# Effects of environmental factors on the activity of metribuzin in plants

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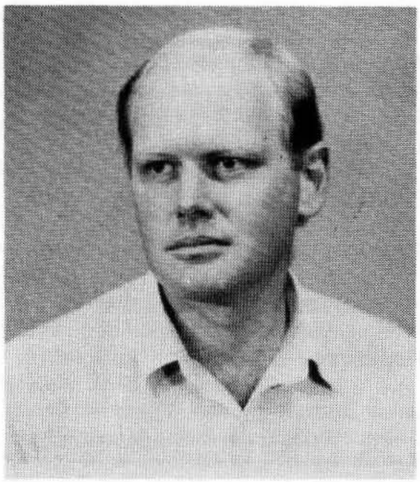

## Summary

**The activity of metribuzin decreases as soil organic carbon or clay content increases, and within the same soil type as pH decreases. Its activity is reduced where topsoil is dry at spraying and for a few days afterwards; its effectiveness may also be reduced by its high rate of degradation. The activity of metribuzin is increased when plants have been subjected to low light intensities or high growing temperatures for a few days before spraying or to high humidity at spraying; activity is reduced when plants have been hardened by stress before spraying. The mobility of metribuzin in the soil may be important in extreme cases; it is reduced in soils of high organic carbon content and increased in highly structured soils.**

## Introduction

Metribuzin (4-amino-6-t-butyl-3-[methylthio]-1,2,4-triazin-5[4H]-one) is currently registered in Australia for use in peas, potatoes, tomatoes, barley and lupins, depending on the product and State. Rates vary from 180 to 700 g ha$^{-1}$ depending on crop, region, soil type and weeds. It is used both pre- and post-emergence. Plant absorption takes place through the seed, roots, shoots and foliage.

Metribuzin is one of the triazinone group of compounds, and its structure is based on a ketone derivative of an asymmetrical triazine ring. It acts by inhibiting the Hill reaction, resulting in the prevention of photosynthesis. Metribuzin is translocated upward in the xylem. Downward movement does not occur (Mullison *et al.*, 1979).

The structure of metribuzin is similar to that of the triazine group of compounds; its mode of action and translocation characteristics appear to be the same as that group, as are the mode of absorption into plants and adsorption onto soil particles (Mullison *et al.*, 1979; Anon., 1979). Much of the basic information on these characteristics which is applicable to triazine compounds is also valid for metribuzin, and vice versa.

Control of weed species that are classed from field experience as moderately susceptible or moderately resistant to metribuzin can vary widely with differing environmental conditions. Important species in these categories in Tasmania include *Polygonum aviculare* L., *P. convolvulus* L., *Trifolium* spp. and *Fumaria muralis* L.. The literature on metribuzin, the triazine group of herbicides and relevant plant physiology studies can explain much of this variation.

## Soil characteristics

In soil comparison studies, decreasing activity of metribuzin was highly correlated with increasing organic carbon content and cation exchange capacity (Swain, 1979; Schmidt, 1973; Liu and Cibes-Viade, 1973). Organic carbon content was highly correlated with cation exchange capacity in all studies. Ladlie *et al.*, (1976) found that metribuzin activity decreased with decreasing soil pH within the same soil type. Swain found that increased clay content in soils relatively low in organic carbon may also have decreased metribuzin activity. Metribuzin activity was reduced by higher clay contents in the soil comparison study by Liu and Cibes-Viade but not in the study by Schmidt.

The activity of metribuzin is related to these soil parameters through soil adsorption (a transient fixation of a dissolved substance on or in the surface of a soil particle) (Hartley, 1976), especially onto organic matter. The matured organic residues are mainly concerned and these are thinly spread, often coating clay particles to the extent that, above a few per cent organic carbon, clay surfaces are effectively blocked as initial adsorption sites (Hartley, 1976; Weed and Weber, 1974). The results of Swain (1979) support this assertion.

Weed and Weber (1974) suggest that at least three mechanisms probably function in soil adsorption of weakly basic pesticides such as metribuzin: ion exchanges which is dependent on protonation and therefore sensitive to pH; hydrogen bonding; and hydrophobic bonding, which may make its greatest contribution at higher pH values when the molecules are not protonated. The first mechanism accounts for the correlation between metribuzin activity and pH in the work of Ladlie *et al.* (1976).

