RESIDUES OF HERBICIDES IN AUSTRALIAN SOILS

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Summary. In order to assess the implications of long-term herbicide usage on Australian soils information regarding herbicide persistence is needed. Overseas studies indicate that herbicide residues in the soil are unlikely to cause long-term problems. However, the factors influencing herbicide persistence are complex and overseas results may not always be applicable to Australian conditions. This paper reviews factors influencing herbicide persistence, recent Australian investigations into herbicide persistence and identifies areas requiring further research. The assessment of herbicide persistence under Australian conditions should be an ongoing area of research. It is important that such research be designed to elucidate the mechanisms involved in herbicide movement and degradation in the soil. The ultimate aim should be to develop techniques to predict herbicide behaviour under differing environmental conditions.

INTRODUCTION

For several decades there has been a rapidly expanding use of herbicides in agriculture for the control of weeds. This has made a significant contribution to increased productivity in Australian agriculture. However, our ability to develop and employ these chemicals far surpasses our ability to assess the implications of their long-term use and to educate the public on their usage. A complete evaluation of the benifits versus the risks of continued herbicide usage cannot be made as there is seldom sufficient information available concerning all the environmental implications. Whilst it is simple to enumerate the benefits of herbicide usage in terms of improved productivity, reduced production costs and improved soil structure through the reduction of soil erosion and conservation of soil moisture and nitrogen, it is less easy to assess their potential to cause adverse environmental effects. The influence of herbicides on the environment is an extremely broad topic and depends on three main factors: the toxicity of the herbicide, the concentration in the environment, and the duration of the herbicide's activity. Hence, a knowledge of herbicide persistence and concentration in the soil is necessary to assess the environmental implications of herbicide applications.

Overseans studies (21, 34) indicate that herbicide residues in soil are generally unlikely to be a major problem, as most herbicides decompose to a low residual level during a single growing season. For most herbicides it is recognised that unless carryover into the following cropping season is greater than 50% of that applied it is unlikely to be a problem for subsequent tolerant crops and that carryover of 10% or less is unlikely to cause problems even for sensitive crop species. Nevertheless, some may persist for longer than a single growing season depending on soil type and environmental conditions. For instance, significant persistence from one growing season to another has been documented for herbicides such as trifluralin, tri-allate, atrazine, picloram, diuron and chlorsulfuron (14, 15, 30, 38).

Persistence studies should be conducted on the major herbicides used in agricultural cropping systems and those exhibiting significant persistence should be further investigated with respect to their potential to cause adverse environmental effects. A knowledge of herbicide persistence in soil is essential to understanding the behaviour of herbicides in the environment. This paper reviews factors influencing herbicide persistence, recent Australian research and identifies areas requiring further investigation.

FACTORS INFLUENCING PERSISTENCE

The factors influencing herbicide persistence are complex and depend on a range of processes such as dispersal, adsorption and degradation. The relative importance of these processes and the rate at which they take place will depend on a number of factors such as: chemical structure of the herbicide; soil moisture and temperature; biological activity of the soil; and soil type. Although the relationship between soil type and persistence is not well understood characteristics such as pH, organic matter content, particle size distribution, cation exchange capacity, bulk density and infiltration characteristics are known to influence the rate of herbicide degradation.

Overseas studies have correlated various soil characteristics with herbicide persistence, however, conflicting evidence in the literature (13), makes it difficult to draw firm conclusions. General trends can be used as a guide, bearing in mind that there are many exceptions and that factors other than those mentioned earlier may have some influence.

Soil properties influence herbicide persistence and phytotoxicity mainly through their effect on the processes of adsorption and degradation. For most herbicides degradation is primarily microbial, although chemical degradation does occur. Generally, it is thought that adsorption onto soil particles or clay minerals decreases the amount of herbicide available in soil solution, which may then result in a reduction in the ability to exhibit biological activity. Herbicide adsorption may be irreversible or reversible, depending on the nature of the herbicide and the adsorption sites. This can affect persitence in two ways. Irreversibly bound herbicides such as paraquat and diquat exhibit increased persistence because they are strongly bound onto the soil particles and hence are protected from degradation. In contrast, since the density of micro-organisms is greater near colloidal surfaces than in the soil solution (5), a reversibly bound herbicide may be more readily degraded due to its close proximity to these micro-organisms. The rate of degradation increases with soil moisture and temperature. Although this has been well documented the extent to which the degradation rate is influenced by soil moisture and temperature depends on both herbicide and soil type (12, 33). It is difficult to separate the influence soil temperature has on degradation from that of soil moisture. For example, in hot dry Victorian summers degradation will be increased as soil temperature rises, but reduced as soil moisture decreases. This is where mathematical models such as those described by Walker and Barnes (35) are invaluable for determining the net result of the opposing effects of such factors.

