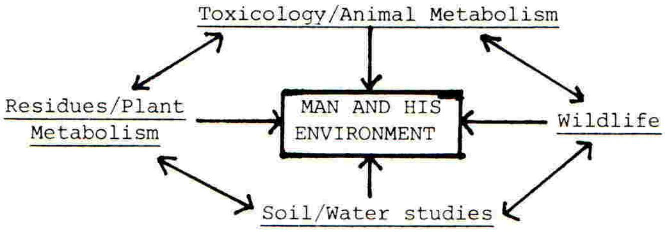

Fig. 1. Inter-relationships of registration data.

THE NEED FOR SOIL STUDIES

Studies on the behaviour of a pesticide in soil are needed to provide information to enable an assessment to be made of the following broad areas of potential effects:-

1) Any direct consequences to man through exposure to pesticide residues which remain after application.
2) Any indirect consequences to man resulting from the presence of pesticide residues which may be widely distributed and persistent e.g. deliterious effects on land, water and wildlife resources.
3) Potential exposure of non-target organisms such as fish, birds, etc., to pesticide residues.

These broad assessment categories, which will be considered in more detail below, re-emphasise the close links which exist between the various groups of data comprising the registration dossier of information. Thus, for example, the behaviour of the pesticide in soil will provide information on the transport of pesticide residues into the aquatic environment. An estimate of the extent of such transportation, when taken in conjunction with the known effects of the compound on aquatic organisms, will enable a risk assessment to be made. The significance of such a potential risk may, in turn, indicate the need for field monitoring studies to supplement the data obtained in the laboratory.

DATA ON THE BEHAVIOUR OF PESTICIDES IN SOILS

The following paragraphs describe in broad outline the basic studies which are required to provide Regulatory Authorities with the data necessary to establish the behaviour of a pesticide in soils and subsequently to predict the potential effects, if any, arising from the proposed uses of the pesticide under practical conditions.

These studies are, however, undertaken and subsequently assessed, against a background of information on the physical-chemical properties of the compound.

Physical-chemical properties

The physical-chemical properties of a pesticide are determined at an early stage in its development and certain of these properties are of value in predicting environmental behaviour. Thus:-

Vapour pressure

This is a major property which can be used to calculate the volatility of a substance and to predict whether a pesticide is likely to enter the atmosphere in any significant concentration and to estimate the distribution between air and other parts of the environment.

Water solubility

The water solubility of a pesticide is an important factor in determining its environmental transport and distribution. In particular it can effect the adsorption and desorption in soils as well as possible transformation by hydrolysis, photolysis, oxidation, reduction and biodegradation in water.

Hydrolysis

Hydrolysis studies are used to establish the significance of chemical hydrolysis as a route for the degradation of a pesticide and, if possible, to identify the hydrolysis products formed. They are normally undertaken in solutions at pH 5, 7 and 9.

Soil metabolism studies

Aerobic metabolism

Pesticides can be metabolically transformed in soil and it is therefore important to determine the nature and extent of pesticide degradation products.

A radiolabelled sample of the pesticide is preferably used for this study which aims to determine the rate, type and degree of metabolism in a sandy loam, silt loam or other soil type representative of the soil at the intended application sites.

Anaerobic metabolism

The information from this study is used to ascertain effects of flooding or water-logging on a well-aerated soil, conditions which may affect the metabolism and fate of the pesticide.

Radiolabelled compound is again used and the study is performed on the same soil selected for the aerobic metabolism study.

Soil mobility studies

Adsorption/Desorption

The adsorption and desorption characteristics of a pesticide in soil contribute to a prediction of the environmental distribution of the compound. Leaching (see below) and volatilization from wet soil surfaces are directly influenced by the adsorption/desorption equilibrium in the soil/water system and this can define the extent to which a chemical is available for degradation.

Batch equilibrium studies, with radiolabelled compound, are undertaken with a number of different soil types (e.g. sandy soil, sandy loam, silt loam, clay, clay loam), the exact number and types depending on the proposed uses of the pesticide and on the requirements of individual Regulatory Authorities.

Leaching

The movement of pesticide residues by leaching through the soil profile may result in contamination of water resources with possible consequential effects on man and wildlife.

Several methods, ranging from simple laboratory tests to more elaborate field studies, are used to simulate the leaching behaviour of pesticides in soils. Soil thin-layer chromatography in which the pesticide is applied to TLC plates prepared from appropriate soil types is a relatively simple and convenient method of testing the mobility of the pesticide. Soil columns can be used to determine vertical distribution of the pesticide in the soil profile and the rate of leaching. Lysimeters may be used to study the fate of pesticides in soil/plant system under outdoor conditions.

Where the pesticide is hydrolysed to a significant extent or where it is metabolised rapidly in soils, then both adsorption/ desorption and leaching studies may also be required on the hydrolysis or degradation products.

Soil photodegradation

Pesticides which are applied to the surface of the soil (and also to the exposed surface of plants) are subject to photodegradation and there is therefore a need to provide data on the nature and persistence of photodegradation products formed on the soil surface.

Radiolabelled material, applied to the soil are exposed to either natural or artificial sunlight conditions and significant amounts of photodegradation products are identified.

Field studies

Dissipation studies

The purpose of these studies is to determine the extent to which the pesticide persists in the soil under conditions of actual use. They are used to support the information obtained from laboratory studies.

Dissipation studies are conducted on at least two sites to which formulated product has been applied at the maximum recommended rate and by the recommended method of application. Soil samples are taken over a period of time so as to obtain a decline pattern for the pesticide and its degradation products. These studies can also supplement the laboratory leaching studies if soil samples are taken at various depths throughout the soil profile.

Rotational crop studies

Data from the studies described above may indicate that the persistence of a pesticide is such that subsequent crops may possibly be affected either in an adverse, phytotoxicity manner or by containing significant residues of the pesticide. In such cases studies involving the growing of a rotational crop on the treated soil are undertaken.

STUDY PROGRAMME

As with other groups of studies which form part of the data package, soil studies are generally undertaken on a step-wise basis over the period of development of the pesticide. This may be about 4 to 5 years but in many cases can be much longer. A schematic representation of the approach to data acquisition is given in Figure 2.

INTERNATIONAL REQUIREMENTS FOR SOIL DATA

The soil studies described above may, with certain exceptions depending on the nature of the compound and its proposed uses, be regarded as a 'basic package' which should enable the pesticide to be registered on a world-wide basis. Individual Regulatory Authorities do, however, differ in their requirements and in the guidance which they provide on the performance of these studies.

A survey of some 80 national registration systems published recently (Pesticide Regulatory Compendium 1982) identified the differences which exist between such systems and their individual data requirements. Data on soil were divided into two categories, namely 'Soil Residues' and 'Movement and persistence in soil' and the requirements for these data within individual geographic regions are summarised in Table 1. These differences in requirements, are of course, not confined to soil data, and similar distributions would be obtained for other areas of the registration data package. In general those Regulatory Authorities which apparently do not require soil data are not normally those which represent the major markets for a new pesticide. Such markets are normally those occurring in the major territories of Europe, North America and the Far East where soil data are a pre-requisite for successful registration.

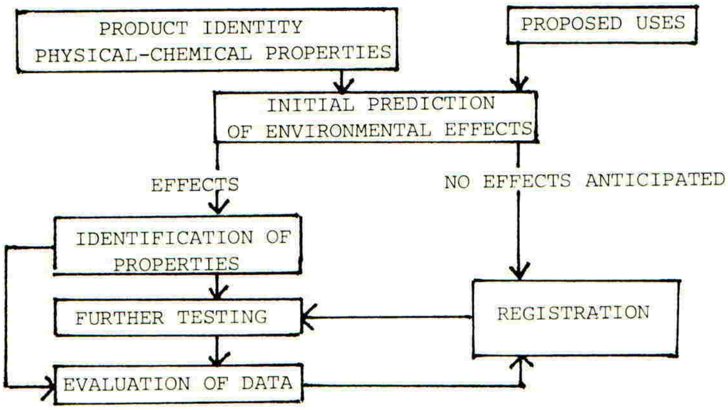

Fig.2. Data acquisition and assessment of environmental hazards.

TABLE 1

Requirements for soil data by National Regulatory Authorities.

Region (and number of territories)	Percentage requiring soil data	
	Soil residues	Movement/Persistence
Europe (26)	65	62
Africa (5)	40	20
Middle East/North Africa (4)	50	0
Far East (13)	54	46
South America (6)	33	33
Central/North America (5)	80	40

As well as differences in requirements between Regulatory Authorities, major differences also exist in the amount of guidance, or in some cases specific instructions, given on how the soil studies should be performed. Thus for example in the U.K., the Pesticides Safety Precautions Scheme (M.A.F.F. 1979) merely specifies the need for:-

a) Method of residue analysis for soil,
b) Residue data in soil and
c) Persistence data in soil including disappearance curves.

It is, however, doubtful whether U.K. registration would be obtained without more data than are apparent from these rather terse guidelines. At the other end of the spectrum are the guidelines published by the American (EPA 1982) and German Registration Authorities (e.g. BBA 1976). These describe in great detail not only the studies required but also the detailed protocols which must be followed.

These two different approaches pose something of a dilemma to Industry. On the one hand the PSPS allows for sufficient flexibility for the necessary data to be obtained in a logical and scientific manner and to undertake studies which are appropriate to the physical-chemical and biological properties of the compound and its proposed uses. Little formal guidance is given, however, on how these studies should be performed. On the other hand the EPA and BBA provide more than adequate protocols but allow for little or no flexibility in approach. Thus in some instances companies have been known to have undertaken a wide range of studies which more than adequately describe the behaviour of particular pesticides in soil and which by any scientific criteria can only be judged as acceptable only to find that further studies conducted strictly in accordance with the protocols are still required. Clearly what is required is a compromise between these two different systems.

CURRENT DEVELOPMENTS AND FUTURE TRENDS

It has already been mentioned that in the area of toxicology, data requirements have more or less reached a plateau and a degree of harmonisation between Regulatory Authorities has been reached.

This is of course not to say that there is universal agreement of requirements in this area and certainly there still remains major differences in the interpretation of data. Although the requirements for soil studies have remained fairly constant over recent years there are nevertheless signs of increasing demands by some Regulatory Authorities, particularly within Europe. These demands would, at least in part, appear to be due to increasingly strong political lobbying by Environmental Groups which manifests itself in other areas as well as pesticides. In many cases this 'political pressure' is reflected in a demand for studies which seems to be justified solely on the grounds that such studies are practically feasible. Very little regard is given to the fact that it may be impossible to interpret the results of such studies in terms of potential environmental impact. For example, the demand for data on soil respiration and nitrogen metabolism is fairly common within Europe. The results of such studies are, however, difficult to interpret, a fact that has been recognised by the EPA who have withdrawn their requirement for such studies as it was felt that the existing experimental systems were inadequate and failed to provide useful conclusions. (EPA 1981). Another example is a request for the effects of a pesticide on 'soil enzymes' in which case, and speaking from personal experience, it was admitted by the Authority making the request, that the results of such a study could not be interpreted but would be 'held in store' until such time as an interpretation was possible! In such cases Industry are, in my view, fully justified in refusing to undertake such studies.

Another major area where the interpretation of data is assuming some importance and giving rise to controversy relates to soil persistence or more precisely that the persistence of a pesticide per se is undesirable and that the quality of soil is damaged by the prolonged presence of a compound. Persistence is not necessarily an undesirable property and all pesticides must have a degree of persistence to be effective against the target pests. It has, however, been suggested that a limit can be used to define 'acceptable' persistence e.g. a half-life of 3 to 4 months. Clearly the question of persistence is complex and any assessment of this issue must take into account a number of factors. Thus the method of measuring persistence is important and it is imperative to distinguish between 'bound' residues and those which may be 'biologically available'. Certain chemicals are so strongly incorporated into the soil matrix that they cannot be removed by exaustive solvent extraction techniques. Provided such residues are unavailable to plants and would not create carry-over problems then they no longer form part of the available pool and its metabolites. Claims that persistent chemicals affect soil quality are not bourne out in practice if quality is defined in terms of crop vigour and yield. Similarly effects of pesticides on soil micro-organisms are usually transient and are generally insignificant in comparison with effects brought about by climatic changes or mechanical disruption of the soil.

There may of course be cases where soil persistence is a potential problem, especially in terms of carry-over to subsequent crops and there will therefore be a need to investigate this fully both in the laboratory and in the field. It is important, however, that any decision regarding the registration of a pesticide is taken on the basis of sound experimental work and not on any arbitrarily chosen half-life limit. The policy of refusing registration merely because a less persistent alternative pesticide is available and in the absence of a realistic appraisal of the properties of the new pesticide is to be regretted.

CONCLUSIONS

Any manufacturer of a new pesticide must invest considerable sums of money in generating data to satisfy the demands of Regulatory Authorities. The length of time taken to generate these data coupled with the intensely competitive nature of the agrochemical industry make the development of a new pesticide a high risk venture. It is imperative therefore that Industry are fully aware of data requirements but it is equally important that Regulatory Authorities maintain sufficient flexibility in their demands so as to allow for the acquisition of data which are appropriate to the particular pesticide and to its proposed uses. It should not be overlooked, as it sometimes is, that Industry itself represents a considerable reservoir of scientific expertise and that such expertise should be made use of in any proposals for new or additional data requirements. The data currently developed to elucidate the behaviour of pesticides in soil are comprehensive but, as in other areas, it is recognised that certain pesticides may require more extensive investigation. The need for such additional studies must, however, be based on sound scientific principles and the specific properties of the pesticide. They must not be demanded on a mere 'check-list' basis or because certain tests, which cannot be interpreted, are currently in vogue.

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SOIL-APPLIED CHEMICALS: THE DECISION MAKING PROCESS

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SUMMARY

Farmers, facing a wide range of soil applied chemicals to choose between, must go through a logical "Decision Making Process" in an attempt to choose a chemical for maximum affect. This paper puts together the process from a practical point of view such as could be adopted by farmers, advisers and distributers.

INTRODUCTION

In the past few years there has been an upsurge in the number of chemicals available to the farmer for soil application. This paper will examine "the Decision Making Process" which the farmer, often in conjunction with an adviser, must go through before a choice of these chemicals is made (as well as choice of application method).

Involved in this "Decision Making Process" are a number of important factors which can be categorised as follows:-

1. Geographical considerations - Soil type & weather.

2. Agronomic considerations - Previous cropping/mapping.
Land preparation.
Crop.
Planting date.

3. Mechanical considerations - Machinery choice/availability.

4. Pest considerations - Weeds.
Diseases.
Insects.

5. Chemical considerations - Pre/post emergence application.
Rate of application.
Choice of chemical.
Mode of action.
Persistence.
Tank mixing.

6. Financial considerations - Cost.

One or, more usually, a combination of these factors can be seen to be important in any particular case, so let us look at each in turn, describing briefly a few thoughts behind them:-

1. GEOGRAPHICAL CONSIDERATIONS

a) Soil type

Here the type of the soil must be considered in conjunction with the preparation. For example, the relative proportions of clay and sand constituents help determine the availability of the chemical by affecting both leaching and chemical binding; a very high or very low organic matter content can reduce the effectiveness of a chemical; and low pH can cause "lock-up" of materials.

b) Weather

Climatic differences can affect the performance and choice of material, and will influence the choice between pre and post emergence application. Thus the effectiveness of the soil applied chemical is affected by e.g. sunlight intensity, soil temperature and speed of germination of both weed and crop. The products' solubility in water, and air temperature at time of application also need to be considered.

2. AGRONOMIC CONSIDERATIONS

a) Previous cropping/mapping

As a crop grows, particularly cereals, it is worth "mapping" any problems (e.g. black grass, wild oat and competing broad-leaved weeds) so that the need for a soil applied chemical, crop manipulation or both, can be anticipated. The ploughing of grass can be expected to lead to serious contamination by grass weeds, insect pests and plant diseases.

b) Land preparation

Soil preparation is important especially, for example where a soil acting herbicide is applied, as in this case the soil must be free of clods and stones, moist and with a reasonably fine tilth to gain maximum benefit from the chemical. The plough is still of great importance as land preparation by ploughing often leads to the improved action of soil applied chemicals.

