

HERBICIDE RESIDUES IN SOILS

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With practically all applications of herbicides some of the compound comes in contact with the soil. Once the target weed species has been destroyed, the herbicide has served its intended function but residues may remain in the soil. For total vegetation control, a herbicide with a long residual life is desired to prevent re-establishment of plants on the treated area. However, herbicide residues in agricultural soils pose several potential problems or hazards:

- (a) they may injure sensitive plants germinating in later years or crops grown in rotation with sprayed crops,
- (b) accumulation of residues may occur as a result of successive applications at rates which exceed the rate of dissipation,
- (c) unlawful residues may occur in crops grown in rotation with treated crops,
- (d) beneficial soil microorganisms may be inhibited.

In this paper the hazards of persistence and accumulation are considered.

ACCUMULATION OF HERBICIDE RESIDUES

With repeated applications of herbicides, accumulation in the soil is determined by the difference between the rate at which the herbicide is added and the rate at which it disappears. The rate of addition is discontinuous and is determined by the application schedule, while the rate of disappearance is continuous and, with most herbicides, is determined by soil and climatic conditions. If the rate of disappearance is assumed to follow first-order kinetics (i.e. at any given time, the rate of disappearance is proportional to the herbicidal concentration in the soil) the maximum residue which can be attained 12 months after application can be calculated.

When herbicidal applications of 1 lb per acre are repeated each year on the same area and when 80 per cent disappearance occurs each year (half life of 5 months), the maximum residue which can accumulate 12 months after application approaches 0.25 lb per acre. Therefore, residue carry-over even after continuous use is small. Such calculations show that for herbicides with half lives of up to one year the maximum residue attained 12 months after application does not exceed the annual

application rate. With longer half lives the maximum residue becomes increasingly greater, until with a half life of 10 years the expected accumulation of residue will approach 14 times the annual addition. Several years of continuous use would be required to accumulate these maximum residues.

Thus, if we have an idea of the half life of a herbicide in a particular soil it is possible to determine the level of residue which will be reached with repeated applications.

The phytotoxic effects produced by soil residues of herbicides will ensure that unnecessarily high residues will not accumulate unnoticed in the soil. In soils cropped regularly any accumulation of residues will cause injury and serve as a warning. In deep rooted perennial crops, however, such as fruit trees, it is possible that herbicide residues may accumulate unnoticed with repeated applications. In this situation the roots of the crop plant occur below the level of penetration of the herbicide.

LOSS OF HERBICIDE RESIDUES

Residues in the soil can occur as a result of carry-over of herbicide from one year to the next or by accumulation with repeated applications, as discussed above. However, all organic herbicide residues eventually disappear from the soil. The processes which govern the fate and behaviour of herbicides in the soil are: decomposition by microorganisms; adsorption by soil colloids; leaching; chemical decomposition; volatilization; photodecomposition; and absorption by plants. Each of these processes will not be considered individually but will be discussed in as far as they relate to the problem of residues.

(a) Short-lived residues

With many herbicides the rate of disappearance from the soil is very rapid. With compounds such as 2,4-D, d,2-DPA and the carbamates the period of persistence is of the order of a few weeks to a few months. These herbicides are readily decomposed by microorganisms in the soil and problems of soil residues are not usually experienced.

Decomposition of such herbicides is usually preceded by a lag phase during which time the soil microorganisms become adapted to utilize the herbicide as a substrate. The length of the lag phase can vary, but once the microorganism becomes adapted to the herbicide subsequent decomposition occurs rapidly.

(b) Medium - and long-lived residues

Many herbicides appear to be decomposed only slowly by

microorganisms and it is with these herbicides that problems of residues can be experienced. The symmetrical triazines and the substituted ureas are slow to be inactivated, which suggests losses by means other than by microbial decomposition. However, specific microorganisms have the capacity to metabolize simazine and diuron. Thus the microorganisms involved must be an extremely minor component of the soil population incapable of increasing under the circumstances, the reaction must be severely repressed by some condition, or the herbicide must be competing with the bulk of the soil organic matter as a substrate (Upchurch 1966).

A herbicide with a half life of one year is usually considered to be very persistent (Sheets and Harris 1965). Under most conditions the ureas and triazines have a half life shorter than one year and accumulation of excessive residues will not occur with repeated applications of these herbicides. However, some residue may persist for more than 12 months and problems could be experienced when a sensitive crop is planted in an area previously treated with one of these compounds.

Although breakdown of the ureas and triazines is relatively slow, these herbicides do not readily move out of the surface layers of the soil into the subsoil. This is due to adsorption by soil colloids, organic matter being the soil component involved to the greatest extent.