Exactly how organic matter influences herbicide persistence and phytotoxicity is unclear since there is much conflicting evidence in the literature. This is possibly due to the fact that organic matter influences degradation through the processes of adsorption and microbial degradation. Generally, increasing organic matter content decreases herbicide persistence (24) and phytotoxicity, as was shown by Savage (29) in a field survey on trifluralin persistence. However, there are usually exceptions and Bardsley *et al.* (2) observed increased trifluralin bioactivity as organic matter increased.

Soil pH may directly affect persistence if the stability of the herbicide is pH dependent, or indirectly through the processes of adsorption and microbial degradation. Although there is some conflicting evidence in the literature most herbicides, particularly the such as atrazine, simazine and chlorsulfuron, degrade more quickly in acidic soils. Ferris (8) reported that atrazine carry over was greater in neutral and alkaline soils and that the degradation of atrazine by hydrolysis increased in acidic soils.

Since soil conditions necessarily vary from site to site and season to season, persistence data is specific to a particular time and location. As shown by an overseas collaborative experiment co-ordinated by the "Herbicide Soil Working Group of the European Weed Research Society" (36), herbicide persistence is extremely variable. Their collaborative project, comprising 21 sites in 11 countries, investigated the persistence of atrazine in a series of laboratory and field experiments. The half-life (time for the herbicide concentration to be reduced to 50% of the original concentration) of atrazine varied from less than 14 days to over 60 days and the percentage remaining after 140 days varied from less than 1% to as high as 40% of the initial concentration. At most sites the half-life was independent of herbicide concentration and the degradation rate could be approximated by first order kinetics. At some sites, however, considerble deviations from first order kinetics occurred, which could imply that different mechanisms of loss were occurring. This variability highlights the need for care when extrapolating data from one site to another, especially when climatic and soil characteristics can be so variable.

COMPARING PERSISTENCE DATA

A recent review by Wardrop (37) has highlighted the difficulties that can occur when assessing and comparing the persistence data available in the literature. In order to make comparisons it is preferable to present persistence data in terms of the half-life of a herbicide. Many studies, however, are conducted for fixed lengths of time and the data are given as the percentage remaining at the end of the experiment.

Often the initial concentration of herbicide in soil (immediately after application) is not determined. This may be due to lack of resources or the cost involved, and yet it is well known that not all the herbicide applied reaches the target. If results are to be expressed as the half-life or as the % remaining, it is critical that the initial amount be accurately determined. Our results, and those from several overseas studies (10, 19, 21), indicate that the concentration found immediately after application, particularly of the volatile soil incorporated herbicides, is much lower than anticipated on the basis of theoretical calculations. An overseas study, using trifluralin and tri-allate, conducted at the University of Manitoba in 1978 and 1979 (21) indicated that the concentration in the soil immediately after incorporation was very much less than anticipated, considering the application rate and soil density. The actual concentration of trifluralin in the top 5 cm of soil immediately after treatment at 0.84 kg/ha was 0.23 ppm and 0.14 ppm. in 1978 and 1979 respectively. This represents only 25-40% of the theoretical amount, indicating that considerable losses may occur during application and incorporation. If the residual concentration found at the end of the 1978 season was expressed in terms of the theoretical amount applied there was an 11% carryover of trifluralin. However, when expressed in terms of the actual concentration determined after the 1978 application the carryover was 30%. Since losses do occur during application the latter value is more relevant when comparing persistence data from different investigations.

RECENT AUSTRALIAN RESEARCH

Until recently there was little Australian data available to allay the mounting public and grower concern over the increased usage of herbicides. As indicated in a survey (22) of farmer attitudes conducted in 1983, this concern is not simply limited to the urban environmental lobby. The response obtained from primary producers in all states indicated that 90% of farmers were concerned about the long-term environmental effects of regular chemical use. Consequently they would prefer to use other methods of weed and pest control if these techniques were as effective and economical as the existing pesticides.