Direct drilling or minimal cultivations can restrict and reduce effectiveness of chemical action. Straw, whether burnt, chopped or incorporated will also affect performance. Possible future legislation on straw burning could have great influence on the choice of soil applied chemicals, maybe causing a swing towards post-emergence application of herbicides.

c) Crop

The availability of soil applied chemicals can influence choice of crop and field selection. Dirty areas of the farm can be cleaned in conjunction with a break crop e.g. bean, peas, maize etc. Residual chemicals can give almost total weed control in a crop.

d) Planting date

Although planting date of a crop remains, by necessity, somewhat flexible, there has been a recent tendancy towards early planting to maximise plant establishment. It must be remembered that early plantings are influenced by weather action, and themselves influence exposure to disease and insect attack, all of which will have a strong bearing on the choice of chemical and timing of application.

3. MECHANICAL CONSIDERATIONS

a) Machinery choice/availability

Important factors to be considered here are e.g. the acreage covered in one day; speed of incorporation if so desired; access to low ground pressure vehicles or floatation tyres and consequently the possibility of applying the chemical pre or post emergence. There is now a choice between conventional and C.D.A. spraying and the possibility of reducing water rates, and depending on timing and soil type, dosage rate could be reduced.

4. PEST CONSIDERATIONS

a) Weed

Before a chemical can be chosen another factor to consider is the type and degree of any weed problem and the consequent influence on the establishment and yield of the crop.

b) Diseases

Particularly where early plantings expose the crop to greater risk of disease, then seed dressings can be of great benefit in providing an early control. Again, mode of action, crop establishment, moisture etc., have to be considered, along with any effects on establishment that might be brought about by the chemical coating on the seed.

If foliar application of a spray is going to be necessary then one could delay application of a soil chemical to enable tank mixing of the sprays for convenience.

c) Insects

Again, tackling any insect problem before crop establishment is reduced, must be the farmers priority. Many soil applied insecticides give control of slugs, leatherjackets, wheat bulb fly, frit fly etc.

As with the disease programme, choice of chemical can be influenced by the convenience of tank mixing with another necessary spray.

5. CHEMICAL CONSIDERATIONS

a) Pre/post emergence application

Soil applied chemicals are available for pre or post crop emergence, or pre or post weed/pest emergence. Some require incorporating into the soil preplanting, which of these is chosen can depend on such factors as cropping programme, size of target, soil type, type of machinery and the type of problem. Post emergence will probably be chosen on farms where climate and soil type do not prevent access to land later in the season.

b) Rate of application

The amount of active ingredient to apply is clearly stated by the manufacturer. Having decided on the extent of the problem, the timing of spraying and the application machinery, then the appropriate rate of application should be chosen.

With improved application techniques opportunity must exist for a reduction in active ingredient.

c) Mode of action /persistence/safety to crop

A clear understanding of how a chemical works is essential in making any decision. For example, how much movement of the chemical can be expected in the soil or plant (and consequently how deep the seed should be drilled); whether the chemical will have adverse affects on some varieties, etc.

The persistence of the chemical could affect (planting of) the next crop and the soil preparation required.

Clear and instructive information about mode of action/persistence/ crop safety should always be sought, as it is often in this area of planning that mistakes are made.

d) Tank mixing

In progressive agriculture, tank mixing will always take place. The soil applied chemical offers little, if any, scope for tank mixing if applied pre emergence. If applied post emergence, however, application of soil chemicals can be made in conjunction with foliar sprays. For example: as long as rules are obeyed there should be no problems.

6. FINANCIAL CONSIDERATIONS

a) Cost

The cost of a soil applied chemical (about £3 to £20 per acre, or £8 to £50 per hectare) is usually accepted by the farmer within a budget for the control of weed, pest or disease.

The problem is how the money is spent to give maximum return. The pre emergence application is an example of "committed cost" - the problem is anticipated and the chemical applied within a programme of relevant control. The post emergence application can in some instances be a "committed cost" but is usually considered as a "selective cost", i.e. the chemical is only applied once the problem has occurred. In this case, there is opportunity for tank mixing with other chemicals to control a wide spectrum of weeds, pests and diseases. Often a combination of "committed" and "selective" costs works well.

Another aspect to consider is that the farmer, in the present financial climate, will keep his money in the bank for as long as possible thus favouring "selective" expenditure.

CONCLUSION

This paper has examined some 15 general factors which must be considered by the farmer to ensure maximum effectiveness of any chosen soil applied chemical. It is necessary to stress that these factors should be examined in a logical order (such as is outlined here) so that no one factor is overlooked - one oversight could lead to complete ineffectiveness of a chosen product.

CROP PROTECTION CHEMICALS AND ROOT GROWTH

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ABSTRACT

The growth of roots can be affected by crop protection chemicals. Symptoms of damage are described and related to the mode of action of the pesticide. There are also comments on damage to roots by other factors that can be confused with chemical damage.

INTRODUCTION

The National Pesticide Residues Unit investigates causes of crop damage caused by pesticides used on farms in England and Wales. Typical damage symptoms have been described in Diagnosis of herbicide damage to crops (HMSO 1981) but these mainly illustrate above ground symptoms. The study of plant root growth is of increasing importance in view of the increase in the use of soi applied pesticides that depend on root and emerging shoot uptake and subsequent translocation in the plant for their effectiveness.

The growth and development of normal roots must be understood before abnormal growth can be recognised and explained. Descriptions and illustrations of roots are to be found in Torrey & Clarkson (1975) and Russell (1977). Descriptions of the effects of herbicides on roots are to be found in Andus (1976), Ashton & Crafts (1981) and Fedtke (1982), but the morphological and anatomical changes in roots brought about by pesticides are generally not well illustrated in the literature.

The uptake of a chemical depends on its position in the soil in relation to the roots. The parts of the root that are absorbing water and chemical are related to the roots' stage of growth, most absorption occurring in a few centimetres behind the root tip. The primary driving force for uptake of nutrients and pesticide into the plant is the transpiration stream which is related to available soil water and atmospheric conditions (Penman 1951). Roots absorb water from the wetter parts of soil before dryer areas and the rate of water movement is greater in periods of high evapotranspiration which is controlled by the weather.

Some movement of pesticide occurs by diffusion in soil water from the site of application but this process is slow and of lesser importance than transpiration. Chemicals that are volatile can reach roots by diffusion through the soil air spaces.

PESTICIDAL DAMAGE SYMPTOMS

Growth inhibition

Many pesticides have a growth inhibition effect without producing morphological changes in roots. Inadequate root growth in a crop may be due to soil fertility or pest and disease so that plants with poor root development require some corroborative evidence such as that provided by chemical analysis or biological assay to confirm pesticide damage.

The rate of growth of pregerminated seeds in petri dishes containing contaminated soil over a 24 hour period can be measured and used as a basis of comparison with known treatments. (Parker 1964).

Plant growth regulator herbicides

Herbicides with hormone activity can inhibit cell elongation; short thick roots are produced due to the radial expansion of cells. There is also an initiation of lateral root primordia from secondary meristems in the root and also in shoots. The symptoms such as those that have been observed in pea roots grown in water with 24D (Andus 1959), are not often seen in the field. This is mainly because hormone type herbicides are applied to leaves and not incorporated into soil. The development of secondary roots into soil may be restricted by the soil imposing a physical barrier that the root primordia have not the energy to overcome, or because the herbicide initiates primordia but prevents their extension. The development of root primordia on stems above ground level with splitting of the epidermis and the development of root callous tissue at soil level are seen following drift of hormone type herbicides. Where soils have been contaminated with more persistent hormone type herbicides such as chlorpyralid root growth can be inhibited to such an extent that plants fail to grow into the affected soil.

Cell division inhibitors

Colchicine was the first compound that was found to affect cell division; other substances which produce similar morphological effects include HCH and a range of herbicides including carbamates, dinitroanilines, chlorthal-dimethyl and propyzamide.

The compounds act on microtubules in cells; blocking mitosis in meristematic tissue. The disruption is seen as a general swelling of the root tip and gives it a club shaped appearance. Pesticides can affect different stages of cell division and the cytological effects seen in meristematic tissue include arrested metaphases, chromosome aberations, polyploidization, bi and polynuclear cells and giant nuclei. In the root cortex cell morphology is irregular, the xylem crushed, increased width to length of cells, reduced secondary cell wall thickening.

It has been noted that calcium concentrations in cells can also be affected by herbicides which act on microtubules.

Herbicide damage from contaminated mother plants

Some herbicides can be carried from a crop into the succeeding crop via bulbs and tubers.

The growth of seed potatoes can be restricted by residues of the sprout suppressants chlorpropham and tecnazene. Tecnazine applied after sprouting has commenced can induce inward growing roots in potato tubers.

Glyphosate and chlorpyralid have contaminated potatoes and bulbs such as onions and tulips, causing abnormal root growth when planted out in the following season.

Seed dressings

The germination of seeds can be affected by excessive applications of some seed dressings.

Organo-mercury compounds such as PMA (phenyl mercury acetate) can damage cereals, roots and shoots being stunted and swollen. The mode of action remains obscure, but mitotic abnormalities have been observed in the root tips of onions at concentrations as low as 0.0001 per cent.

Seed dressings of gamma-HCH can prevent the emergence of roots and can cause abnormal nuclear division of meristematic tissue.

The effects and symptoms of overdoses of up to five times the recommened rate on wheat and barley seed were studied at Cambridge. Roots and shoots showed no recognisable symptoms of phytotoxicity at emergence but growth was delayed depending on the chemical and the amount applied.

NON PESTICIDAL DAMAGE SYMPTOMS

Soil acidity

Crops that are susceptible to soil acidity may have roots that are short and thickened with the development of many secondary roots; affected plants could also show leaf chlorosis. Soil from crops such as barley and sugar beet should be tested for pH when chemical damage is suspected.

Boron deficiency

The meristems of roots are damaged by a deficiency of boron; cell division is inhibited and the root tips may die.

Straw residues

The development of seedling cereals may be inhibited by the presence of decaying straw residues. Roots of affected seedlings are shorter with swollen apices and a marked proliferation of root hairs immediately behind the tips. The condition has been observed in direct drilled winter cereal crops when straw debris was incorporated at seedling depth, especially when the soil was wet (Ellis et al 1975).

Soil Structure

Soil compaction can prevent roots developing down to soil profile; affected roots may be thickened and twisted. The restriction of rooting may confine roots to the soil surface where the likelihood of absorbing chemical is greater.

Anaerobic conditions

Anaerobic soil conditions can prevent roots growing into poorly drained soils and periods of wet weather in summer can reduce soil oxygen supply deficiency to kill roots and cause chlorosis.

Drought

Some crops, especially brassicas, produce short thickened roots in the top few inches of soil during periods of drought. These roots, filled with starch, are storage organs which elongate rapidly into normal roots when the plant is supplied with water (Vartanian 1981).

Pests and diseases

Crop pests and diseases cause extensive damage to roots but these cannot be dicussed in any detail here. The pattern of damage is generally random and patchy, in contrast to chemical damage which is often related to the method of application.

CONCLUSION

The abnormal root growth that may be caused by some pesticides can be an aid when investigating damage problems, but they must be used in conjunction with field observations and laboratory analysis.

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2.

Factors Affecting Activity

The principles that govern the activity of chemicals in the soil and some ways in which they may be manipulated.

Chairman:
Professor J. W. PARSONS
University of Aberdeen

Session Organiser:
Dr. T. R. ROBERTS
Shell Research Ltd

FACTORS AFFECTING THE UPTAKE OF SOIL-APPLIED CHEMICALS BY PLANTS AND OTHER ORGANISMS

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ABSTRACT

Vertical redistribution of chemicals is related to the octanol-water partition coefficient (K_{OW}) of the chemical and the soil organic matter content. A range of log K_{OW} from 1 - 3 is shown to be necessary for pre-emergence translocated herbicides and no single chemical in this range is likely to be reliable over the organic matter content range from 1 - 10 per cent. Systemic insecticides and nematicides with log $K_{OW} < 0$ may be less effective under wet conditions. Strongly adsorbed chemicals are active by vapour action, must be incorporated to the depth of the target organism and are less effective in soils with high organic contents.

INTRODUCTION

Previous reviews have discussed the effects of soils on herbicide activity (Riley & Morrod, 1976; Walker, 1980; Eagle, 1976; Hance, 1983.). Similar effects of soil would be expected with other biologically active chemicals because the movement and uptake of chemicals in soil depend on the physical properties of the chemical not on its biological activity which is only expressed when the chemical reaches the active site in the organism.

The main factors which modify the intrinsic activity of a soil applied chemical are adsorption by soil, the vertical distribution in soil and its persistence, factors normally controlled by the molecular structure of the chemical although the initial vertical distribution can be controlled by placement or incorporation. Environmental factors affecting activity such as soil organic matter content, soil structure, pH, rainfall and temperature are largely fixed for a given site and time of application.

Successful use of a soil-applied chemical depends on matching the vertical distribution of the chemical and the target organism. The distributions of some chemicals used to control them are shown in Figure 1. The widest distribution is found for root nematodes and root pathogens. Nematicides for potato cyst nematode are incorporated to about 15 cm for effective use. Fungicides for controlling diseases such as take-all would require similar incorporation but present fungicides are ineffective in soil despite high activity *in vitro* (Bateman, 1980). Insecticides for pests such as carrot root fly are distributed as granules in the top few centimetres of soil although the optimum distribution is not known (Suett, 1984). Surface treatments or shallow incorporation of herbicides acting on shoot growth give a well matched initial distribution. The greatest mismatch of distributions is for pre-emergence translocated herbicides. Although some shoot uptake occurs most uptake is through the roots and movement below the soil surface is therefore required and it is with this class of herbicide that the greatest variability occurs either because there is insufficient movement and poor weed control or too much movement causing failure of weed control or crop damage because selectivity partly depends on a vertical separation between weed and crop roots.

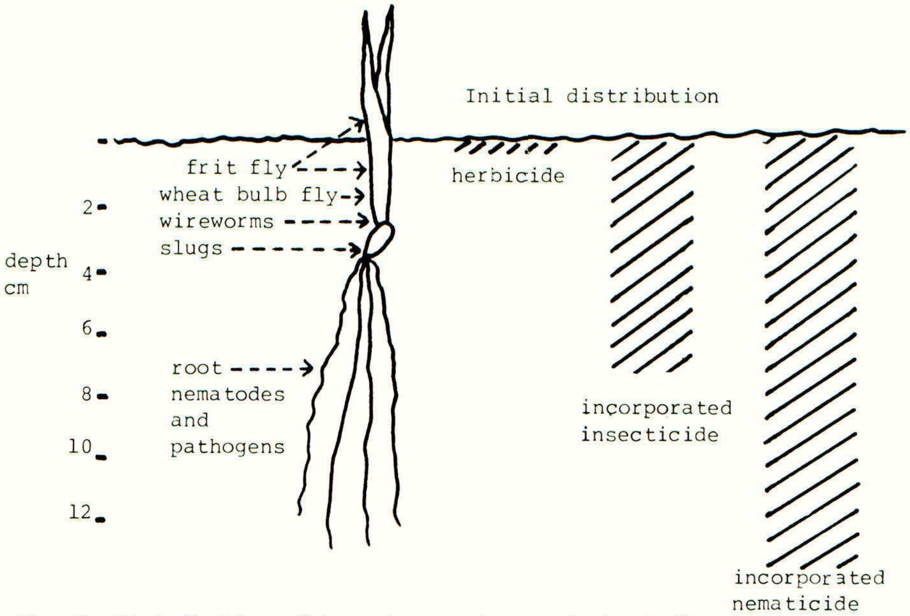

Fig. 1. Distribution of target organisms and chemicals.

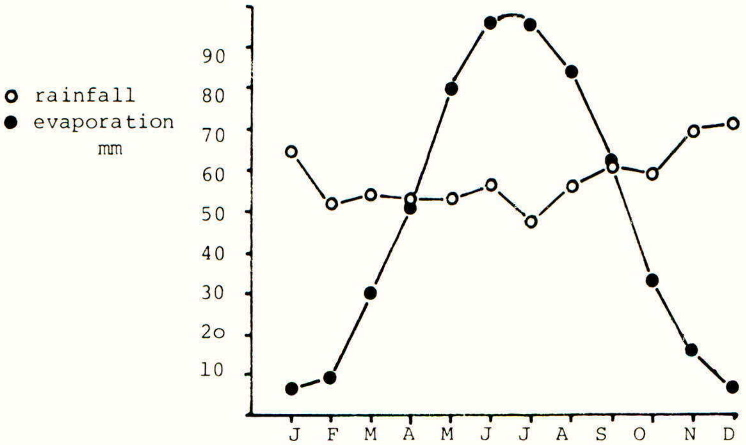

Fig. 2. Monthly rainfall and evaporation at Rothamsted.

