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# Weed control with atrazine and chlorsulfuron is determined by herbicide availability and persistence in soils

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*Abstract.* Effectiveness and length of weed control with atrazine and chlorsulfuron can be variable in the field. While some of this may be due to climatic variations, differences in soil properties may also be important. We tested this by recording changes in control of mintweed (*Salvia reflexa* Hornem.) and turnip weed (*Rapistrum rugosum* L.) with time in different soils, and comparing these results with the measured changes in plant-available herbicide in the soils. Length of weed control with the same herbicide rate varied from 0 to >15 weeks. Mintweed and turnip weed were controlled (85–100%) only when the soils had $\geq 0\cdot 1$ $\mu$g available atrazine/g and $0\cdot 8$ ng available chlorsulfuron/g, respectively. This agreed with the sensitivity data for these weeds when grown in a soil-free system. The herbicides were initially more available in grey clays than in black earths, and soil pH accounted for most of the variations in the persistence of the available residues. Thus, the efficacy of these herbicides in different soils could be estimated if the available residues in the root-zone could be predicted and the sensitivity of different weeds was known.

*Additional keywords:* degradation, herbicide residues, efficacy, soil pH, soil-free system.

## Introduction

Atrazine is used extensively in grain sorghum (*Sorghum bicolor* L. Moench) for the residual control of broadleaf and grass weeds in the north-eastern grain region of Australia. A recent survey estimated that 264 tonnes of atrazine was applied annually to sorghum crops in the Condamine catchment, which covers most of the Darling Downs of Queensland (Rayment and Simpson 1993). Rates vary for the target weed species, ranging from $1\cdot 15$ kg/ha for mintweed (*Salvia reflexa* Hornem.) to $2\cdot 25$–$3\cdot 25$ kg/ha for barnyard grass (*Echinochloa crus-galli* L.) (Parsons 1992), but these rates do not take into account differences in soil types or properties.

Chlorsulfuron is also used extensively for the residual control of broadleaf weeds and paradoxa grass (*Phalaris paradoxa* L.) in wheat (*Triticum aestivum* L.). Application rates vary from 11 g/ha for turnip weed (*Rapistrum rugosum* L.) to 15 g/ha for paradoxa grass control (Parsons 1992). These rates are independent of soil properties, although the length of re-cropping intervals takes into account soil pH.

Field performance of these herbicides can be variable for both effectiveness and length of weed control across the north-eastern grain region. Differences in seasonal conditions are often thought to be the main reason for these variations, but perhaps differences in soil properties could also be important. Recent incubation studies have shown that the initial activity and the persistence of atrazine and chlorsulfuron varied greatly among different soils of southern Queensland (Walker *et al.* 1993, 1994).

The sensitivity of some major crops to herbicide residues has been measured in a soil-free system (Ferris and Haigh 1992; Jettner *et al.* 1993) and used for predicting the safety of re-cropping. However, little information is available on the sensitivity of weeds to fully available herbicide residues or on the usefulness of such data for predicting field performance of herbicides.

In the current study we measured the effectiveness and length of weed control by atrazine and chlorsulfuron in different soils, and compared this with both the measured or estimated plant-available residue in the soils and weed response to residues in a soil-free

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Table 1. Site location, soil properties, and persistence and availability of atrazine (At) and chlorsulfuron (Ch)

| Site | Location | Great Soil Group | Soil pH | Clay (%) | Half-life (days) | | | Avail. portion (%) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Avail. At[A] | Total At | Total Ch | At[B] | Ch[C] |
| A | Kingaroy | Krasnozem | 6·0 | 56 | 24 | 42 | 27 | — | 8 |
| B | Nangwee | Black earth | 7·6 | 69 | 31 | 61 | 84 | 14 | 8 |
| C | The Gums | Grey clay | 8·0 | 46 | 42 | 65 | — | 38 | 27 |
| D | Mt Irving | Black earth | 8·1 | 70 | 43 | 105 | 105 | 23 | 15 |
| E | Roma | Grey clay | 8·2 | 53 | 44 | 55 | 135 | 62 | 39 |
| F | Pirrunuan | Black earth | 8·7 | 71 | 63 | 143 | — | 13 | 8 |

[A] Atrazine residues extracted in water.
[B] Ratio of residues extracted in water and those extracted in methanol (total residues) at 1 day after application.
[C] Ratio of $ID_{50}$ for maize primary root inhibition in sand (non-adsorbing medium) and soil.

system. This was done to determine the importance of soil properties on herbicide availability and persistence, and the subsequent variability of weed control under constant soil water conditions.