Although Australia's soils, climate and cropping systems are different to those in the U.S.A. and Europe, we have been relying on the extrapolation of overseas data to predict persistence in our environment. In the past most Australian studies have been conducted in isolation on a single herbicide for a single soil type. These studies tended to be qualitative, relying on the response of weeds or crop plants as indicators of herbicidal activity. Whilst such studies are useful in identifying potential residue problems, they do not allow quantitative interpretation of the residue level causing crop damage, and hence they are of limited value for advisory purposes.

In 1981, a National Workshop on Tillage Systems recognised that a more structured and integrated approach was essential when investigating herbicide persistence in Australian soils. Apart from studies conducted by Welsh (38) and Marley (18) into picloram persistence, and those by Bowmer (3, 4) into atrazine, simazine and diuron persistence there was very little information available on herbicide persistence in Australian cropping situations.

Since 1981, the Wheat Research Council of Australia has actively supported a number of investigations around Australia. A recent workshop funded by the Wheat Research Council (1) highlighted the progress that has been made in herbicide residue research since 1981. Research programmes have been established in the major wheat growing states to investigate the persistence of herbicides in Australian cropping systems. These investigators have adopted a more integrated multi-disciplinary approach in order to investigate the fate of several herbicides (chlorsulfuron, trifluralin, simazine, diclofop-methyl, picloram and diuron) on a range of soil types. Whilst each program is influenced largely by regional practices, they also complement each other, particularly with respect to the range of soil types and climates encountered in Australian wheat growing areas. Particular emphasis has been given to chlorsulfuron, one of the new sulfonylurea herbicides which are active at extremely low application rates (<20 g/ha). Chlorsulfuron persistence is also greatly influenced by soil and climatic conditions. Instances of chlorsulfuron residue carryover have been documented (15) and its persistence can be a drawback in cropping rotations involving sensitive crops.

The variability of the herbicide concentration in the soil immediately after application has been investigated in Victoria and W.A. Using a fluorescent dye as a tracer, the W.A. investigation (25, 26) showed that mechanical incorporation can increase the variability of the deposition pattern. Tyned implements tended to cause banding of trifluralin, which under the moist conditions of that season did not affect weed control. However banding, or uneven incorporation may affect efficacy in drier years. In the Victorian study (19) the variability in herbicide deposition across a plot was assessed by measuring the concentration of trifluralin or diclofop-methyl in individual cores. It was observed that the herbicide concentration in the soil across individual plots immediately after application was extremely variable, and was influenced by both the type of herbicide and the site. The coefficients of variations for trifluralin varied from 56-129% and for diclofop-methyl from 32-52%. This variability must be taken into consideration when sampling to ensure that a representative sample is abtained. When the concentration found immediately after application is expressed as a percentage of the theoretical value it is obvious that the theoretical value can be misleading. When using trifluralin, for example, the concentration immediately after application ranged from 0.11-0.32 ug/g, which converts to 32-84% of the theoretical amount. This agrees with the work previously described (10, 21).

Herbicide persistence trials need to be conducted over a number of years so that persistence can be assessed for a sufficient range of climatic conditions. Both the Victorian and W.A. projects have found that herbicide persistence can be dramatically influenced by climatic variations. Piper (27) observed no herbicide carryover or damage to the subsequent crop in the W.A. trials conducted between 1982 and 1984. Since then however, the 1985 dry season has produced some herbicide residue problems that were not previously seen. Similar results were observed in Victoria, where much higher trifluralin carryover was found following the dry 1984 summer than had occurred after the previous summer (16). These results highlight the importance of conducting long-term trials to assess persistence over a sufficient range of climate conditions. This is essential if the long-term implications of regular herbicide application are to be assessed.

The use of herbicides in reduced tillage systems - both long fallows (8-10 months) and short fallows (1-5 months) - is being investigated in S.A. (6). This project will identify the herbicides that are of practical and economic significance in reduced-tillage fallow systems. The rates of herbicide needed to effectively control weeds on important cropping soil types and under a variety of rainfall patterns will be assessed. Residual herbicide activity is being monitored in relation to long-term weed control, as well as crop and pasture growth.