MOVEMENT IN SOILS

Long distance movement of solutes in soils is with the bulk flow of water except for the highly volatile fumigants. Redistribution depends on the flow of water through soil and the adsorption of the chemical by the soil.

$$\text{Chemical adsorbed by soil} \overset{K_d}{\rightleftharpoons} \text{chemical in soil solution}$$

Adsorption by soils is usually expressed as K_d, the ratio of chemical adsorbed by soil and the soil solution concentration determined in soil-water slurries. K_d is in the range 0.01 - 1000 for most agricultural chemicals. Except for soils containing ash from burning of crop residues or straw (Embling et al, 1983) adsorption is proportional to soil solution concentration and K_d is constant over a range of solution concentrations.

The flow of water through soil is highly seasonal. The climate of the cropping areas in Britain is relatively uniform (Smith, 1976). Rainfall is spread fairly evenly over the year, annually in the range 600 - 850 mm, the minimum rainfall in the March - May period being about 70 per cent of the maximum although monthly rainfall varies widely from year to year. Annual evaporation from an open water surface is about 500 mm but increases from 0 in December to about 90 mm in June. Differences in evaporation between years is relatively small.

Evaporation begins to exceed average rainfall in March/April and rainfall to exceed evaporation in September/October (Figure 2). These are the main periods of application of pesticides to soil, autumn-applied chemicals at the beginning of a six month period when the soil is usually close to field capacity and spring applications at the beginning of a six month period of drying. However because of the year to year differences in rainfall, but not evaporation, the net flow of water varies widely and is the main reason for differences in performance of those chemicals which depend on movement, or lack of it, for effectiveness.

The effect of differences in K_d and the evaporation rate of water on vertical movement under wet conditions is shown in Figure 3. The distributions were simulated using the computer model CALF (Nicholls, et al. 1982) for a clay loam soil at Rothamsted for an application date of January 3rd, 1984. Actual weather data for the period January 3rd - February 14th was used for the winter simulation which gave accurate simulations for 3 chemicals with K_d 0.1, 0.8 and 2 measured in the field. Wet conditions in spring/autumn when rainfall exceeds evaporation were simulated by setting evaporation at 1.5 mm per day and wet conditions in summer when rainfall and evaporation are comparable were simulated by setting evaporation at 3 mm per day. Degradation was neglected.

For these wet conditions which represent the greatest leaching found in most years it is apparent that movement is limited when $K_d > 5$ and may remove all but traces from the surface layers when $K_d < 0.5$. Simulations with other soil textures which differ in the pore size distribution shows rather more movement in light textured soils and less movement in very structured soils. Under lower rainfall conditions movement in each season is correspondingly decreased. Aged residues dissolve less readily or appear to be adsorbed more strongly (Hance & Embling, 1979; Boesten & Van Der Pas, 1983) so that conditions at the time of application and the subsequent rainfall pattern will also influence vertical movement. The conclusion from the simulations is that K_d

Fig. 3. Computed distributions 42 days after application: rainfall 105 mm; evaporation 10 mm winter, 63 mm autumn/spring, 126 mm summer

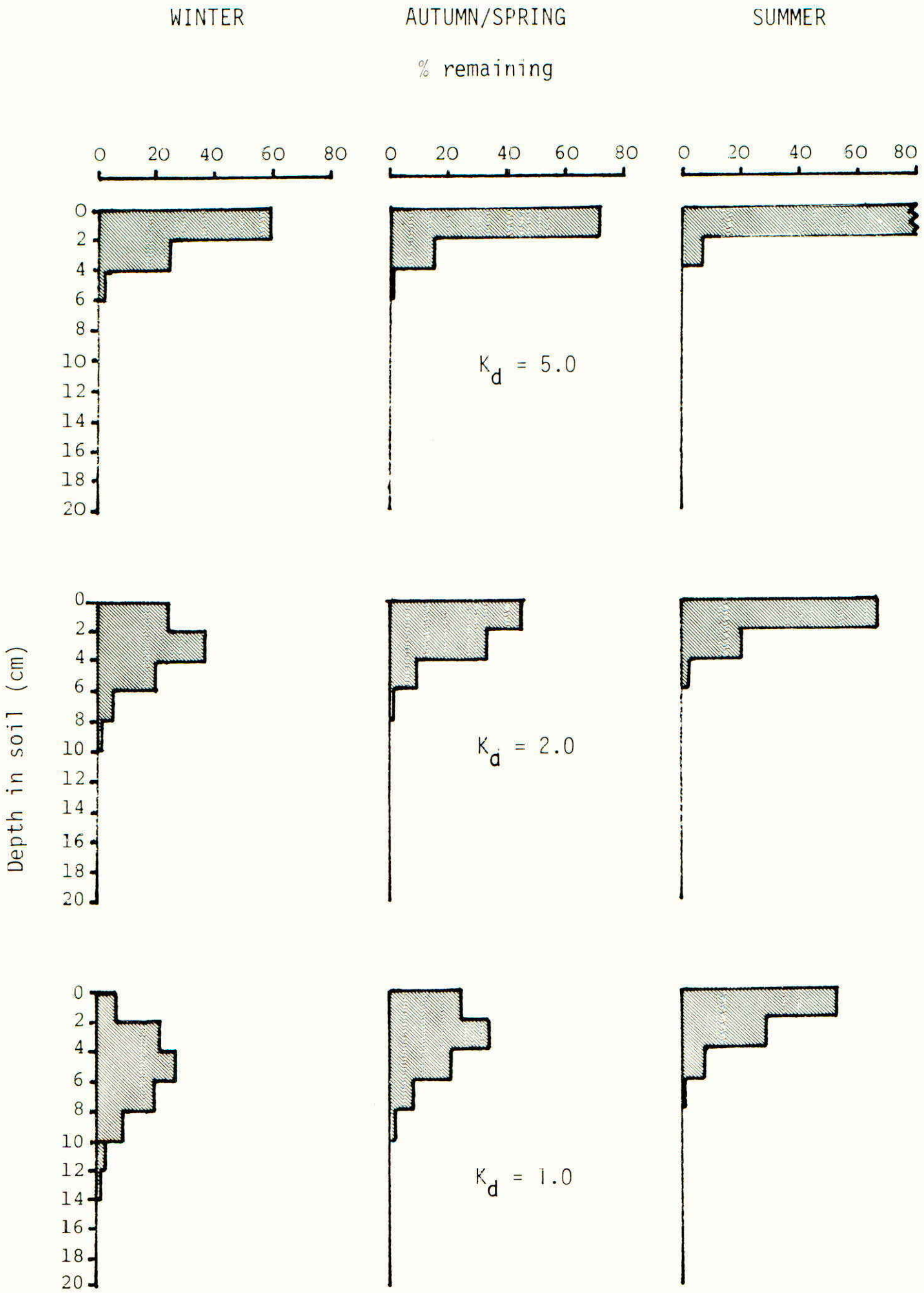

Fig. 3. continued

in the approximate range 0.5 - 5 is required for limited movement in soils and that redistribution throughout the plough layer by leaching could not be reliably achieved.

K_d and soil properties

Much early work showed that for non-ionised chemicals (and virtually all soil applied chemicals are of this type) K_d was closely proportional to the soil organic matter content. The general use of texture for recommended rates of application relies on the correlation between texture and organic matter content (Eagle, 1983). Organic matter is generally greater in heavier soils although this depends on the history of the site, in particular the time in arable cropping. The classical sites at Rothamsted for example after more than 100 years arable cropping on a clay loam soil have organic matter contents close to 1 per cent, the level generally associated with very light soils.

Assuming that K_d is proportional to organic matter content the variation of K_d with o.m. is given in Table 1. Experimentally K_d is distributed over a range of half to twice the mean value for a particular organic matter content.

TABLE 1

Variation of K_d with organic matter content

% o.m.	K_d						
1	5	2	1	0.5	0.2	0.1	0.01
2.5	12.5	5	2.5	1.25	0.5	0.25	0.025
5	25	10	5	2.5	1.0	0.5	0.05
10	50	20	10	5	2.0	1.0	0.10

Over a 10-fold range of organic matter content K_d also varies 10-fold and chemicals moving little in soils with high organic matter content may be very mobile in soils with low organic matter and activity is unlikely to be reliably achieved over the whole range of organic matter contents and textures if it depends on vertical distribution.

K_d and properties of the chemical

Because K_d is proportional to organic matter content, adsorption of a particular chemical can be expressed as a soil organic matter - water distribution, K_{om} or Q (Furmidge & Osgerby, 1967).

$$K_{om} = \frac{100\ K_d}{\%\ \text{o.m.}}$$

K_{om} for a chemical is relatively constant for soils throughout the world, with variation, as for K_d, over about a 4-fold range in comparison with a range of at least $0.1 - 10^6$ for different chemicals (Briggs, 1981a). K_{om} is related to the octanol-water partition coefficient of the chemical (Briggs, 1973, 1981a) by:

$$\log K_{om} = 0.52 \log K_{ow} + 0.65$$

For example K_{om} calculated for chlortoluron (log K_{ow}, 2.41) is 80 compared to the mean value of 71 found by Embling et al.(1983). Thus K_d expected for a range of organic matter contents can be calculated from K_{ow} a single, easily measured property of the chemical

$$K_d = 0.045\ K_{ow}^{0.52}\ .\ \%\ \text{o.m.}$$

Equally the value of K_{ow} giving an appropriate K_d can be calculated as shown in Table 2.

TABLE 2

Values of log K_{ow} of chemicals appropriate for K_d at different organic matter contents

K_d	% organic matter 1	 2.5	 5	 10
	log K_{ow}			
10	4.5	3.8	3.1	2.6
5	3.9	3.2	2.6	2.0
2	3.2	2.4	1.8	1.2
1	2.6	1.8	1.3	0.7
0.5	2.0	1.2	0.7	0.1
0.2	1.2	0.5	-0.1	-0.7
0.1	0.7	-0.1	-0.7	-1.3
0.01	-1.2	-2.0	-2.6	-3.0

The extent to which a chemical of known log K_{ow} will match its required vertical distribution (Figure 1) for different types of biological activity can be obtained from Table 2 and Figure 3. For example with pre-emergence systemic herbicides applied in autumn with winter leaching conditions to follow, K_d should be in the range between 0.5 and 10 and therefore log K_{ow} between 2 and 3. For application in spring with summer conditions to follow, K_d should be between 0.2 and 5 hence log K_{ow} in the range 1 - 3. For both times of application there would be limitations for light soils and high organic matter contents because of seasonal differences in rainfall, and the natural variability in adsorption by organic matter.

Herbicides taken up by shoots are required close to the soil surface, thus K_d should be above 2 and log K_{ow} above 3. Table 3 lists soil-acting herbicides, including some post-emergence treatments, from the 1984 Approved List (MAFF 1984) with indications of limitations on use and those chemicals thought to have vapour activity. The generalisations outlined previously are followed. The autumn-applied herbicides are the ones with log $K_{ow} > 2$ except for simazine, metoxuron and chlorsulfuron. Chlorsulfuron anion is the only herbicide with log K_{ow} less than 1 and considerable leaching, particularly in soils of higher pH, would be expected (Nicholls et al., 1983). Most chemicals with log $K_{ow} > 3$ act on shoot growth and are vapour active. Table 4 lists the properties of soil acting chemicals of other types from the 1984 Approved List together with some seed dressings and additional chemicals for comparison. There are few limitations on use except for organic soils and high pH soils where some insecticides are less effective. The range of log K_{ow} is much wider than for herbicides although the chemicals with log $K_{ow} > 3$ are again all vapour active.

WATER SOLUBILITY

Water solubility is often thought of as an indicator of adsorption and leaching. This can be misleading because although for liquids there is an inverse relationship between solubility and K_{ow} and hence K_d, for solids an additional factor is the energy required to disrupt the crystal structure.

TABLE 3

Log K_{ow}, main season of application, vapour activity and limitations on use of herbicides

Chemical	log K_{ow}								limitations on use		vapour activity
	<0	0-1	1-1.5	1.5-2	2-2.5	2.5-3	3-3.5	>3.5	light soil	high o.m.	
bromacil				s							
chloridazon				s					x	x	
chlorsulfuron				a					x		
" anion	-1										
cyanazine				s					x		
fenuron			s								
lenacil				s					x	x	
metamitron			s							x	
metoxuron				s,a							
metribuzin				s					x	x	
simazine				s,a					seed > 7cm		
terbacil			s						x		
atrazine					s						
aziprotryne						s,a			x	x	
chlortoluron					a					x	
diphenamid					s				x	x	
isoproturon						a				x	
linuron						s,a			x	x	
methabenzthiazuron						a				x	
methazole						s				x (for pre-em action)	
propachlor					s						
propham						s			x		+
chlorbromuron							s			x	
chlorpropham							s		x		+
ethofumesate, napropamide							s		x	x	
dichlobenil,EPTC							s				+
propyzamide							s,a			x	
cycloate, bifenox, trifluralin								3.6, 5, 5	x	x	+
chlorthal dimethyl, pendimethalin, triallate								4.8, 5, 5		x	+

TABLE 4

Log K_{ow} of insecticides, their biologically active metabolites, fungicides and vapour activity

Chemical	log K_{ow}							vapour activity
	<0	0-1	1-1.5	1.5-2	2-2.5	2.5-3	>3	
Insecticides/Nematicides								
oxamyl	x							
omethoate	x							
aldicarb			x					
" s'oxide	x							
" s'one	x							
dimethoate		x						
ethiofencarb					x			
" s'oxide		x						
thiofanox					x			
" s'oxide		x						
bendiocarb				x				
carbofuran				x				
mephosfolan				x				
chlorfenvinphos							3.8	
chlorpyrifos							5	+
diazinon							3.8	+
disulfoton							4	+
" s'oxide				x				
fonofos							4	+
iodofos							5	+
phorate							3.8	+
" s'oxide				x				
quinalphos							4	+
BHC							3.9	+
dieldrin							4.1	+
aldrin							6	+
Fungicides								
triadimefon						x		
triadimenol						x		
propiconazole							3	
bitertanol							4	
prochloraz							4.2	
Nitrification inhibitor								
nitrapyrin							3.2	+

This is related to the melting point, Tm ^{o}C. The equation

$$\log \text{ water solubility (mole } ^{-1}) = -\log K_{ow} - 0.01\ (T_m - 25)$$

(Briggs 1981a) or closely similar ones (Bowman & Sans 1983) show that there can be a 1000 fold variation in water solubility between a liquid and a high melting solid of the same K_{ow} and a corresponding 36 fold difference in K_d for compounds of the same water solubility. As shown by Nicholls et al., (1984) there are few chemicals for which water solubility per se is an important feature of their behaviour in soil. After an initial equilibration period all soil applied chemicals are present either adsorbed or dissolved at normal field rates water solubility being a factor only for simazine and lenacil each with log $K_{ow} < 2$ and a high melting point.

UPTAKE BY TARGET ORGANISM FROM SOIL

Assuming that the distribution of the chemical and target organism are matched uptake by the organism can be through the water or vapour phase.

$$\begin{tikzcd}
\text{chemical adsorbed by soil} \arrow[r, shift left, "K_d"] & \text{chemical in soil solution} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & \text{organism} \arrow[l, shift left] \arrow[dl, shift left] \\
 & \text{chemical in soil air} \arrow[u, shift left, "K_{aw}"] \arrow[ur, shift left] &
\end{tikzcd}$$

The concentration in soil water depends on K_d and the concentration in soil air on K_d and the air-water concentration ratio, K_{aw}. The air-soil concentration ratio is K_{aw}/K_d which is given approximately by (Briggs 1981b).

$$K_{as} = \frac{\text{vapour pressure } K_{ow}^{0.5}}{765\ \%\ \text{o.m.}}$$

Therefore for a particular compound where vapour pressure and K_{ow} are fixed the concentration available for uptake by either the water or vapour route is inversely proportional to organic matter content. Thus effectiveness decreases for both herbicides and insecticides with increase in organic matter content (Upchurch and Mason, 1962; Nicholls et al., 1981).