## Materials and methods

### *Soils*

Surface soil (0–10 cm) was collected from 6 sites in southern Queensland. The soils, which had no residual herbicides applied within at least the previous 5 years, were a krasnozem, 2 grey clays, and 3 black earths with soil pH(1 : 5 soil : water) ranging from 6·0 to 8·7 (Table 1). Each soil was air-dried, sieved (5 mm), and mixed uniformly prior to use in the pot experiments.

### *Weed response to soil-incorporated herbicides*

Untreated soil was added to the lower half of 16-cm-diameter pots, and watered to field capacity. The surface 10 cm of soil was mixed prior to adding to the pots with either atrazine at 0, 0·05, 0·1, 0·25, 0·5, 1·0, 2·5, and 10 $\mu$g/g soil, or chlorsulfuron at 0, 0·5, 1·0, 2·5, 5·0, 10, 25, and 100 ng/g soil in sufficient water to bring each soil to field capacity. Treatments were replicated 3 times and kept in a glasshouse. Seeds of mintweed or turnip weed were mixed in the surface 0·5 cm of the atrazine or chlorsulfuron treated soils, respectively. Seedlings were thinned to 2 per pot, and shoot fresh weights were recorded at 4 (atrazine) or 5 (chlorsulfuron) weeks after sowing. Immediately following the harvest, seeds were sown again in the same pots and harvested 4 or 5 weeks later. This was repeated 4 times over an interval of 16 or 20 weeks. Growth of mintweed in soil A was very poor, and the data are not presented. Dates of sowing were 22 January, 18 February, 18 March, and 16 April 1993 for atrazine pots, and 10 June, 15 July, 20 August, and 23 September 1992 for chlorsulfuron pots. Mean air temperatures in the 4 growing intervals were 23·1, 21·4, 21·4, and 18·7°C for atrazine pots, and 15·5, 16·2, 17·7, and 18·8°C for chlorsulfuron pots. All pots were maintained at approximately field capacity with regular watering.

Atrazine at 0·5 $\mu$g/g and chlorsulfuron at 5 $\mu$g/g were also mixed in extra pots of each soil, except for Soils C and F for chlorsulfuron. These were sampled to measure the herbicide residues remaining at each time of sowing. The chlorsulfuron rate was higher than those used in the pots sown with weeds, as these rates could not be detected by chemical assay. However, degradation was assumed to follow first-order kinetics, and therefore, half-life was independent of initial concentration (Hurle and Walker 1980).

### *Herbicide analysis*

Total atrazine was extracted in hot methanol–water (80 : 20) for 2·5 h, whereas available atrazine was extracted by shaking for 1 h in an aqueous 0·02 M KCl solution (Ferris and Haigh 1987). Atrazine concentration in both extracts was determined by using reverse phase high pressure liquid chromatography (HPLC) with a methanol–water mobile phase (60 : 40) and UV detection at 223 nm. Stalder and Pestemer (1980) showed that water-extractable residues estimated the fraction of herbicide available to plants (hereafter referred as available herbicides). Total chlorsulfuron was extracted by shaking for 1 h in methanol–water–acetic acid (80 : 20 : 0·5), and measured by HPLC (Walker *et al.* 1989). The available portion of the total chlorsulfuron was estimated from the ratio of herbicide dose for 50% inhibition of maize root length ($ID_{50}$) growing in treated sand and soil. Bioassay techniques and analysis are reported in Walker and Robinson (1996).

### *Weed response to herbicide residues in a soil-free system*

The sensitivity of mintweed to atrazine and turnip weed to chlorsulfuron was determined in a soil-free system that was described in detail by Jettner *et al.* (1993). It consisted of a 2-pot system; the larger pot held the nutrient and herbicide solution, and the weeds grew in sand in the smaller pot, which was supported above the top of the larger pot by a pot saucer with an appropriate sized hole. The solutions, which were drawn up into the sand by a cotton wick, were 0, 0·01, 0·025, 0·05, 0·1, 0·25, 0·5, 1·0, 2·5, and 10 $\mu$g atrazine/mL, and 0, 0·1, 0·25, 0·5, 1·0, 2·5, 5·0, and 25 ng chlorsulfuron/mL. Treatments were replicated 5 times and kept in a glasshouse with mean air temperatures of 23·1°C (atrazine) and 17·6°C (chlorsulfuron). Seedlings were thinned to 2 per pot, and shoot fresh weights were recorded at 4 (atrazine) or 5 (chlorsulfuron) weeks after sowing.