The marked differences shown in the activity of metribuzin on different soil types in glasshouse experiments (Black, 1982) may not be carried over to the field. Light soils typically dry out in the surface layers faster than heavy soils and thereby reduce the availability of the herbicide; such behaviour can override the influence of soil type (Black, unpublished data). This effect is not shown in normal pot experiments, which are frequently returned to field capacity.

In practice the effect of soil type on the efficacy of metribuzin is partially overcome by altering the rate of application, as with many other herbicides.

## Mobility

Mobility is important in the extreme cases where a herbicide either remains in the very top layer of soil above the bulk of weed seeds or where a toxic dose is leached beyond the roots of weeds. The mobility of metribuzin was found to be less in soils high in organic carbon (Swain, 1979; Jarczyk, 1972; Sharom and Stephenson, 1976). Swain found it to be more mobile in highly structured soils.

Mobility will be reduced as soil adsorption increases, because only the herbicide that is free in soil solution will be carried down in descending water (Hartley, 1976). High mobility in strongly structured soils (i.e. those with fine particles that are strongly aggregated) which are initially wet has been explained by postulating that the mass flow of soil solution during leaching is around rather than through aggregates. Results may differ if the herbicide is leached through initially dry soil (Swain, 1979; Hartley, 1964). Poor weed control resulted on krasnozems (strongly structured soils with high organic matter) when metribuzin was applied to wet soils just before heavy rainfall (J. Ward, personal communication, 1979), indicating that the pulse of herbicide concentration had been leached beyond the weed roots.

### Soil moisture at spraying and afterwards

The relatively poor performance of metribuzin on moderately susceptible to moderately resistant weed species in a 1977 experiment in Tasmania has been attributed to dry topsoil conditions (R. S. Smith, personal communication, 1980). In the corresponding experiment in 1978, the topsoil was deliberately kept moist at and after herbicide application by frequent light irrigation, and metribuzin activity was excellent (Table 1). In small plot studies, Wax (1977) found that control by metribuzin of *Abutilon theophrasti* Medik. and *Datura stramonium* L. was good when there was abundant rainfall within 10 days after spraying but poor under limited rainfall.

**Table 1** Percentage control of wireweed and clovers by metribuzin 0.3 kg ha$^{-1}$ applied pre-emergence to dry and wet soils

| Treatment | Wireweed *(Polygonum aviculare)* (% control) | Clover *(Trifolium* spp.) (% control) |
|---|---|---|
| **1977–78** | | |
| dry soil surface at spraying and for 2 weeks afterwards | 7 | 62 |
| **1978–79** | | |
| soil surface kept moist at spraying and for 2 weeks afterwards | 49 | 81 |

After R. S. Smith (personal communication, 1980)

Hance and Embling (1979) applied a wettable powder formulation of metribuzin to soil at either field capacity or air dry and wetted the air dry treatments to field capacity immediately or after 24 hours (Table 2). Soil solutions were removed using a pressure membrane apparatus at intervals up to 96 hours after wetting. When sampled soon after spraying, the concentration of metribuzin in soil solution from the dry soil not wetted for 24 hours was only about half the theoretical equilibrium concentration. The concentration increased only slightly in the first 24 hours before falling again by 96 hours. In contrast, the concentration of metribuzin in soil solution from the wet soil was about two and a half times the theoretical adsorption equilibrium concentration, and that from the dry soil wetted immediately was about twice the equilibrium concentration when sampled soon after spraying. In each case it took approximately 24 hours for the concentration to drop to the theoretical adsorption equilibrium. These authors state that the low concentration following spraying of dry soil which was not wetted for 24 hours is possibly the result of spray solution being drawn into particles so as to be inaccessible to water when the soil was wetted subsequently.

Walker (1976) studied stem uptake of atrazine (a triazine herbicide) in turnips (*Brassica rapa* var. *rapa*) in the laboratory. The herbicide was localized in the top centimetre of soil by applying surface irrigation in only 3 mm amounts; the amount of herbicide in the seedling markedly increased following watering of surface soil and was proportional to the length of time the soil was wet. In another experiment, as the interval between seedling emergence and the first irrigation increased, the same uptake through the stem resulted in a lower shoot concentration due to the greater size of the turnip seedlings (Table 3). Walker suggested that stem uptake of the herbicide could only take place when there was effective contact between the stem and soil water.