UPTAKE BY PLANTS

Soil influences uptake by plant roots and shoots only through its effect on soil water or air concentrations. Plant roots accumulate chemicals from water in proportion to K_{ow} of the chemical (Briggs et al., 1982). For polar compounds (log $K_{ow} < 0$) concentration within the root is about 0.8 times the external concentration increasing to over a hundred times when log $K_{ow} > 4$. For subsequent translocation to leaves there is an optimum log $K_{ow} = 2$. Chemicals with log $K_{ow} > 4$ are poorly translocated despite high accumulation in the roots. For plants growing in soil, adsorption by soil lowers the optimum for translocation to about log $K_{ow} = 1$. Soil systemic activity is therefore unlikely for chemicals with log $K_{ow} > 3.5$. Analogues of translocated herbicides with log $K_{ow} > 5$ have great intrinsic activity as inhibitors of photosynthesis (Kakkis et al, 1984) but no herbicidal activity because of the requirement for translocation and soil mobility. The same upper limits apply to systemic soil applied insecticides and nematicides but the range is much wider because leaching is less crucial, although control could fail under high rainfall conditions.

Aldicarb sulphoxide, rapidly formed from aldicarb in soil has K_d close to 0.01 and aldicarb has failed when applied during a dry period in February followed by high rainfall, probably because it was leached below the zone where insects could be controlled (Figure 3). Uptake by shoots depends on diffusion of chemical there being no mass flow of water as there is to roots. Vapour diffusion is 10,000 times faster than diffusion in water and vapour concentrations are greater for chemicals with high vapour pressure and high K_{ow}. Shoot-acting chemicals are therefore generally volatile and not translocated, high values of K_{ow} giving large vapour activity and no leaching through soils. Very wet conditions and slow growth may lead to increased uptake through the water phase from the high surface concentrations and damage to crops normally protected by rapid emergence.

SOIL INSECTS AND OTHER ORGANISMS

Movement of chemicals to soil insects and other organisms is dependent entirely on diffusion. Uptake from water increases with increasing K_{ow} in parallel with the decrease in soil water concentration caused by increased soil adsorption so that at equilibrium all chemicals would accumulate to similar levels in soil living organisms. (Lord et al., 1980). However equilibrium may take several weeks to be achieved for lipophilic compounds (Lord et al., 1980; Reinecke & Nash, 1983) because of slow diffusion. Only relatively weakly adsorbed chemicals, log $K_{ow} < 2$ would be effective by uptake from water. Oxamyl and aldicarb sulphoxide and sulphone are so weakly absorbed that they can be used in organic soils but require incorporation in all soil types. Uptake from water depends on moisture content as shown for earthworms by Briggs and Lord (1983).

As for herbicides lipophilic insecticides would depend on vapour activity (Nicholls et al., 1981) which all except chlorfenvinphos of the compounds in Table 4 do. Soil incorporation is necessary to achieve the desired depth distribution of the target insect. Metabolism of disulfoton and phorate to their sulphoxides and sulphones converts the vapour acting parent molecule to mainly water acting systemic products.

In the case of fungicides, the ergosterol biosynthesis inhibitors shown in Table 4 are not very active as soil-applied materials because they are too lipophilic and involatile so transport to the organism would be slow. Hide and Cayley (1982) found that incorporation of high rates of strongly adsorbed involatile fungicides was necessary to control potato diseases. Incorporation to depth is not practical to control cereal root pathogens and redistribution by rainfall to the required pattern is unlikely.

CONCLUSION

Movement of chemicals vertically in soils and to target organisms in soil depends largely on the physical properties of the chemical and the soil organic matter content. The range of seasonal weather conditions and organic matter contents mean that, particularly for translocated herbicides, variability in performance and limitations in use are inevitable. As Riley and Morrod (1976) concluded, the only way to change behaviour is to change the chemical.

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FORMULATION AND APPLICATION FACTORS INVOLVED IN THE PERFORMANCE OF SOIL-APPLIED PESTICIDES

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ABSTRACT

Pesticides are applied to soil as sprays, granules, seed dressings or baits. Formulation and application of these products affect the initial distribution of the pesticide, and the rate at which the formulation releases the toxicant into the soil environment. Both these factors affect performance through their influence on losses of toxicant by volatilisation, chemical, photo-chemical or microbial decay and by modifying the rate of leaching of toxicant into the soil. In some cases adverse effects may be overcome by modifying the formulation, in other cases changes in the application systems are required. The possibilities for the greater control of release of pesticide through formulation are considered.

INTRODUCTION

A formulation can be considered as a vehicle that allows a biologically active compound to be transported to its site of action in the biological system that is to be modified or destroyed. Many different types of formulations can be devised for most toxicants and the formulator has to consider a large variety of input data to select the type and to design the most appropriate formulation within that type (Furmidge, 1979). For the purpose of the present discussion, the following factors can be considered as the most important in selecting the formulation:

1. the nature of the target,
2. the type of biological activity involved,
3. the type of application equipment available,
4. the physical and chemical properties of the toxicant,
5. safety and regulatory requirements,
6. cost.

While all these are important, the most critical in determining the type of formulation are the first three; the last three factors are most important in determining the physical form in which the selected formulation is developed.

The target of concern is an organism in, or on, the soil and the types of biological activity involved may be insecticides, fungicides, herbicides, nematicides, PGRs, safeners etc. The application has to ensure the effective distribution of the formulation over the soil surface, or within certain volumes of soil where the target organism exists. The types of formulation that are of practical value are sprayable formulations, granular formulations, injection products, seed treatments and baits. The first three of these can be considered with all soil-applied toxicants, seed treatments can be used with most toxicants other than herbicides, while baits are likely to be of use only against mobile insects in soil. The availability of local application equipment may limit further this selection.

Having selected the type of formulation, one can consider the different ways the particular type of formulation can be designed and how the performance is likely to be modified by the design.

PERFORMANCE OF SOIL-APPLIED FORMULATIONS

The preceding paper has considered the complex interactions of adsorption, leaching, diffusion and degradation that govern the availability of toxicants to biological organisms in soil. It is generally assumed that a toxicant in the soil can be taken up by an organism only via the water or air phases in the soil; any formulation must release its toxicant to the soil before any activity will be observed. Once released the toxicant will be subject to the interactions with the soil components regardless of the application system used to distribute it and of the type of formulation in which it was applied. Attempts have been made to modify properties such as adsorption by soil and rate of water transport through soil by addition of surface-active agents but such vast quantities of additive are needed to produce any significant effect that the use of such additives in formulations can be ruled out on grounds of cost alone. Note this is a different situation from that encountered in applications to other types of target, such as to foliage or to inanimate surfaces in buildings etc., where the formulation can be used to modify the physical interactions between toxicant and surface and thus to change the availability of the toxicant to the pest organism. This does not imply that formulation has no effect on the performance of pesticides in soil but that, with certain exceptions, the effect is limited to modifying the release of the toxicant into the soil. Similarly, application may affect performance, but only in terms of the initial distribution of the toxicant in the soil.

Properties that may be affected by the initial distribution and by rate of release include losses through volatilisation, through chemical or microbial decay and the rate of redistribution of the toxicant in the soil by leaching and diffusion.

Sprayable Formulations

These can be developed in a variety of different forms; simple solutions (in water or organic solvents), emulsifiable concentrates (e.c.), suspension concentrates (s.c.), wettable powders (w.p.) or water-dispersible granules (w.g.). The formulator is limited in his choice of formulation by the physical and chemical properties of the toxicant, particularly by its solubility characteristics and its chemical stability.

They are very versatile formulations, designed to be diluted or dispersed in varying quantities of water to provide a wide range of spray concentrations that can be matched to the spray volume desired to give the correct application rate of the chemical. A typical set of application data is given in Table 1 for an e.c. and a w.p.; an s.c. would be similar to the e.c. and a w.g. similar to the w.p.

So many drops are produced by the spray formulation applied at a drop size of 200 μm and 100 litre ha^{-1} that, with reasonable care in application, a uniform layer of the formulation will be applied over the whole exposed soil surface.

TABLE 1

Application Data*

	Formulation (%a.i.)		
	Wettable Powder (75%m/m)	Emulsifiable Concentrate (40%m/v)	Granule (10%m/m)
Active ingredient (g ha^{-1})	500	500	500
Total formulation (g ha^{-1})	667	1250	5000
Av. particle diam. (μm)	6	1.3	500
Particle number (ha^{-1})	$1.2x10^{13}$	$1.1x10^{15}$	$3.8x10^{7}$
Particle number (cm^{-2})	$1.2x10^{5}$	$1.1x10^{7}$	0.38
Active ingredient (g cm^{-2})	$5x10^{-6}$	$5x10^{-6}$	$5x10^{-6}$
Carrier application rate (ha^{-1})	100 litre water	100 litre water	5kg
Carrier particle size (μm)	200	200	500
Carrier particles (ha^{-1})	$2.4x10^{10}$	$2.4x10^{10}$	$3.8x10^{7}$
Carrier particles - av. distance between (cm)	0.06	0.06	1.7
Content of each carrier particle	ca. 500 powder particles	ca.10000 emulsion drops	1 granule

* All systems are assumed monodispersed, and the application surface to be smooth

It is also obvious that, from the vast number of the dispersed particles that are distributed as point sources, the toxicant will be released from such formulations almost instantaneously and will then be subject to the environmental influences of the atmosphere above, and the soil below, the applied layer. Gückel _et al_ (1974) measured the evaporation of deposits from e.c. and w.p. formulations of gamma-HCH, diallate and endosulfan from glass plates; the rate of loss was similar for the two formulations and to the pure toxicant, suggesting that spray formulations do release their toxicant almost immediately and that it is most unlikely that differences in performance will be noticeable when different spray formulations are applied to the soil surface under practical conditions.

Although the release of the toxicant on to the soil surface will be very rapid, equilibration of the released toxicant with the surrounding environment will be slower. Diffusion of the compound will commence upwards into the atmosphere (volatilisation), downwards in the soil air and downwards in the soil water. If precipitation occurs there will also be movement downwards in the water phase due to bulk flow. The situation is illustrated in Figure 1.

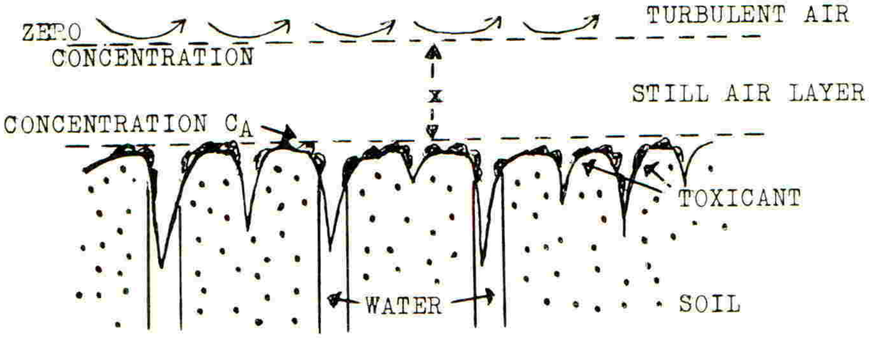

Fig. 1. Spray deposit on soil surface

Volatilisation

Since the applied toxicant is spread fairly uniformly over the surface and is effectively released from the formulation almost immediately, the initial concentration at the soil surface (see Fig. 1) C_A = SVC. If we assume that atmospheric turbulence will reduce the concentration to zero at a distance x above the surface, then the system can be treated by analysis of diffusion across a layer with constant concentration at each surface (Crank 1975) which shows that, at a given temperature and at a steady state:

$$M_A = \frac{D_A . SVC . t}{x} + \frac{x . SVC}{6}$$

where M_A = total loss of compound due to volatilisation (g cm^{-2})
D_A = diffusion coefficient for the compound in air ($cm^2 s^{-1}$)
x = depth of the still air layer (cm)
SVC = saturated vapour concentration of compound (g ml^{-1})

For most organic molecules, the value of D_A at 20°C lies between 0.04 and 0.1 $cm^2 s^{-1}$ and a value of 0.07 provides a reasonable approximation for most pesticides in air (Hartley & Graham-Bryce 1980).

If it is assumed that x = 0.2 cm the steady state will be established within 1 second and this equation then predicts the potential evaporative losses for a few typical pesticides given in Table 2. These losses represent the maximum that can occur from a plane surface of pure compound. In practice, roughness of the surface, the actual thickness of the still air layer and some degree of non-uniformity of the deposit will all affect volatilisation but to a limited degree. The extent of loss will also vary with temperature, approximately ±5% for every 1°C change.

TABLE 2

Potential losses of pesticide through volatilisation from 1 ha of plane surface at 20°C

Compound	Vapour pressure (Pa)	SVC* ($g\ ml^{-1}$)	Loss in 1 hour
Naled	2.7×10^{-1}	4×10^{-8}	5kg
Diallate	1.2×10^{-1}	1.3×10^{-8}	1.6kg
Dichlobenil	3.8×10^{-2}	2.7×10^{-9}	340g
Diazinon	1.9×10^{-2}	2.3×10^{-9}	290g
Triallate	1.4×10^{-2}	1.8×10^{-9}	220g
Trifluralin	7.3×10^{-3}	9.9×10^{-10}	125g
Ethalfluralin	5.6×10^{-3}	7.6×10^{-10}	96g
Parathion	7.8×10^{-4}	9.4×10^{-11}	12g
Ametryne	5.1×10^{-5}	4.7×10^{-12}	0.6g
Simazine	8.3×10^{-7}	7.1×10^{-14}	8.9mg

* Figures taken from Hartley & Graham-Bryce (1980)

Gückel et al (1982) measured the evaporation of uniform deposits of several pesticides from glass surfaces and developed an equation relating volatility with vapour pressure. Their figures are very similar to those calculated in Table 2 and the differences are due probably to the particular conditions of their measurements.

Diffusion into the soil air will be equally rapid initially but will be limited by the relatively small volume of air available within the soil and by the rate of establishment of equilibrium in the partitions at the air/water and at the air/solids boundaries. Diffusion into the soil water will be governed by the rate of dissolution of the compound in the available soil water, by the rate of diffusion through the water phase (which is some 10000x slower than through air) and by the establishment of adsorption equilibrium between the soil water solution and the solids phase. A crucial aspect here is the amount of water present at the surface of the soil at the time of spraying. The water provided in the spray itself is not likely to be significant; 100 litre ha^{-1} would evaporate completely from a moist soil surface within 5 minutes on a typical summer day in the UK, though at high r.h. it may take a little longer.

The real imponderable is the extent to which a spray application does indeed provide a surface layer of essentially pure toxicant and how rapidly any such surface excess can be absorbed and adsorbed into the bulk of the soil, i.e. what is the value of C_A after application and how does it vary with time?

There is little published work that helps; many papers reporting on the persistence of spray deposits give 'zero time' figures measured an hour or so after spraying which are of little value in assessing initial losses after spraying. In applications of insecticides to foliage, Ritcey et al (1981) measured deposits one hour after spraying and looked for correlations between the measured deposit and the vapour pressure of the insecticide. Very little naled or dichlorvos (SVC at $20^oC = 1.4 \times 10^{-7}g\ ml^{-1}$) was detected as a spray deposit; increasing initial deposits were found with decreasing vapour pressure up to parathion, beyond which deposits appeared fairly constant. Until more direct evidence becomes available, one must anticipate that losses of spray deposits from soil surfaces may be considerable with toxicants having an SVC greater than 10^{-10}.

As the remaining toxicant diffuses, or is leached, into the soil and is then adsorbed on to the soil solids, the amount of 'free' toxicant on the soil surface that is available for volatilisation will decrease to a relatively low level controlled by the 'steady state' conditions of the partition equilibria between soil air, water and solids. These are the conditions normally used in studying volatilisation from soil surfaces (see e.g. Hance et al, 1973); there are still significant losses of the more volatile toxicants but these are a function of the soil/toxicant interactions after the toxicant has left the formulation and not, therefore, governed by formulation/application variations.