A research program in northern N.S.W. was undertaken in response to grower concern that atrazine use in summer crops may cause injury to subsequent winter cereals. This program aims to investigate the effect of atrazine residues on soil fertility, and to establish the reasons for variable efficacy and carryover of phytotoxic residues. The effect of atrazine on soil fertility was assessed by monitoring the carbon cycle (9). Carbon loss was lower in the no-tillage treatments than in the mechanical cultivation treatments. The use of atrazine and glyphosate in the no-tillage treatments had no adverse effects on the overall soil biomass.

Investigations into variable atrazine persistence and performance in N.S.W. indicated that the time of application had an important influence on the loss of atrazine. Using the Walker and Barnes herbicide loss simulation model (35), Ferris (8) showed that the below average rainfall and temperatures in the 1984/85 cropping season could be expected to reduce the rate of atrazine degradation. A June application could be expected to have a half-life of 105 days compared with 46 days for a December application in the 1984/85 cropping season.

Whilst recent investigations into herbicide persistence have greatly increased our knowledge of herbicide residues in Australian soils they have also highlighted the deficiencies in our understanding of the complex processes involved.

THE FUTURE

The assessment of herbicide persistence under Australian conditions should be an ongoing area of research. As new herbicides are introduced, especially new classes such as the sulfonylureas and imidazoloinones, they will require appropriate long-term assessment. The recent trend towards the development of products requiring much lower application rates makes it essential that we continue to increase our knowledge of herbicide behaviour in soils.

The assessment of herbicide persistence should involve monitoring the long-term effects of repeated herbicide application on soil residue levels and investigating the effect of leaching and run-off on herbicide loss and distribution in the soil profile. Once this basic information has been obtained the environmental implications of these residues should be assessed. This could involve investigating whether or not interactions occur between residues of different herbicides, or between herbicide residues and other agricultural chemicals. Also the impact of herbicide persistence on soil flora and fauna and the potential of herbicide residues to adversely affect non-target organisms should be assessed.

Due to the cost of investigating such a complex system at a number of sites on a range of herbicides, it is imperative that a more integrated multi-disciplinary approach to persistence investigations be adopted. It is important that such research be designed to elucidate the mechanisms involved in herbicide transport and degradation in the soil, and ultimately to determine the way in which they are influenced by soil properties and climatic conditions. This is essential in order to extrapolate from one herbicide to another of similar structure, or from one site to another.

Standardisation. The development of standardised monitoring and reporting procedures is of major importance. It is essential that a practical and cost-effective procedure be developed in order to monitor the initial soil concentration immediately after application. This is necessary if valid comparisons between different application rates at different times and locations are to be made. Further, it must be remembered that the rate of herbicide degradation is not always independent of concentrations. A knowledge of the degradation rates is necessary before comparisons can be made between investigations involving different locations and rates of application. Marley (18), for instance, demonstrated that picloram degradation on a heavy black clay was faster at the lower application rates than the higher rates.

Methodology. It is important that resources continue to be allocated for the improvement of techniques for determining and verifying herbicide soil residues. This is of particular concern given the potential usefulness of the sulfonylurea group of herbicides. These herbicides are applied at rates of less than 20 g/ha, and this necessitates detection of residue concentrations in the parts per billion and parts per trillion range. These concentrations stretch current analytical techniques to their limits. Bioassay procedures have been introduced as an analytical technique to enable the detection of these chemicals at the parts per billion level. However, although these procedures give a measure of herbicidal activity they are relatively non-specific and unable to distinguish between chemicals acting by similar mechanisms.

The only other alternative presently available for detecting such minute concentrations is enzyme linked immunoassays. The development of enzyme linked immunochemistry techniques to detect herbicide residues has the potential to revolutionise herbicide residue analysis. If such techniques live up to their potential, it will be possible to detect herbicide residues in soils quickly and accurately. Whilst filling the present gap in our ability to detect and identify sulfonylurea herbicides, this technique has important implications for both farmers and researchers. It will enable the cost-effective analysis of large numbers of samples which will greatly facilitate research into the factors influencing herbicide degradation. Also, it has the potential to be marketed as a kit which would allow farmers to tailor their applications and plant-back times to individual seasons.