The implication from the work of Hance and Embling (1979) and Walker (1976) is that soil moisture at the time of metribuzin application may affect both its availability and the amount taken up via the soil through the stem. A moist soil surface at application, or rainfall immediately afterwards, will result in relatively large amounts taken up through the stem in the first 24 hours (before the soil solution concentration drops to the adsorption equilibrium). On the other hand a dry soil surface at and after application could decrease the long term availability in the soil solution and the amount of uptake through the stem (this may account for most of the uptake via the soil when there has been insufficient rainfall after application to move the herbicide down into the root zone). Finally, the longer surface soil wetting is delayed, the less effective is stem uptake because of the greater size of the plant compared to the stem surface area in contact with the soil.

### Plant hardening before spraying

Tomato plants that were hardened before spraying by a combination of water and nutrient stress and increased light intensity were more resistant to metribuzin injury than plants grown under normal conditions (Nelson and Ashley, 1978). This confirms observations that certain weed species are more resistant to metribuzin under conditions leading to plant hardening. The

**Table 2** The concentration of metribuzin in soil solution ($\mu$g mL$^{-1}$) extracted from soils of different moisture status

| Treatment | Hours after wetting 0 | 2 | 4 | 6 | 24 | 96 | SE |
|---|---|---|---|---|---|---|---|
| Field capacity at spraying | 52.1 | 37.7 | 35.7 | 33.9 | 25.3 | 19.6 | 3.1 |
| Air dry at spraying, wetted after spraying | 42.9 | 44.6 | 45.4 | 34.1 | 23.0 | 17.2 | 4.0 |
| Air dry at spraying, wetted after 24 hours | 10.0 | 11.7 | 12.3 | 14.0 | 14.1 | 10.0 | 2.5 |
| Theoretical equilibrium concentration: 22 | | | | | | | |

After Hance and Embling (1979)

**Table 3** Shoot concentration of atrazine in turnip seedlings ($\mu$g g$^{-1}$ fresh weight) under different soil moisture conditions

| Treatment | Timing of first irrigation At emergence | 3 days after emergence |
|---|---|---|
| Dry topsoil, no irrigation | 0.40 | 0.20 |
| One 3 mm irrigation on first day | 1.40 | 0.35 |
| 3 mm irrigations on two consecutive days | 2.15 | 0.45 |

Total herbicide uptake was approximately the same in equivalent watering treatments. All samples were taken 19 days after emergence.
After Walker (1976)

effects of water stress on plant growth have been documented in a number of recent reviews and considerable research has shown that plants are capable of adapting to moisture stress by both morphological and physiological processes. Adaptations to moisture stress which may decrease the foliar uptake of herbicides include the thickening of cuticular waxes and an increase in the number of cuticular appendages, closure of the stomata, reduction in leaf area and an increase in the root-shoot ratio. In addition wilting increases the contact angle between spray droplets and leaves, with consequent decreased wettability (Crafts, 1968; Cates, 1968; Hsiao, 1973; Hsiao and Acedevo, 1974; Begg and Turner, 1976; and Fischer and Turner, 1978).

Brouwer (1966) found that root growth was relatively insensitive to moderate levels of water stress and hence root development *per se* was unlikely to affect herbicide uptake at such levels. However, Crafts (1968) pointed out that roots in the surface layers will die by desiccation at stress levels approaching permanent wilting. Roots in the top layers of soil are also unlikely to contribute much to water uptake when the surface has been dry for some time, because the root growing points will tend to explore the lower layers of moister soil. As absorption of water is normally greatest in the region of the root hairs (which are situated in a limited zone behind the roots tips), water uptake will be at lower soil levels even if functional roots are present in the surface layers. Since the level at which moisture is taken up is critical in relation to the amount of metribuzin taken up by the roots (because of the distribution of herbicide in the soil), it follows that there is likely to be less herbicide taken up by the root system of moisture stressed plants.

It is not known how much plant hardening occurs in young seedlings, since most observations have been made on much larger plants. Very young seedlings may not have time to adapt fully to moisture stress before spray application, although some hardening of older seedlings obviously occurs in the field. The deleterious effects on metribuzin activity of a dry soil surface at spraying and plant hardening may be augmented by the effect of dust on leaves (often associated with these conditions), since the dust will adsorb a proportion of herbicide that lodges on foliage and render it unavailable for plant absorption. There appears to have been little work on this aspect.