Leaching

The uniform distribution over the soil surface will facilitate leaching of the toxicant by rainfall. The amount required to leach a surface deposit into the bulk soil depends on the rate of dissolution of the toxicant and the rate at which the rain percolates through the surface layers of the soil; up to 1 cm of rainfall should be ample to leach any toxicant with a solubility greater than 2-3 mg $litre^{-1}$. The easier the leaching, the more concentrated the initial band of toxicant entering the soil will be; inturn this will increase the rate of degradation of the toxicant by any chemical or microbial mechanism that is concentration dependent. Thus spray formulations should provide a rapid action, particularly after rain, but decay of the toxicant may be noticeably faster following a spray application than following other types of application that provide a less uniform deposit and a less immediate release of toxicant.

Photochemical breakdown

A deposit spread uniformly over the soil surface will be subject to photochemical breakdown. The importance of photochemical decay, as with volatilisation, will be critically dependent on the length of time the deposit remains on the soil surface. Penetration of the surface will protect the compound from direct sunlight, dissolution in surface water will not provide any protection and it is uncertain whether adsorption to exposed solid surfaces would provide any degree of stabilisation or not.

There is little hard evidence on the importance of photochemical breakdown on soil surfaces. Klehr *et al* (1983) sprayed thidiazuron at 150g ha^{-1} on to the surface of soil, and, at a temperature of ~30°C and using 3x the energy in natural sunlight, approximately 60% of the applied dose was photolysed in 2 hours and 20% was lost through other processes. The remaining 20% showed no further loss and was assumed to have moved into deeper soil layers. Burkhard & Guth (1979) examined methidathion, diazinon and profenofos. At 45°C, using 2x the energy of natural sunlight and a concentration of $10\mu g\ g^{-1}$ in moist soil, approximately 54% of diazinon, 22% of profenofos and 18% of methidathion was lost in 24 hours. In dry soil the losses were somewhat less, the differences being attributed to differences in adsorption on the soil solids.

The information is too sparse to draw firm conclusions but it appears that photochemical breakdown can cause significant losses of surface spray deposits on soil.

Granular formulations

The behaviour of conventional granular formulations can be affected by their method of manufacture. They are usually prepared in one of three ways: spray impregnation, agglomeration, or by surface coating.

Spray impregnation

A solution of the toxicant or, if liquid, the toxicant itself is sprayed on to pre-formed adsorptive granule cores.

This process has its limitations. The toxicant content of the formulation is limited by the concentration of the toxicant in the spray solution and by the amount of liquid that can be absorbed by the granules before they become sticky (though dusting with a sorptive dust will reduce this problem). The granular carrier must be chemically compatible with the toxicant to ensure a good storage life and these two requirements frequently conflict since highly sorptive clays are often highly reactive to pesticides and catalyse their breakdown. The sorptive nature of the granule base will affect the extent to which the toxicant solution penetrates the granule and initially, the concentration of toxicant is likely to decrease from the outside to the centre of the granule.

A good granule base should be hard and tough so that attrition of the granules during application is minimal.

Agglomeration techniques

The toxicant and a powdered filler, together with suitable binding agents, are moistened with water or other suitable liquid and the resulting dough is formed into granules and dried.

This method is more versatile than spray impregnation since the formulator has a wider choice of ingredients. High toxicant contents are possible, a filler base can be selected that is chemically compatible with the toxicant and variation of the binding agent can provide some modification of the rate at which the roxicant is released (Furmidge *et al* 1968). Initially the concentration of toxicant should be uniform throughout each granule.

Good binding agents will provide tough granules but, since they are prepared from powdered ingredients, attrition during handling and application is a potential problem in poor application equipment.

Surface coating

An impermeable granular base is used, such as sand, and the toxicant is applied as a viscous slurry to the outside of the particles. The formulation is then dried or dusted with a sorptive clay to ensure the granules are free-flowing.

This method is relatively cheap but not very versatile. The toxicant content is limited by the thickness of the layer than can be stuck to the outside of the granule core and the total toxicant is initially exposed on the surface of the granule. The granule core is not subject to attrition during application, but the surface covering of toxicant may be readily removed as dust; this may present a greater hazard in use than attrition of other types of granule.

Other methods of production, such as encapsulation and dissolution or dispersion in polymeric matrices can be used but such refinements are normally reserved for the building of specific control mechanisms in the release of the toxicant and will be considered later.

Application

The efficient and uniform distribution of a granular product is mechanically a more difficult job than distributing a liquid in the form of a spray. The problems involved were reviewed by Nation (1972). Many machines are available on the market; the best of these are very good but there are many types of applicator that cause serious attrition of the granules in the machine and produce a poor distribution pattern.

Data for an idealised, broadcast application of a granular formulation are compared with the spray data in Table 1. The major differences between the two systems lie in the less-uniform initial distribution of the granular application and the fact that the toxicant has to be released from the granule before it can show biological activity.

To be released, the toxicant must diffuse to the surface from where it can volatilise or be dissolved in the soil water, or it may be leached by rain percolating through the granule, particularly with agglomerated granules. The situation is more complicated than the spray situation and is illustrated in Fig. 2. Apart from the non-uniform distribution, the most striking difference in behaviour is the effect that the 'topography' of the soil surface is likely to have on the initial behaviour of the granules. The tendency will be for granules to lodge in crevices in the soil surface where they may be surrounded by air, or by water depending on the soil structure and its water content.

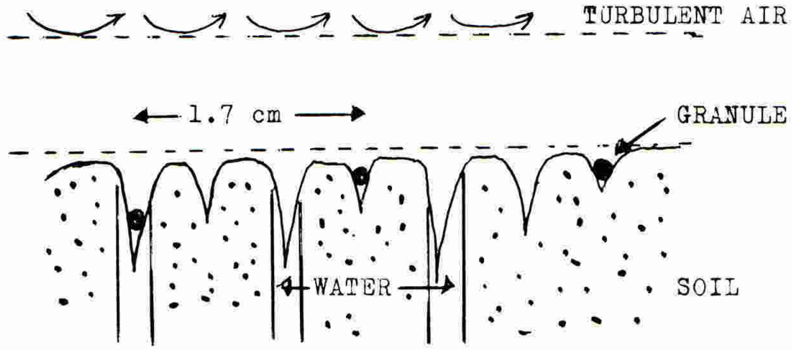

Fig. 2. Granular application (as in Table 1) on soil surface

Volatilisation

The situation illustrated in Fig. 2 is not amenable to any simple diffusion treatment, but some general predictions can be made. Spray coated granules present the simplest case since the toxicant is initially on the surface of the granule. The rate of volatilisation depends on the surface area of the granules, their distance apart and on the thickness of the still air layer. As the concentration of vapour in the still air layer increases, the large uncovered areas of soil surface will act as a 'sink' for solution or adsorption of toxicant vapour. Consequently the value of C_A at the soil surface will not build up to the SVC value as rapidly as in the spray situation. This must reduce the loss of toxicant through evaporation. The toxicant content, size of granules and application rate are all critical factors in this; if the granule size were halved to 250 μm and the toxicant content reduced to, say 2%, the initial rate of volatilisation could again approach the rates given in Table 2. Using agglomerated or spray impregnated granules, volatilisation losses are likely to be slower than for coated granules. An exception to this would be agglomerated granules that disintegrate readily when wetted since the toxicant would then be released very rapidly.

Leaching

Figure 2 shows that a considerable volume of rain can fall on the soil surface without directly impinging on a granule. In addition, with spray impregnated granules and with agglomerated granules containing non-water soluble binders, rain has to penetrate into the granule to leach toxicant out. The combination of these factors means that the rate of leaching of toxicant from granular formulations is always slower than from spray formulations but that it will vary to a considerable extent with the type of granule used and with the number applied - the latter being controlled by the toxicant content and the size range of the granules. Slower leaching will lead to lower concentrations as the toxicant is absorbed within the soil and this, in turn, will tend to reduce rates of chemical and microbial decay. Thus granular formulations will tend to be slower acting than sprays but should provide an increase in the persistence of the toxicant.

The non-uniformity of the treatment might be expected to lead to a non-uniform biological response and, carried to extremes, it must do so. However, it appears that most toxicants are sufficiently mobile within the soil to overcome a considerable degree of non-uniformity. Graham-Bryce _et al_ (1972) examined the activity of phorate and disulfoton granules applied to field beans and found the performance improved with increasing frequency and duration of simulated rain. Addala _et al_ (1984) applied four herbicides, chlortoluron, nitrofen, propyzamide and terbutryne to soil in the field using two types of spray application and as discrete drops from a dribble bar set at 2 cm intervals. No real differences in biological activity were found except with nitrofen which is known to be very strongly sorbed to soil and relatively immobile (Fadayomi & Warren 1977).

Photochemical breakdown

Granular formulations will largely protect photosensitive toxicants from breakdown while the toxicant remains within the formulation. Once released, vapour diffusion will tend to redistribute material across the soil surface where it will be exposed to photolysis but it will also be more available for leaching. Overall, one would expect less photochemical breakdown from granular applications than from sprays, particularly under wet conditions, but there is no evidence in the literature to prove this hypothesis.

Bait formulations

As formulations, baits are similar to granules. They can be made by similar processes, though agglomeration is usually preferred. In action, they differ in that the toxicant has to move from a granule to the target pest whereas with a bait the pest moves to the toxicant. The bait does not have to be distributed as widely as granules and the toxicant should be held in the bait and not released. Their use is obviously limited to mobile pests and they need to be more attractive to the pest than the other natural attractions that surround them. On the other hand, they must not attract beneficial organisms and the bait must be largely waterproof so that the toxicant is not leached out.

They are potentially a very attractive formulation where they can be made to conform to these requirements since they require lower application rates than sprays or granules and they suffer from none of the potential disadvantages outlined for these broadcast applications. Developments in pheromones are likely to increase their use in future but raise the additional problem of controlling the release of the pheromone.

Seed dressings/coatings

Seed dressings have been widely used with contact insecticides and fungicides but their use has increased considerably with the increasing number of systemic pesticides that are available. Not that all systemic compounds are suitable for use as seed dressings; they must possess a reasonable persistence, both in the soil and in the plant, if they are to provide protection during the growing period of the plant. Weed control is one major area of pesticide application that has not been amenable to the use of seed dressings but herbicide safeners applied as seed dressings could prove a very attractive way of using these compounds. Seed dressings provide the ideal 'placement' application, at least in the case of systemic materials, since the toxicant is positioned in the soil exactly where it is of greatest value. Losses due to volatilisation and photodecay immediately after application are minimal.

Application

A major difficulty with seed dressings is in applying a uniform dose to each seed and in ensuring the active ingredient adheres to the seed during handling, storage and drilling. Historically, dry powder dressings were very popular, largely because the pesticides originally used were not soluble in non-phytotoxic solvents. However, adhesion of these dressings to seeds is weak and uniformity of treatments is poor.

Most solid seed dressings can be replaced by liquid formulations prepared either as solutions or, if the toxicant is insufficiently soluble in non-phytotoxic solvents, as suspension concentrates. Spray applications to the seed, followed by removal of surplus liquid, allows more uniform treatment and better adhesion, as shown in a survey of commercial treatments by Lord et al (1971). Of 33 samples treated with powders taken from different seed merchants, only 5 samples showed more than 50% of the target dose on the seed and 12 samples had less than 10%; of 17 samples treated with liquid dressings, 10 had more than 50% and only 1 sample less than 30% of the nominal dose. Even with liquid dressings there were large differences in the dose on individual seeds and there is scope for very considerable improvement; much closer collaboration is required between the companies producing seed dressings and application equipment manufacturers.

Performance

The biological performance might be expected to depend on the degree of adhesion between toxicant and seed, and therefore to vary with the formulation. There is little evidence of this in the literature but the lack of uniformity in most practical seed dressings could provide variations in performance that swamp any formulation effects. Graham-Bryce et al (1980) applied various fungicides as w.p. and as powdered technical material with a sticker to barley seed; no obvious differences in performance were observed in field trials. Collier <u>et al</u> (1979), using a formulation of ethirimol in methanol, noted some penetration of the toxicant into the embryo of the seed either during treatment or immediately after application. If this effect could be promoted without causing phytotoxicity, losses of toxicant into the soil could be reduced and efficiency still further improved. A full review of seed dressings, their application and performance is given by Jeffs (1978).

Seed coating or pelleting is a more elaborate treatment in which successive layers of adhesive and nutrients, or toxicants, are sprayed on to seeds and dried. It makes possible much higher loadings of material than conventional dressings and would be of considerable value where mixtures of toxicants are required or where control of release is desired. Their use has been limited by cost but, as better techniques are developed, these systems will warrant attention.

Controlled release formulations

A considerable amount of attention has been given to controlled release formulations over the last few years; the present position regarding their commercial use has been reviewed by Wilkins (1983). Despite this interest, very few controlled release products have been developed commercially for use in soil.

There are many definitions of controlled release and its role in crop protection but it is usually understood to imply an extension to the persistence of a toxicant so that less can be applied to give the same performance as a conventional product, or that a longer period of biological control can be achieved with equivalent application rates. However, as McFarlane (1976) points out, control over persistence alone is not sufficient for improved performance; the available toxicant needs to be matched to the pest infestation and life cycle in space and in time. This requires a considerable knowledge of the pest dynamics which is not always available. It also implies a wide range of product specifications to meet specific crop/country/pest requirements and if these specific requirements can be met then the control of secondary pests (which may be taken for granted when using more conventional applications) may not be achieved. More specific products also increase the time and effort required on development, increase registration costs, and are often more expensive than conventional formulations and require more skilled advice in their use. With all these potential limitations it is not, perhaps, surprising that few commercial products have yet appeared.

The situation is rendered more difficult in soil applications since the soil itself, through its sorption, diffusion and leaching characteristics, acts as a huge 'controlled release' system. The rate at which a toxicant, once released from its controlled formulation, becomes available to a target organism is governed by the composition and structure of the soil, by temperature and by rainfall; all factors beyond the control of those who design or apply the formulation. Nevertheless, there are some controlled release products available, or under development, for soil application and the basic technology is becoming well established to provide many possibilities for the future.

Microencapsulation is a technique that has received a lot of attention; such products can be sprayed as suspensions of individual microcapsules or agglomerated into granules, baits or coating materials. Release is either by diffusion through the capsule wall (for theory, see McFarlane & Pedley, 1978) or by degradation of the capsule wall. The processes used for production are described by Scher (1977). The technique has been developed by Stauffer for formulating fonofos as a soil insecticide to control its loss by volatility and to render it safer to handle. Phillips et al (1976) have examined microencapsulated pyrethroids to delay their rapid action in bait formulations for leaf-cutting ants.

A simpler type of controlled release formulation can be prepared by dissolving, or dispersing, the toxicant in a polymeric matrix. This type of product has been developed mainly as granules though it could be used for coating materials on conventional granules or on seeds (providing germination was not affected). Lignin has been used as the polymeric base to overcome the high volatility of ethoprofos nematicide (Dellicolli, 1977) and to develop long-persistence 2,4-D granules and carbofuran granules (Wilkins et al, 1984). Starch xanthide matrices have been reported to reduce the volatilisation of butylate from soil surfaces and a number of soil insecticides and fungicides formulated in polymer granules are being tested in Australia (McGuffog & Anderson, 1983).

Some of the most successful commercial applications of controlled release have been in the use of attractant pheromones in cotton, orchard and forestry pest control (Plimmer, 1983). Suitable pheromones are not available, as yet, for soil insects but, if they can be developed and combined with suitable toxicants such as pyrethroids, they could provide effective bait formulations or traps for soil insect control.

CONCLUSIONS

The behaviour of soil-applied pesticides is dominated by the interactions between the active material and the soil itself. The effects that application/formulation have on behaviour are limited to controlling the initial distribution and modifying release of the active compound into the soil. Prediction of the importance of these effects is difficult since they depend on the rate at which the active material is released from the formulation, which, in the case of conventional formulations, is largely uncontrolled, and on the rate at which the released material reaches the steady state conditions imposed by the soil/pesticide interactions. This latter rate is controlled by the rate at which the pesticide can achieve an equilibrium partition between soil air, water and solids which is itself governed by the initial distribution in, or on, the soil and by the soil composition and structure, and climatic factors such as rainfall and temperature. Once the pesticide has reached this steady state, its behaviour, though complex, is more amenable to prediction. In a situation containing so many unknowns, any statements on behaviour must be considered as opinions, rather than as facts, and generalisations must be subject to many exceptions depending on specific environmental situations.