Herbicides such as picloram, 2,3,6-TBA and fenac, which are relatively resistant to microbial breakdown are able to persist at biologically active levels for more than a year, particularly if they have been used at non-selective rates for the control of hard-to-kill weeds. These compounds are adsorbed to a limited extent only and are thus mobile in the soil and may be moved downwards, the depth of movement being determined by the depth of water percolation. At levels below the plough layer, organic matter is usually extremely low, pH may be different, and oxygen concentrations are often lower than in surface soils. These soil properties can influence the decomposition of herbicides indirectly through their influence on soil microorganisms. Thus it is likely that conditions at depths of two feet or more in the soil may be unfavourable for herbicide decomposition because of poor growth of microorganisms. What then is the fate of herbicides, such as picloram, fenac, and 2,3,6-TBA, which are readily moved downward by water and which are decomposed slowly (if at all) by microorganisms? Considerable work has been carried out on the persistence of picloram but the question of the fate of this chemical in the subsoil still has not been answered.

PERSISTENCE OF PICLORAM

As picloram is an extremely active chemical, even very small residues in the soil can affect susceptible crops. Many studies have indicated that residues sufficient to affect crops remain in the soil several years after treatment.

Losses after one year of 60 to 90 per cent of the original amount applied to the soil have been reported, while after two years 80 to 100 per cent loss has occurred (Goring *et al.* 1965, Keys and Friesen 1968). Estimates of the half life of picloram have ranged from 1 to 13 months (Goring *et al.* 1965, Grover 1967) and thus unnecessarily high residues should not build up with repeated applications. However, because of its high activity even minute residues of picloram will affect susceptible crops.

Extensive studies have shown that picloram is decomposed by soil microorganisms (Grover 1967, Youngson *et al.* 1967). One report indicates that a lag period precedes decomposition (Grover 1967) while Youngson *et al.* (1967) conclude that a lag period is not involved in decomposition over a wide range of concentrations. Attempts to isolate organisms that can utilize picloram as an energy source have been unsuccessful and it has been concluded that the decomposition of picloram is an incidental process in the breakdown of soil organic matter, requiring the loss of approximately 10,000 to 100,000 pounds of organic matter per pound of herbicide (Youngson *et al.* 1967).

The assumption that dissipation follows first order kinetics is valid for many herbicides. However, with picloram it has been observed that the rate of decomposition is greater at low concentrations than at high concentrations (Herr *et al.* 1966, Grover 1967, Youngson *et al.* 1967, Hamaker *et al.* 1968). In other words, the rate of decomposition is not proportional to the concentration in the soil. By a mathematical analysis of the rate of decomposition Hamaker *et al.* (1968) concluded that half order and Michaelis-Menton kinetics most satisfactorily describe the detoxification of picloram in soil.

Sorption studies, using soil slurries, have shown that picloram can be extensively sorbed by highly organic soils and also by red and acidic soils (Hamaker *et al.* 1966). The data suggest that sorption is primarily due to organic matter and hydrated metal oxides, with clays probably playing a minor role.

Movement of picloram through the soil involves sorption and desorption from the percolating solution. Thus the degree of sorption and rate of desorption indicate the rate of movement

to be anticipated. In a trial using soil columns, picloram leached slowly through soils in which sorption was high, whereas rapid leaching occurred where sorption was low (Hamaker *et al.* 1966).

From field trials it has been reported that picloram will move downwards in the soil (Scifres *et al.* 1969). In other work, the highest concentration was found to occur in the surface 6 inches one year after application to medium and heavy textured soils, while on light textured soils the greatest concentration was found at the maximum sampling depth of 2 feet (Herr *et al.* 1966).

On plots treated with various rates of picloram in several areas of Victoria, most residues have been located in the surface 18 inches of soil up to one year after application. With longer treatment periods (4 to 5 years) picloram residues have been detected to a depth of at least 5 feet with the highest concentrations occurring below about 3 feet.

Attempts have been made to correlate the rate of decomposition and the phytotoxicity of picloram to various soil and climatic factors. Hamaker *et al.* (1967) found that the rate of decomposition was most closely related to rainfall and temperature, while Grove (1968) found that phytotoxicity was correlated with soil organic matter content and concluded that soil organic matter content and soil pH affect the availability of picloram to plants.

Although considerable picloram may be lost from the soil during the year following treatment, the small residues which carry over can affect susceptible crops because of the high activity of this chemical. Microbial decomposition occurs slowly but is apparently an incidental process in the breakdown of soil organic matter, while adsorption is not important except in organic soils and soils high in hydrated metal oxides. Thus picloram is readily moved downwards in the soil by percolating water and residues can persist in the subsoil for many years because of the lack of decomposition in the subsoil. More information is required on the decomposition and fate of herbicides in the subsoil, especially with herbicides with characteristics similar to picloram, 2,3,6-TBA and fenac.

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