### Light intensity before and at spraying

In experiments where high or low light intensity was imposed on tomato plants 3 to 4 days before metribuzin application, both Phatack and Stephenson (1973) and Fortino and Splittsoesser (1974) found that low light intensity markedly increased phytotoxicity. Da Silva and Warren (1976) produced field evidence to support these results. Pritchard and Warren (1980) found that after 3 days of cloud, 2 or 3 days of sunshine were needed to restore the full tolerance of tomatoes to metribuzin. All three pairs of authors postulated that the ability of plants to inactivate metribuzin is related to the level of food reserve (phytosynthate) immediately before application, which in turn is related to light intensity.

The work on the effect of light intensity on metribuzin activity in tomatoes needs caution before extrapolating to other species. In an exploratory experiment using three-leaf wheat seedlings as indicator plants, reduced light intensity before spraying did not increase the activity of metribuzin (Black, unpublished data), perhaps because the large carbohydrate reserves in the seed buffered the effect of lower photosynthate accumulation under reduced light intensity.

### Growing temperature before spraying

Phatack and Stephenson (1973) and Fortino and Splittsoesser (1974) grew tomato plants under differing day/night temperature regimes ranging from 16/16°C to 27/18°C and found that phytotoxicity increased with temperature. Phatack and Stephenson suggested that the response was due to lower reserves of available carbohydrate resulting from the higher rates of growth at the high temperature, whilst Fortino and Splittsoesser suggested that the differences were due to greater metribuzin uptake at the higher temperatures. Thus there is little doubt that the phenomenon occurs, but there is disagreement about its cause.

### Humidity around plant foliage at spraying

Fortino and Splittsoesser (1974) found that tomato plants were more susceptible to injury from metribuzin when grown in a relative humidity of 80% than when grown at 58% relative humidity. They postulated that since a high moisture content prevents rapid drying, the chemical remains in solution longer on the leaf surface, promoting absorption and therefore increasing effectiveness. Humidity around the plant foliage is the critical factor and depends on wind as well as relative humidity. The changes in relative humidity that accompany diurnal variation may therefore be a factor affecting metribuzin activity, depending on the time of application.

### Plant density

High plant density may affect uptake via the foliage because of a shielding factor and may marginally reduce uptake via the soil because the theoretical amount available to each plant depends on plant density. A higher seedling density may result in greater evapotranspiration per unit area of soil surface and so decrease topsoil moisture, thereby affecting the activity of metribuzin.

### Rate of metribuzin degradation in the soil

The rate of degradation will have an important effect on bio-activity because it affects the theoretical amount available to plants through the soil at any given time after spraying. Webster and Reimer (1976) found that degradation of metribuzin within the first 3 weeks after application to a sandy loam was both rapid and temperature dependent. Less than half the applied metribuzin was intact after 3 weeks at soil temperatures which ranged over 13 to 30°C during the period. Both these workers and Hyzak and Zimdahl (1974) found that the rate of metribuzin breakdown over the warmer months agreed well with first-order kinetics.

Walker (1978) simulated the degradation of eight soil-applied herbicides including metribuzin in the top 8 cm of a light sandy soil. His model incorporated components for the effect of both soil moisture and temperature and assumed that degradation of all herbicides would follow first-order kinetics. The fit of the predicted values was in general agreement with the field data, but varied somewhat according to the herbicide. The predictions were at greatest variance with the most mobile herbicide (metribuzin) and least with the least mobile herbicide, and Walker ascribes this to the effect of rainfall leaching the more mobile herbicides below the 8 cm level of the soil profile.

The implication from these studies is that metribuzin breaks down rapidly under typical growing conditions. It is degraded by light radiation as well as by microbial activity (Webster and

Reimer, 1976) and may therefore break down even faster if sprayed onto dry soil where it may remain undissolved or adsorbed on the surface. For these reasons it is important to spray in conditions that maximize the probability for quick absorption of a lethal dose by the target weeds.

## Discussion

The instructions on the metribuzin labels allow for alteration of the rate according to soil type and advise spraying when the topsoil is moist, so reducing major sources of environmental variation in the activity of the herbicide. Unfortunately the instruction on application to moist topsoil cannot always be adhered to when the crop and weeds are growing rapidly and when the farmer is busy. The toxic dose for most of the weed species claimed to be susceptible is probably quite low, and there may be little or no effect of environment on the activity of metribuzin on these species, except in extreme conditions.

The experience of the author and others in the Tasmanian Department of Agriculture is that instances of poor performance of metribuzin are most often associated with weed species considered to be only moderately susceptible to metribuzin and with spray applications to dry soil surfaces under dry conditions leading to dusty leaves and plant hardening.

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