With conventional spray formulations, the type of formulation (solution, e.c., w.p., s.c., or w.g.) is unlikely to have any noticeable effect on field performance. The toxicant will be released from such formulations very rapidly and, when applied uniformly to the soil surface, these formulations may give rise to high losses through volatilisation and through photochemical breakdown. They represent the least desirable formulation/application system except where rapid action is required and when using relatively involatile and chemically stable toxicants that are not particularly mobile in soil. However, spray applications are relatively cheap and convenient and most of the potential disadvantages can be removed by incorporation of the spray deposit into the soil; this incorporation should be immediate and not delayed.

Conventional granular formulations applied broadcast to the soil surface minimise the losses that would be incurred with a spray application of the same material. The degree of improvement shown will be affected by the formulation of the granule and by the way it is produced, by agglomeration, by spray impregnation or by coating. The initial activity of such formulations will be slower than with sprays, particularly under dry conditions, and the initial distribution of toxicant will be less uniform. These may prove to be important limitations with highly immobile toxicants, or when using systemic toxicants under dry conditions in crops having a limited root development. They tend to be more expensive than spray formulations and more care is needed in selecting the appropriate equipment that will provide as uniform a distribution as possible without causing undue attrition of the granules, particularly important when using agglomerated or coated granules.

Directed applications, e.g. in-furrow treatments during drilling, are by far the best means of using both spray and granular products unless uniform treatment of the whole soil is essential.

Seed treatments are the most efficient and desirable means of applying pesticides in soil. Powder seed dressings suffer from poor adhesion to the seed but these can be replaced by liquid seed dressings which, with further refinements in equipment used for applying them to seed, should result in uniform, consistent treatments combining good performance with economy and safety in use. Developments in seed coating techniques and controlled release will further improve the flexibility of seed treatments and should enable them to be used to a wider extent than hitherto. Greater collaboration is required between chemical manufacturers, equipment manufacturers and seed merchants to exploit this type of application to the full.

Controlled release formulations for use in soil are beginning to appear, particularly as granular products. The technology is developing to a stage where considerable control can be exercised over the chemical but this is not always matched by an equivalent understanding of the best way to use this 'controlled' chemical to control the pest. This, coupled with the fact that the environment in which the product is used is uncontrolled, and frequently ill-defined, and the increased costs of developing such products in specific (and therefore relatively small) outlets means the introduction of such products will continue to be fairly slow. However, it is possible that new compounds will be developed on the assumption that they will be used in controlled release formulations; plant growth regulators and herbicide safeners to be used as seed treatments or as in-row placement treatments of granules, and pheromones to be used in bait formulations, are all possibilities in this respect.

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RELATIONSHIPS BETWEEN SOIL CULTIVATION AND PESTICIDE PERFORMANCE

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ABSTRACT

Some of the interactions between cultivation systems, soil conditions, plant growth and pesticide performance are reviewed. It is concluded that at the moment only minor effects on pesticide performance can be attributed directly or indirectly to the effects of cultivation system on the gross properties of the soil although this is based on very little published information. Local effects close to the soil surface, particularly those concerned with adsorption seem to be of more significance. There is good evidence that the adsorptive capacity of the surface soil increases when the soil is not ploughed, particularly in cereal growing systems where the straw residue is burnt. Under these circumstances soil organic carbon content is not a good guide to adsorption characteristics. A simple test for adsorption, using the dyestuff methylene violet (Bernsthen), is described which could be developed for use in the field.

INTRODUCTION

The cultivation, or lack of it, given to a field affects a variety of soil properties several of which might be expected to influence pesticide activity directly or indirectly. In practice the only pesticides whose performance has been noticeably affected in the UK, are the substituted urea herbicides used for the control of grass weeds in winter cereals. In considering reasons for this it might be useful to review the processes that could be modified by the method of cultivation and which are relevant to pesticide performance. For this purpose it is perhaps sufficient to consider just two systems of soil management, direct drilling and mouldboard ploughing (together with the subsequent operations needed to produce a seed bed) as these represent the extremes of the range of possibilities.

CULTIVATION, SOIL CONDITIONS AND PLANT GROWTH

In general it appears that after a period of direct drilling the surface soil is more friable, the soil is more compact with lower porosity and the earthworm population is higher than when the soil is ploughed and cultivated (Allen, 1981). However, although ploughing increases soil porosity there is better continuity of pores in direct drilled land so that roots and water usually can penetrate more easily to the lower layers of the soil. At the same time the changes in structure at the surface, accompanied by increased organic matter levels which result from direct drilling, frequently lead to increased water retention in the upper layers (Van Ouwerkerke & Boone, 1970). These effects of cultivation on water movement will undoubtedly affect pesticide redistribution in the soil and, as Allen (1981) noted, often influence root-distribution as well. Therefore differences in pesticide uptake by plants might be expected. This has indeed been reported by Parrish et al. (1983) who found that 0.56 kg/ha of metribuzin caused damage to spring wheat in a no tillage system with a high surface plant residue but not in a conventional system. The degree of injury was correlated with the moisture content of the surface soil. In a pot experiment they showed that mulching increased the metribuzin concentration 5 cm below the surface by 80%.

CULTIVATION AND PESTICIDE BEHAVIOUR

Surface structure and trash residues

If crop residues are left on the soil surface then clearly they will intercept a fraction of any pesticide application intended for the soil. The variability involved makes measurement difficult but the observations of Addy (1982) and Bauman & Ross (1983) suggest that some 20-30% of an application may not reach the soil initially although Ghadvi et al. (1984) put the figure somewhat higher at around 60%. Even so, Erbach & Lovely (1975) found that about 6 tonnes of maize trash per hectare did not affect the performance of recommended rates of atrazine and alachlor. The practice of stubble burning of course circumvents any difficulties that may result from spray interception but may introduce another problem which is discussed later.

The condition of the surface soil is likely to affect the agronomic if not the phytotoxicological performance of herbicides. Roberts and Hewson (1971) studied the performance of two herbicides in seedbeds of different degrees of fineness obtained by cultivation and Roberts et al. (1981) examined the effect of the soil conditioner cellulose xanthate on the weed control given by a range of soil applied compounds. In both cases the number of weeds germinating was dependent upon seedbed conditions but the fraction killed by any particular herbicide was about the same regardless of seedbed. Thus with a highly effective compound the number of weeds which germinate will be relatively unimportant but if the weed population possesses some tolerance then the number of survivors will be closely related to the number germinating. Hence the cultivation regime may affect herbicide performance as measured by the number of surviving weeds. Whether direct drilling or ploughing provides the best germinating conditions depends upon the weed. For example broad leaved annuals seem to be more abundant on ploughed land whereas Alopecurus myosuroides and Poa spp. are favoured by direct drilling (Cussans, 1975). Perennial weeds are also encouraged by direct drilling but since they are normally controlled with foliar applied herbicides this is a consideration outside the scope of this paper.

Pest and disease incidence is also affected qualitatively and quantitatively by cultivation system (Allen, 1981, Akobundu, 1982, Ungar & McCalla, 1980), but evidence for effects on insecticide, fungicide or nematicide activity seems to be lacking. Presumably seed dressings, which account for a substantial part of the non-herbicide soil-applied sector, are not much affected by soil tilth, but compounds with appreciable vapour-phase activity might be sensitive to changes in the distribution and quantity of air spaces.

Effects on persistence

The improved surface structure resulting from direct drilling is a consequence of the higher organic matter levels and greater aggregate stability which have been reported from many parts of the world (see reviews by Allen, 1981, Ungar & McCalla, 1980, Phillips & Young, 1973). These changes in turn represent evidence for increased microbial activity. On the assumption that pesticide degradation rates in the soil are at least to some extent dependent upon overall microbiological performance, then differences in persistence related to cultivation might be anticipated. However, the higher organic levels also imply greater adsorption, an effect that could be increased by the presence of carbon residues if the trash of the previous crop was burnt, and so reduced availability could counteract the microbiological potential for enhanced degradation. There is little direct evidence concerning these possibilities specific to the effect of cultivation system. Experiments with soils of different organic matter levels or with soils amended to change adsorptive characteristics or microbial activity have been reviewed by Hurle & Walker (1980). Their conclusions that "results are conflicting and it is clear that adsorption does not always protect a chemical from degradation, nor does it always lead to increased rates of loss" and "... no general conclusions can be made. In order to understand the results .... we require information on the specific involvement of microorganisms in degradation of particular compounds" do not give much hope of predicting general differences between cultivation systems.

Hurle (1982) found in a laboratory study that DNOC and atrazine degradation rates were reduced in soil amended with straw ash and that for atrazine there was a linear relationship between the Freundlich adsorption constants of the amended soil samples and herbicide half life.

In our laboratory we have measured the rates of degradation of chlortoluron in soil from adjacent plots of a site at Compton Beauchamp where winter wheat had been grown for 6 years using either ploughing or direct drilling. During this period straw disposal was by burning with both cultivation systems. Samples were taken with a spade from the top 2.5 cm. Some characteristics of the two soils are given in Table 1.

TABLE 1

Soil properties

	Ploughed	Direct Drilled
Sand %	2.2	2.2
Silt %	39.7	39.7
Clay %	58.1	58.1
Organic C %	3.9	4.6
Water holding capacity %	45.5	46.8
pH	6.3	5.4
Water soluble carbon %	0.017	0.016
Freundlich K (chlortoluron)	5.8	17.1

Samples were treated with chlortoluron at a rate of 10 µg/g, made up to one of 4 water contents and incubated at various temperatures. Chlortoluron was determined at intervals up to 84 days and half lives calculated assuming that first order kinetics were followed. The results are shown in Table 2.

TABLE 2

Persistence of chlortoluron incubated with soil that had been ploughed or direct drilled.

Treatment		Ploughed		Direct Drilled	
Water content (% of WHC)	Temperature($^{\circ}$C)	Half life (days)	r	Half life (days)	r
90	10	28.8 (0.5)	0.99	30.7 (0.9)	0.99
90	30	24.2 (1.0)	0.99	25.7 (1.5)	0.94
90	20	24.7 (1.0)	1.0	27.8 (1.7)	0.98
60	20	25.7 (1.2)	0.99	26.5 (1.2)	0.97
40	20	24.1 (2.1)	0.97	26.6 (0.4)	0.97
20	20	28.7 (2.3)	0.97	30.1 (0.7)	0.97

Figures in parenthesis are standard deviations.
r is the correlation coefficient of log chlortoluron concentration with time.

These figures show no differences that can be ascribed to the cultivation history of the soil nor to its adsorption capacity for chlortoluron and thus are not consistent with Hurle's observations with atrazine and DNOC. The two sets of results do, however, accord with those of Moyer et al. (1982) who found that adding charcoal to soil increased the adsorption of both atrazine and linuron but atrazine degradation was slowed while that of linuron was not.

However, all these results were obtained in the laboratory so must be treated with caution. In particular, differences in compaction and water infiltration rate will have been eliminated by the treatments needed to homogenise the soil samples. In addition, under field conditions, the water contents will probably be different and there may be some differences in soil temperature due to the insulating effect of unburnt trash on the surface of direct drilled soil and the difference in albedo resulting from the carbon and ash layer at the surface which will caused unploughed land to be darker than ploughed. Finally, the constraints and manipulations necessary in laboratory experiments are likely to diminish any differences in the activity and composition of the soil microflora.

Published field evidence for the effect of cultivation on pesticide persistence is limited. Burnside and Wicks (1980) concluded that atrazine carryover in a reduced tillage system in Nebraska was less than in systems conventional to the region but they did not have directly comparable plots and they used an oat bioassay procedure which could have been affected by changes in adsorption. Bauman & Ross (1983) found that atrazine was less persistent after one year following coulter cultivation (that is the 2.5 cm coulter on a maize planter) than chisel or mouldboard ploughing, but in a longer study, the herbicide residue was highest in the coulter system after 5 annual applications. Otherwise there seems only advisory experience, which suggests that crops sown after minimum or no-tillage are most at risk from residue damage (Eagle, 1981), although here we may be dealing with a dilution rather than a persistence effect.

Thus the gross effects on the soil of cultivation system discussed so far either have small or ambiguous effects on pesticide performance or, more frequently, have not been investigated seriously. What remains are local effects close to the soil surface, in particular those concerned with adsorption. It is a consideration of these that will occupy most of the rest of this paper.

Cultivation and soil adsorption characteristics

It is often accepted that adsorption of non-ionic organic molecules by soil is closely correlated with soil organic matter content. Many workers following Furmidge & Osgerby (1967), Lambert (1967) have therefore expressed adsorption distribution constants in terms of weight of organic matter (K_{oc}) rather than weight of soil. The variability from soil to soil is much less than for constants calculated on a total soil basis and the concept has been particularly valuable in deriving general relationships. For example Kenaga & Goring (1979) aand Briggs (1981) have used it in connection with other partition properties and chemical structure to give a preliminary assessment of the environmental behaviour of a compound. Similarly, Sabljic & Protic (1982) have shown that molecular connectivity indices, which are calculated from the number and types of atoms and bonds and their adjacent environment, can be used to predict adsorption of a compound by soil if the organic carbon content is known. On a different theoretical plane, Wauchope & Koskinen (1983) developed a thermodynamic interpretation of adsorption based on a standard state which assumed that soil organic matter forms a standard solution with the herbicide.

These examples, however, are general approaches and the relationship between adsorption and soil organic matter is less useful in specific circumstances. As Calvet (1980) points out, the correlation is high only when the range of organic matter content is large; over the range 0-4% which covers many temperate agricultural soils it may be low and it is different for ureas and triazines. Table 3 illustrates the point.

TABLE 3

Relations between the Freundlich adsorption constant and soil organic matter content (Calvet, 1980).

	Organic matter < 4%			Full range of organic matter		
	n	regression	r	n	regression	r
Atrazine	23	(1.7)+(0.6) OM%	0.11	29	(8)+(7.4) OM%	0.93
Diuron	17	(3.4)+(2.9) OM%	0.92	27	(0.2)+(4.1) OM%	0.98

n = number of observations

r = correlation coefficient

It is thus not surprising that the adsorption-organic matter relationship becomes more unreliable when applied to the surface of direct-drilled soils where the straw has been burnt so that charcoal is present. The figures in Table 1 demonstrate this, as although the respective organic carbon figures for the ploughed and direct drilled soils are relatively close (3.9% and 4.6% respectively) the Freundlich K values for chlortoluron are 5.8 and 17.1. Cussans *et al*., (1982) provided practical evidence. They collected surface soil samples from 44 fields throughout the UK and subsequently recorded the control of *Alopecurus myosuroides* by either chlortoluron or isoproturon. They found that an adsorption measurement gave better prediction of poor herbicide performance than did soil organic matter content and the relationship between adsorption and carbon content was particularly unreliable with direct drilled fields (Fig. 1). Although these observations did not show that adsorption was the only factor involved when these herbicides performed poorly it was clearly a major influence.

Consequently, Embling *et al*., (1983) studied some of the properties of straw ash and the effects on adsorption of heating soil to temperatures similar to those occurring under a straw burn. Atrazine adsorption was not greatly affected by heat treatment of the soil even at 250°C for 5 minutes. Chlortoluron adsorption was not much changed by preheating a soil containing 1.3% organic matter but in soils containing 8.45 and 43.1% organic matter a 5 minute treatment at 250°C more than doubled the Freundlich K value and even 1 minute at 100°C gave substantial increases.

Burnt straw residues were highly adsorptive of both compounds as shown in Table 4.