Enzyme linked immunoassay techniques coupled with a knowledge of the 'no effect level' for a particular crop will greatly increase management options. Farmers will be able to ascertain if the concentration of residue carried over into the subsequent cropping season will be harmful to a particular crop.

Crop tolerance. Until recently very little definitive work had been done in Australia on herbicide persistence and its effects on subsequent sensitive crops. Whilst considerable work has been undertaken to determine the tolerance of cereals to a range of recommended herbicides, very little has been done on sensitive crop species. Field investigations conducted in N.S.W. on cereals by Lemerle (17) have shown that herbicide tolerance can vary between cultivars and is influenced by climatic conditions. As highlighted by Wardrop (37), in a review on the environmental effects of herbicides in conservation cropping systems, this type of investigation needs to be conducted on a range of rotation crops, both tolerant and sensitive.

Instances of carryover and subsequent injury to sensitive crops have been documented overseas for herbicides such as atrazine, chlorsulfuron, picloram, trifluralin and tri-allate. However, at present even when herbicide damage is suspected and chemical analyses undertaken, it is impossible to assess confidently the significance of the concentrations found. Ferris (7) has conducted a series of glasshouse and field trials to determine the significance of atrazine residues and link them to plant-back periods for sensitive crops. The 'no effect level' was determined using a water extraction procedure developed by Stalder and Pestemer (31). More research needs to be undertaken to validate this work under a range of environmental conditions and extend it to soil and crop options in other parts of Australia.

Similar work should be undertaken for chlorsulfuron as its residual activity can often limit rotation options. Many farmers find the two year plant-back period for lupins and peas to be limiting. If a 'no effect level' could be combined with a rapid enzyme linked immunoassay test, then it would be possible for a farmer to determine when this two year plant-back period was excessive.

Modelling. Computer models have the potential to simulate the complex interactions that affect herbicide persistence. Modelling studies need to be undertaken to complement and extend the usefulness of long-term persistence investigations. Computer simulation models can be used to predict herbicide degradation and movement under a range of environmental conditions. If years having a high risk of residue carryover can be predicted, then management practices may be altered, if necessary to minimise damage to subsequent crops.

A number of useful models have been developed overseas. These generally rely on empirical relationships which must be established for all soil and herbicide combinations. Whilst this limits the usefulness of such models, they are still a powerful tool when applied to a known set of conditions or parameters.

A herbicide persistence model developed by Walker and Barnes (35) in the United Kingdom allows the complex relationship between soil temperature and soil moisture to be accounted for. Overseas experiments have tested the model with a number of herbicides (33, 36) and although the model has limitations its general predictive ability is promising.

Simulation models may involve relatively few parameters such as the Walker and Barnes model (35) or they may be more complex such as those developed by Troester *et al.* (32), Nichols *et al.* (23) and Ross *et al.* (28). The latter take into account additional factors such as volatilisation, adsorption, UV degradation and herbicide movement.

Investigations into the applicability of such computer models to Australian conditions are being undertaken in N.S.W. (11) and Victoria (20). These models will enable us to better utilise research data, and to more readily predict the behaviour of herbicides in the field. Such information will improve weed control practices by allowing better optimisation of application timing and improved forecasting of safe plant-back periods.

CONCLUSIONS

All herbicides used in Australia require registration by the appropriate State Authority. Registration is granted on the basis of data on the efficacy and safety of the herbicide from field trials conducted overseas and in Australia by the chemical company, often in conjunction with the various Departments of Agriculture. Overall, herbicides function effectively and safely. Whilst the chances of significant unforeseen effects to non-target organisms are slight they must not be ignored. This was discussed in detail in a review by Wardrop (37) into the environmental effects of the herbicides used in conservation cropping systems. The complete assessment of the impact of herbicides and their metabolites on the environment is difficult because of the many complex interactions that occur between the different biological systems of the environments.

Recent research programmes conducted by the State Departments of Agriculture and supported by Research Council funds have significantly contributed to our knowledge of herbicide behaviour in Australian soils. However, it is important that we do not become complacent regarding the impact of herbicide usage on the environment. The assessment of the impact of herbicides on the Australian environment must be an ongoing area of research.

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