TABLE 4

Freundlich constants for chlortoluron and atrazine with straw ash and carbon contents of the ash (Embling *et al*., 1983)

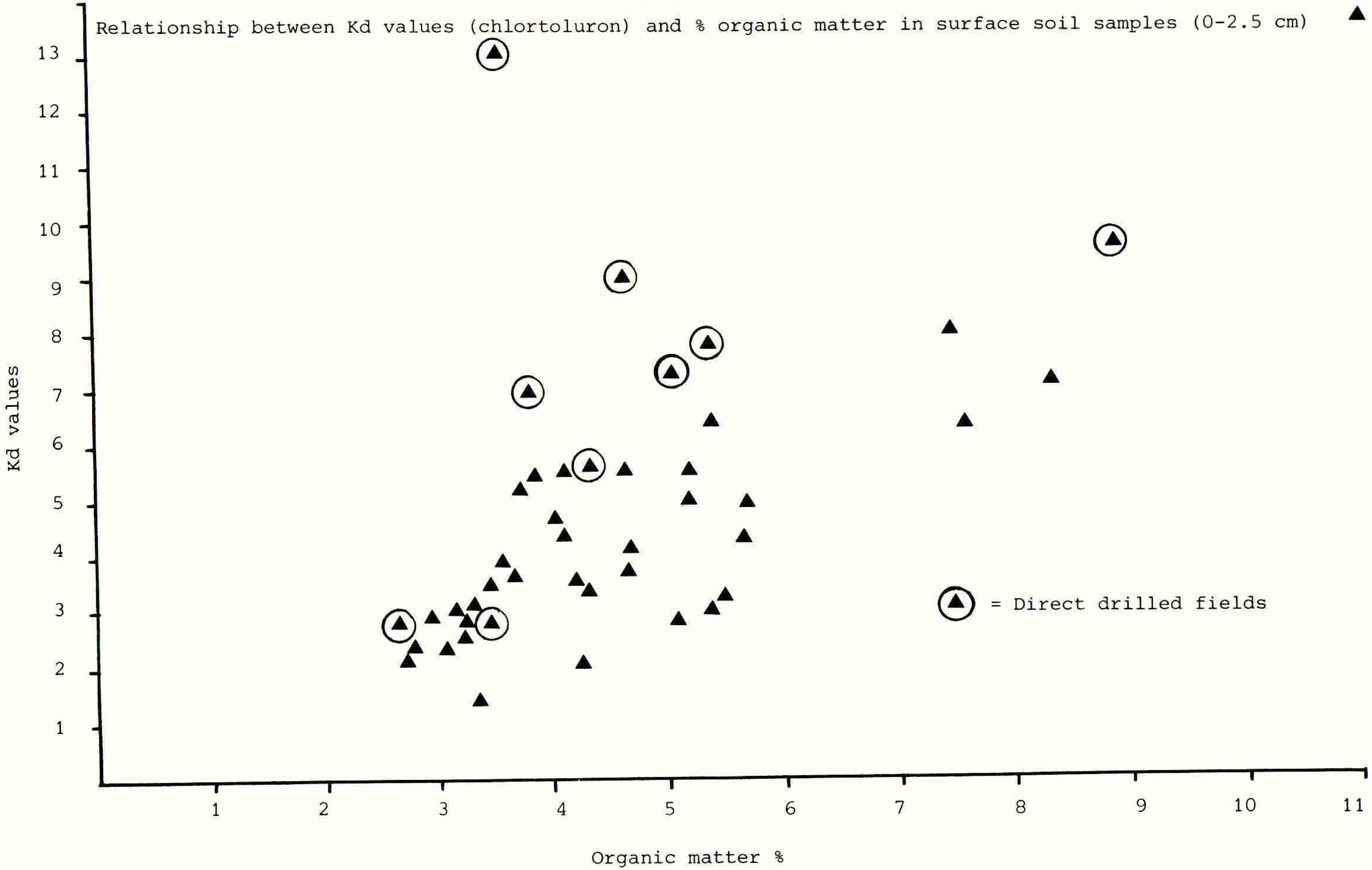
	Heating time (min)							
	1			5				
Temperature (°C)	%C	K	$\frac{1}{n}$	%C	K	$\frac{1}{n}$	K	$\frac{1}{n}$
	Chlortoluron						Atrazine	
Untreated		35	1.05				15.7	0.57
500	55.1	67	0.57	36.1	211	0.42	195	0.55
600	53.3	229	0.40	38.2	258	0.42	223	0.43
700	39.6	700	0.33	22.8	452	0.32	235	0.38

They calculated that a soil containing 10% organic matter, the upper limit for which chlortoluron is recommended by the manufacturer, would have a Freundlich K value of about 7 for chlortoluron. Heating the soil containing 8.45% OM at 109°C for 1 minute raised its K value close to this level. They also calculated that burning 5t/ha of straw might well leave residues that would increase the adsorptive capacity of the surface soil above the level equivalent to the manufacturer's upper limit.

There are, however, a number of restrictions that prevent us drawing simple quantitative conclusions from this work. One is that the observations were made with freshly burnt straw ash but Hurle (1978) showed that the activity of straw ash mixed with soil declined with time and subsequent work at WRO (Cotterill unpublished) confirms this and shows that the initial decline is quite rapid but a steady state, with the adsorption

Fig. 1

Relationship between Kd values (chlortoluron) and % organic matter in surface soil samples (0-2.5 cm)



about 15% of the initial level, is reached after 5-10 days. The results nevertheless do provide support for the idea that direct drilling and straw burning over a number of years could lead to a loss of herbicide performance. It is also worth noting that Lichtenstein et al. (1971) found that the addition of activated carbon to reduce the uptake by plants of residues from heptachlor and aldrin treated soils was effective for the 4 years that their study lasted.

Possible field test of adsorption

The figures in Table 4 show why Cussans et al. (1982) found that organic matter content is an unreliable guide to chlortoluron adsorption, particularly in direct drilled fields, as the adsorptive capacities of the straw ash samples were certainly not correlated with their carbon contents. It is now clear, therefore, that if we wish to identify fields where substituted urea herbicides may be unreliable some sort of adsorption measurement is needed.

It seems likely that if this is to be done both economically and reliably a two stage procedure may be required. The reason lies in the way in which adsorption varies with the solute concentration.

For most practical purposes the adsorption of pesticides by soil can be adequately described by the well known Freundlich relationship which may be written

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log c$$

where x is the quantity of solute adsorbed by a mass m of soil, C is the equilibrium solute concentration and K and n are constants.

If the value of $\frac{1}{n}$ is 1 then the ratio of $\frac{x}{m}$ to C is the same at all values of c. For most pesticide adsorptions the value of $1/n$ lies in the range 0.7 - 1 (Hamaker & Thompson, 1972). Taking the value of $1/n$ to be 0.7 and K to be 10 we find that at C = 1 unit, the value of x/m is 10 but at C = 10, x/m is 50. Thus if we wish to have a reliable estimate of adsorption it is necessary to measure it over a range of concentrations if the value of $1/n$ differs greatly from 1. For this reason the use of K_D value, that is $x/m/C$ measured at one concentration only, is to be discouraged. This is particularly important in the case of soils whose properties have been modified by straw ash since Table 4 shows that the value of $1/n$ for the adsorption of chlortoluron bv straw ash lies in the range 0.32 - 0.57. Taking the value of 0.4 for $1/n$ in the example calculated above we see that a K_D value of 10 where C = 1 would be 2.5 at C = 10 and 40 at C = 0.1.

Thus it would be sensible to do a rough screening observation using at least 2, preferably 3 solute concentrations to classify the soil into one of 3 categories; low adsorption - no likely problems; high adsorption - substituted ureas unlikely to be successful; intermediate adsorption - uncertainty therefore justifying the measurement of a full adsorption isotherm. The screening observation could be made with any solute but if it were carried out in the field it would need to be with a coloured solution so that a visual estimation could be made. Where a full isotherm is necessary it should be carried out with the pesticide of interest.

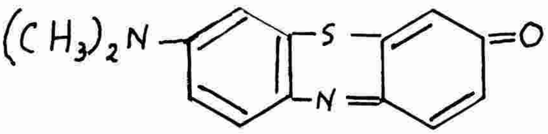
The use of such a procedure will require an initial phase to correlate adsorption measurements with field experience. A start has been made in the work of Cussans et al., (1982) and by ADAS but unfortunately, for reasons of economy and convenience, this work has used only K_D values obtained by shaking 1 g soil with 10 ml of a solution containing 10μg/ml chlortoluron. As discussed above this could produce misleading results.

The second requirement is a suitable colorimetric method so that the preliminary assessment can be made in the field. Unfortunately most dyestuffs are ionic and therefore are not appropriate models for soil-applied pesticides which are usually non-ionic. Nevertheless Hata et al., (1982) reported that piperophos adsorption was highly correlated with the adsorption of Methylene Blue (Colour Index 52015) Acid Rhodamine B (Colour Index 45100) and on soils of low adsorptive capacity, Solar Pure Blue AFX (Alphazurin A, Colour Index 42080) although these are all ionic dyes. They found that Solar Pure Blue AFX gave promise in a prototype field test kit.

Hance et al., (1968) could not find a suitable dye so suggested that dimethylaminobenzaldehyde could be used as a model compound since although it is colourless itself it can be converted to a coloured Schiff base by reaction with primary aromatic amines such as aniline. This gave a satisfactory indication of adsorption in the laboratory but was never developed for field use because they found that differences in weather from place to place overrode differences in herbicide performance that could be ascribed to soil characteristics (at a time when most farmers used traditional methods of soil cultivation). Following the indications given by the work of Cussans et al., (1982) that adsorption could be important in minimum tillage systems, the subject of a field test of adsorption was re-examined at WRO.

For visual assessment of the colour of a solution in comparison with reference colours a blue or green dye is desirable since colours at the red end of the spectrum can easily be confused by the straw coloured solution frequently obtained when soil is extracted with water. Two non-ionic blue dyes were considered, indophenol blue and methylene violet (Bernsthen). The latter was chosen because of the very low solubility of indophenol blue in water although subsequent events showed that to obtain approximately the correct adsorption characteristics, solutions of methylene violet (Bernsthen) must contain 50% ethanol.

Methylene violet (Bernsthen) Colour Index 52041; hereafter termed MV(B) is:



It must not be confused with methylene violet RRA or 3RA (Colour Index 50205) or with methylene violet 3RAX conc (Colour Index 50206) which have quite different structures and, being ionic, are unsuitable for this purpose. MV(B) behaves as a fat-soluble dye and partitions from acid solutions into chloroform or ether.

The use of this dye as a model adsorbent cannot yet be regarded as a reliable and established procedure, but this Symposium is an appropriate place to outline the preliminary findings.

Adsorption isotherms for MV(B) have been obtained in aqueous solution and in 10%, 20% and 50% ethanol. Freundlich constants for these solutions with five soils together with those for aqueous chlortoluron are shown in Table 5.

TABLE 5

Freundlich constants for MV(B) and chlortoluron

	Methylene violet (Bernsthen)								Chlortoluron	
	% ethanol									
	5		10		20		50			
Soil	K	1/n	K	1/n	K	1/n	K	1/n	K	1/n
Deal	189	0.90	207	0.87	126	0.82	8.3	0.92	1.46	1.07
Boddington Barn	132	0.85	118	0.92	67	0.93	6.7	0.80	1.74	1.05
Triangle	978	1.09	948	1.02	532	0.84	44.1	0.99	7.22	0.86
Compton Beauchamp (direct drilled site)	414	1.09	259	1.08	246	0.65	30.5	0.69	10.19	1.03
Fen peat	1230	0.96	1146	1.07	770	0.76	73.4	0.80	15.52	1.10

Thus even in 50% ethanol, MV(B) is adsorbed more than chlortoluron. However, for this purpose it is important to have an easily seen colour change. In addition the correlation between MV(B) and chlortoluron is only 0.93 for the small group of soils.

The ratio of Freundlich K for chlortoluron to Freundlich K for MV(B) in 50% ethanol is 4.7 on average (range 3-6.1). The lower value of 3 will be taken so as to err on the side of safety. The calculation of Embling *et al.*, (1983) mentioned earlier, indicates a Freundlich K value for chlortoluron with a soil containing 10% organic matter to be about 7. Cussans *et al.*, (1982) concluded that values in their k_d test of above 6 were associated with poor control of *A. myosuroides* by chlortoluron. For the purposes of a preliminary field screening test it would be prudent to take a lower figure, perhaps 5, so that the MV(B) K value above which chlortoluron performance is likely to be poor would be about 15.

A suitable procedure for use in the field might be as follows:-

1) Take 5 ml samples of surface soil (assumes a bulk density of about 1) into screw-capped cylindrical bottles.
2) Add 50 ml of 50% ethanolic solutions containing 5 μg/ml and 15 μg/ml of MV(B).
3) Shake 1 min and allow soil to settle.
4) Compare the colour of the supernatant liquid with that of respectively 2 μg/ml and 6 μg/ml standard solutions of MV(B) held in similar bottles. These are equal to the concentration that would remain

if the K value of the soil were 15.

5) If the colours of both the supernatant solutions are darker than the corresponding reference solutions then the adsorptive capacity of the soil is likely to be acceptable as far as chlortoluron performance is concerned. If the colour of either solution is lighter, then soil samples should be taken back to the laboratory for direct measurement of its adsorption isotherm for chlortoluron.

Two stages remain in the development of this procedure: The first is to establish that it is possible for operators to make the visual assessment reliably. This process is underway currently. The second will be to show that this simple procedure gives a useful indication in practice of soils where herbicide performance may be uncertain. This will involve verification that adsorption is of critical importance, that the somewhat arbitrary choice of the limiting adsorption value is suitable and that adsorption of MV(B) is reasonably well correlated with that of herbicides of interest.

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THE INFLUENCE OF CULTURAL PRACTICES ON THE ACTIVITY OF SOIL-ACTING HERBICIDES

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ABSTRACT

Annual grass weed infestations in winter cereal crops tend to be more severe when minimum cultivation systems are used. Therefore better weed control is required than in a system based on ploughing. Unfortunately, soil-acting herbicides tend to be less effective in conditions associated with minimum cultivations. The main reason for this seems to be adsorption of herbicides onto burnt straw residues which are concentrated in the surface soil. Other factors such as pH and soil nutrient distribution may also be partially responsible. It is suggested that where such problems occur, it is better either to use foliar acting herbicides or to plough once every 4 or 5 years to prevent a build-up of adsorptive surface soil.

BACKGROUND

Annual grass weeds, such as *Alopecurus myosuroides* (black-grass) and *Bromus sterilis* (sterile brome) are greatly encouraged by minimum cultivation systems of growing winter cereals (Froud Williams, 1983; Moss, 1979,1981; Pollard *et al*., 1982). This is mainly because such systems retain weed seeds close to the soil surface from where seedlings can readily emerge. In contrast, ploughing tends to bury seeds to a depth from which emergence is unlikely. Therefore, because minimum cultivations encourage weeds in this way, it follows that better weed control is required from herbicides than in a conventional ploughing system. A population model for *A. myosuroides* has been developed (Cussans & Moss, 1982) from which it is possible to determine the % weed control required to maintain a static weed population (Table 1).

TABLE 1

The annual percentage kill by herbicides needed to maintain a static population of *A. myosuroides*
(from Cussans & Moss, 1982)

	STRAW BURNT	NOT BURNT
PLOUGHED	50	65
DIRECT DRILLED	88	92

Unfortunately, although there is a requirement for better weed control in minimum cultivation systems, there is increasing evidence that some herbicides may be less effective in such situations which can result in inadequate weed control and rapid weed build-up.

RESULTS FROM CULTIVATION EXPERIMENTS

Results from several field experiments (Moss, 1979,1984) showed that all the soil-acting herbicides studied were less effective on plots direct drilled for a number of years than on ploughed land (Table 2).

Diclofop-methyl, applied at 1.13 kg a.i./ha early post emergence, was the only herbicide to give a good (>95%) level of weed control on direct drilled land. Although diclofop-methyl is partially active through the soil, (Kocher, 1981), foliar uptake is of more importance with post-emergence applications (Schluter & Duke, 1979). Foliar acting herbicides have obvious advantages where soil conditions impair the performance of soil acting herbicides. There may be scope for reformulation or the use of additive to increase the foliar activity of those herbicides that are partly soil and partly foliar acting (Ayres, pers. comm.). However, increasing the foliar activity may increase damage to the crop as well as to the weed.

TABLE 2

The effect of cultivation on herbicide performance
(from Moss, 1984)

% reduction of the numbers of *A. myosuroides* heads		PLOUGH	DIRECT DRILL
Pendimethalin	pre-emergence	100	72
Terbutryne	"	96	71
Trifluralin + linuron	"	89	42
Triallate granules	"	86	42
Chlortoluron	post-emergence	97	53
Isoproturon	"	99	72
Metoxuron	"	93	73
Propyzamide	"	96	78
Carbetamide	"	80	49
Diclofop-methyl	"	97	96
Kd (chlortoluron)	surface soil	3.7	14.4
% organic matter	"	3.0	5.1
pH	"	7.4	7.0
Phosphorus (ppm)	"	10	76
Potassium (ppm)	"	257	716

WHY DOES CULTIVATION SYSTEM INFLUENCE HERBICIDE PERFORMANCE?

Cultivations can influence many soil properties that may affect herbicide performance. Physical factors such as cloddiness of seedbed or surface straw may prevent uniform herbicide distribution and result in inadequate weed control. Other changes are more complex. Three factors that can be influenced by cultivation system, and which can affect herbicide performance are adsorption, pH, and nutrient distribution (Table 2).

Adsorption

It is generally accepted that organic matter is the most important soil property governing the relative extent of adsorption of non-ionic herbicides in different soils, whereas clay content is usually of much less importance (Calvet, Terce & Arvieu, 1980; Grover, 1975; Hance, 1965; Kozak & Weber, 1983). Many studies have shown that the organic matter content of the surface soil tends to increase with long term minimum tillage (Bakermans & de Wit, 1970; Douglas & Goss, 1982; Fleige & Baeumer, 1974).

The relationship between adsorption, measured as Kd values for chlortoluron, and organic matter for 10 winter cereal fields sampled in autumn 1982 is shown in Fig. 1 (Moss & Cotterill, 1984). The 'no ash' samples comprised soil from the surface of ploughed areas or from 10-15 cm depth on direct drilled or shallow tine cultivated areas. The 'ash' samples consisted of surface soil (0-2.5 cm) from areas where straw was burnt and subsequently direct drilled or shallow tine cultivated. Both sets of soil samples were collected from the same 10 fields. It is important to recognise that Kd values are a relatively crude measure of adsorption and that for comparative purposes measurement of the Freundlich isotherm for adsorption is more accurate (Hance & Cotterill, 1984).

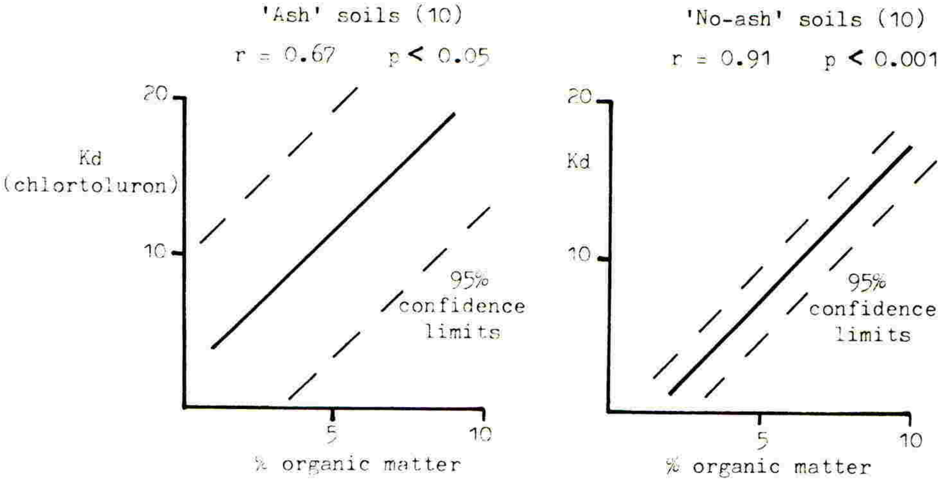

Fig. 1. Relationship between adsorption (as Kd values) and organic matter in soils containing ash and ash free soils collected from within the same ten fields.(from Moss & Cotterill, 1984)

The close relationship between adsorption and organic matter for the 'no ash' soils supports the conventional view that adsorption is mainly dependent on organic matter content. However, the relationship for 'ash' soils is much poorer, although still statistically significant, and the ratio Kd:%OM is higher indicating that the adsorption levels on such soils are greater than organic matter levels alone would suggest. These effects seem to be due to the presence in the surface soil of a concentration of burnt straw residues which have been shown to be highly adsorptive to herbicides (Embling et al., 1983).

It appears that such residues are considerably more adsorptive per unit weight than other soil organic matter. Thus, while burnt straw residues may comprise only a small proportion of the total soil organic matter, they may have a much greater effect on total adsorption.

In a study made during 1980, field performance of chlortoluron and isoproturon was more reliably indicated by adsorption measurements (Kd values) than by organic matter content (Cussans et al., 1982). In that study, poor herbicide performance was particularly associated with soils where the Kd value for chlortoluron was over 6.0 (Fig. 2).

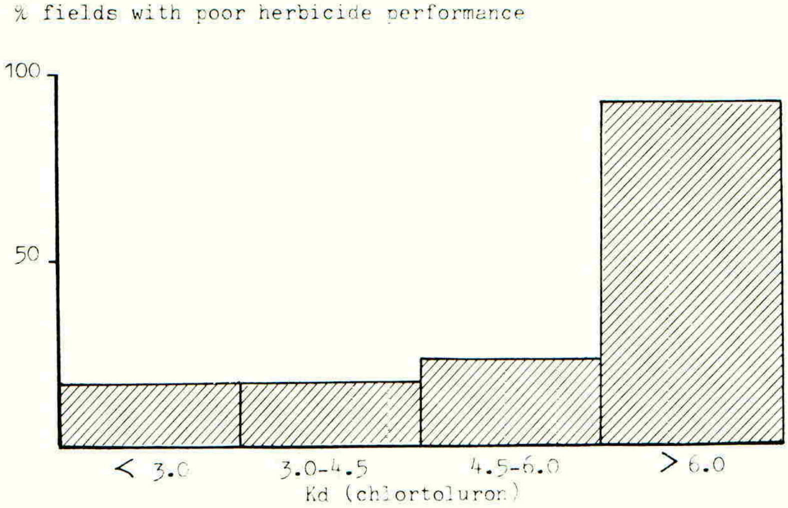

Fig. 2. Relationship between adsorption levels of surface soil (as Kd values) and herbicide performance in the field (from Cussans et al., 1982)

Further studies have demonstrated that a much higher proportion of soils containing ash have a Kd value (chlortoluron) of over 6.0 than ash free soils (Table 3) (Moss & Cotterill, 1984).

TABLE 3

The influence of ash on adsorption level

Numbers of fields in each category	'Ash soils'	'No ash soils'
Kd > 6.0	11 (92%)	4 (29%)
Kd < 6.0	1 (8%)	10 (71%)

One implication of these results is that where ash is absent, organic matter levels alone may be a suitable measure on which to base herbicide recommendations. Where ash is present, organic matter figures alone have less relevance and it may be better to base recommendations for use on direct adsorption measurements (Hance & Cotterill, 1984). However it must be stressed that many other factors, apart from adsorption, can influence herbicide performance.

It appears that where burnt straw residues accumulate in the surface soil, the performance of soil-acting herbicides may be reduced by adsorption of the herbicide. Nyffeler and Blair (1978) have also shown in pot experiments that ash can reduce the activity of chlortoluron and isoproturon. The effect of burnt straw residues is likely to be greatest where they are retained close to the soil surface, as occurs with direct drilling. On several fields direct drilled annually for the past five years, visual observations indicated that residues were largely confined to the surface 5.0 cm of soil. Ploughing, if good inversion is achieved, should bury virtually all surface residues below 5.0 cm. Tine cultivations are likely to disperse burnt straw residues to a depth dependent partly on the depth of cultivation. The greater the dispersion, the greater will be the dilution factor and consequently the less the likely effect on herbicide performance. It would be predicted that the adsorption level of the surface soil following tine cultivations would be intermediate between ploughed and direct drilled soil. This has been found to occur at one of the Letcombe tillage sites where the same cultivations had been carried out annually for 9 years (Table 4) (Moss & Cotterill, 1984).

TABLE 4

Effect of cultivation type on adsorption of surface soil

Cultivation Depth	Plough 20 cm	Tine 10 cm	Direct Drill 3 cm	S.E.
Kd (chlortoluron) (surface 2.5 cm)	7.7	11.7	13.8	± 0.52

Cotterill (pers. comm.), has shown that the adsorptive capacity of fresh straw ash declines very rapidly. Most, but not all, of this adsorptive capacity can be lost in 10 days if the samples are subjected to three wetting and drying cycles. In field sampling, no evidence has been found of a decline in adsorption between autumn and spring, where sampling has been done at least 7 days after burning (Moss, 1984).

It appears that there may be two distinct components to burnt straw residues. One can be rapidly deactivated within a period of a few days whereas the other component appears to be very persistent. The high adsorption levels recorded in fields that have been direct drilled for many years are probably a result of a gradual build up of burnt straw residues.

The rate of increase of adsorption level has implications for herbicide performance. At one site, changes in adsorption level have been studied where direct drilling has followed ploughing (Table 5).

TABLE 5

Effect of cultivation on changes in organic matter and adsorption of surface soil, measured as Kd values for chlortoluron
(from Moss & Cotterill, 1984)

		Oct 1980	Sept 1981	Oct 1982	Oct 1983
Ploughed 1980					
Direct drilled	Kd	2.7	4.6	6.7	5.9
1981 & 1982;	% OM	2.9	-	-	3.6
Disced 1983					
Direct drilled	Kd	11.6	12.3	13.8	11.8
1973-1982;	% OM	4.3	-	-	4.4
Disced 1983					

The results demonstrate that adsorption levels increase more rapidly than organic matter levels and that the increase is a gradual process (Moss & Cotterill, 1984). The adsorption levels after two years direct drilling were still substantially less than those after ten years continuous direct drilling. The decline in adsorption between 1982 and 1983 was probably a result of the stubble cultivations carried out in September 1983, which may have incorporated some ash below the surface layer.

These results demonstrate that increases in adsorption occur over a prolonged period and that consequently any reduction in herbicide performance is likely to be a gradual process. The extent of herbicide adsorption is likely to be dependent on both the innate organic matter content as well as the amount of ash present. With long term minimum tillage, herbicide performance is likely to become inadequate sooner on soils which have a relatively high organic matter content , prior to the addition of adsorptive ash following straw burning.

More information is required on the speed of build-up of adsorptive components and their progressive effect on herbicide performance. Fig. 3 shows a simple model for A. myosuroides showing what would happen if herbicide performance declined from 95% kill by 5% each year (Cussans & Moss, 1982). In these circumstances A. myosuroides populations would remain at a low level for four or five years with no sign of any future problem. Eventually, the exponential increase in weed populations would lead to severe infestations and considerable loss of crop yield. While this phenomenon has only been observed on a few farms the results obtained from the model closely resemble what has actually occurred.

Because so many other factors are involved in determining herbicide activity, it is unlikely that the level of performance will decline steadily year by year. However, it is likely that the probability of herbicide failure will increase with increasing adsorption level.

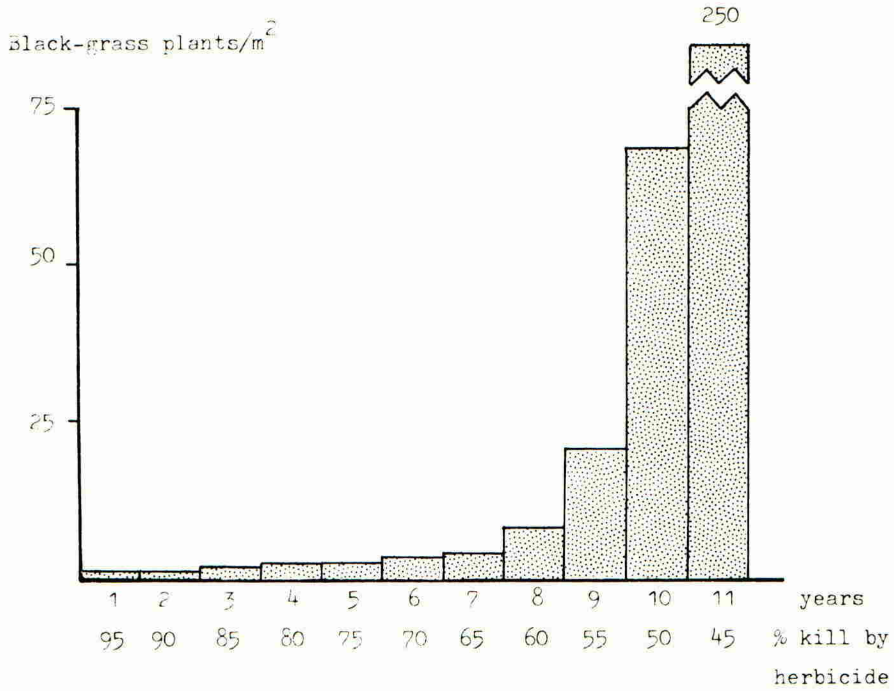

Fig. 3. A model for A. myosuroides populations on direct drilled land which assumes kill by herbicide to be 95% initially but declines by 5% for each year of direct drilling (from Cussans & Moss, 1982)

pH

Long term minimum tillage and direct drilling can result in increased acidity of the surface soil (Shear & Moschler, 1969; Blevins et al., 1977). Differences in pH between soils have been shown to affect the performance of many herbicides (Banting et al., 1976; Eagle & Rahn, 1982). Lower pH tends to be associated with poorer performance of herbicides. However, in some cultivation experiments substantial differences in herbicide performance have occurred between cultivations when there has been little difference in the pH of the surface soil (Moss, 1984). This suggests that pH is unlikely to be the major factor causing poor herbicide performance in minimally cultivated soils.

Soil nutrient distribution

Minimum cultivation, and direct drilling in particular, tend to result in a concentration of nutrients in the surface soil (Bakermans & de Wit, 1970; Cannell & Finney, 1973; Ellis & Howse, 1980; Moss, 1984). Results from a preliminary pot experiment at WRO indicate that increasing concentrations of N, P and K are associated with poorer performance of isoproturon against A. myosuroides (Table 6).

TABLE 6

The influence of soil nutrient level on the performance of isoproturon (0.05 kg/ha) against A. myosuroides grown in sand culture (Smith & Moss, unpublished)

% reduction of foliage fresh weight				
Nitrogen	0	50	100 ppm	(Phosphate = 50 ppm) (Potash =400 ppm)
% reduction	94	87	76 %	
Phosphate	0	50	100 ppm	(Nitrogen = 50 ppm) (Potash =400 ppm)
% reduction	93	87	81 %	
Potash	0	400	800 ppm	(Nitrogen = 50 ppm) (Phosphate = 50 ppm)
% reduction	93	87	86 %	

However, the effects were relatively small and it seems unlikely that surface nutrient levels are a major influence on herbicide performance in the field. Other studies have also shown no clear relationship between nutrient level and herbicide performance in the field (Cussans et al., 1982).

Changes in tillage may result in changes in several soil properties and in plant root growth, any of which could affect herbicide performance. The evidence indicates that adsorption by burnt straw residues is the main factor involved in reducing herbicide performance. However, it is difficult to isolate a single factor as responsible because interactions between soil factors can occur. For example, Mahler & Harder, (1984) found that the major factor determining surface pH was the amount of N fertiliser applied. The additive effects of adsorption, pH and nutrient levels on herbicide performance, the influence of climate and interactions between all these factors, have not been adequatly investigated and warrant further study.

PRACTICAL CONCLUSIONS

Where soil factors result in inadequate weed control by soil acting herbicides, the following solutions are recommended:

1. Use foliar acting herbicides. More research could be directed towards maximising the foliar activity of predominately soil acting herbicides.

2. Rotational ploughing, once every 4-5 years, should bury the adsorptive surface soil layer and provide an environment in which soil acting herbicides are likely to be more effective (Cussans & Moss, 1982). This would also have the benefit of burying any acidic surface layer in which nutrients were concentrated.

THE FUTURE

If straw burning is restricted, or perhaps even banned, it is probable that herbicides will have to work in an environment in which substantial quantities of straw are present. Little information is available on the effect that decomposing straw residues may have on herbicide performance. Limited work (Addala et al., 1984; Moss, 1979) showed that the presence of stubble near the soil surface resulted in poorer weed control than where stubble was buried by ploughing, although the reasons for this were not clear. The effect of straw on herbicide performance is an area worthy of further work.

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