### *Data analysis*

A logistic equation was fitted to the weed response data (in soil and solution) as a function of herbicide dose by nonlinear regression (Streibig 1988) using GRAPHPAD (Version 3·1):

$$\mathrm{SFW} = A + [(B - A)/\{1 + (10^C/10^X)^D\}]$$

where SFW is shoot fresh weight (mg), $X$ is logarithm of herbicide dose (ng or $\mu$g/mL or g), $A$ and $B$ are the lower and upper asymptotes, $C$ is $\log(ID_{50})$, and $D$ is slope at $ID_{50}$, the dose for 50% response. The logistic equations were used to calculate herbicide concentrations for 85–99% control, and percentage control for several applied concentrations. The changes in herbicide residues (HC) with time ($t$) were fitted by the function $\mathrm{HC} = \mathrm{HC_o e}^{-kt}$, and the first-order half-lives ($t_{1/2}$) were calculated as $t_{1/2} = 0 \cdot 69/k$ (Hurle and Walker 1980). Regressions between half-lives and soil pH were analysed by using STATISTIX (Version 3·1).

## Results

### *Weed response in soils*

Initial response and length of herbicide effectiveness varied considerably between the different soils. Atrazine at 0·5 μg/g, which is equivalent to 0·75 kg/ha, was ineffective for mintweed control in Soil B, but gave 85–100% control for up to 4 weeks in Soil D, 8 weeks in Soils C and F, and 12 weeks in Soil E (Fig. 1*a*). This level of control was achieved when the available atrazine was ≥0·1 μg/g at the time of sowing (Fig. 1*b*). The exception was Soil F, in which 85–100% control was achieved with less residues.

Chlorsulfuron at 10 ng/g, which is equivalent to 15 g/ha, gave 85–100% control of turnip weed for up to 5 weeks in Soils A and B, 15 weeks in Soils D and F, and >15 weeks in Soils C and E (Fig. 2*a*). This high level of control was achieved when the estimated available chlorsulfuron was ≥0·8 ng/g at the time of sowing (Fig. 2*b*).

The logistic model gave good agreement with the combined weed efficacy and available herbicide data for the different soils ($R^2 = 0 \cdot 82$ for atrazine, $R^2 = 0 \cdot 70$ for chlorsulfuron), excluding the data for atrazine in Soil F. Mintweed control increased from no control at 0·01 μg available atrazine/g to 85–100% control at ≥0·12 μg/g (Fig. 3*a*) as estimated from the logistic equation. Similarly, efficacy of chlorsulfuron on turnip weed increased from no control at 0·1 ng available chlorsulfuron/g to 85–100% control at ≥0·93 ng/g (Fig. 3*b*). These estimated concentrations for 85–100% control are very similar to those measured in Figs 1 and 2.

### *Herbicide persistence and availability in soils*

Persistence varied greatly between the different soils. Atrazine half-lives for total residues ranged from 42 days for Soil A (pH 6·0) to 143 days for Soil F (pH 8·7), whereas half-lives of available atrazine were considerably shorter in the same soils (Table 1). Chlorsulfuron half-lives ranged from 27 for Soil A to 135 days for Soil E (pH 8·2). Persistence of both herbicides increased exponentially with soil pH, but the relationship with atrazine was much better with available than total residues (HL, half-life):

$$\text{Total atrazine HL} = 4 \cdot 15 \ \exp(0 \cdot 37 \ \text{pH}) \quad (R^2 = 0 \cdot 58, \ P = 0 \cdot 078)$$

$$\text{Available atrazine HL} = 3 \cdot 02 \ \exp(0 \cdot 33 \ \text{pH}) \quad (R^2 = 0 \cdot 87, \ P = 0 \cdot 007)$$

$$\text{Total chlorsulfuron HL} = 0 \cdot 42 \ \exp(0 \cdot 69 \ \text{pH}) \quad (R = 0 \cdot 99, \ P = 0 \cdot 006)$$

The available portion of the applied herbicides was <25% for the black earths and krasnozem, but was 27–62% for the grey clays (Table 1). The ratio of available to total atrazine residues decreased with time (data not presented).

### *Weed response in solution*

The logistic model gave very good agreement with the response data of the 2 weeds grown in the soil-free system ($R^2 = 0 \cdot 99$ for atrazine, $R^2 = 0 \cdot 96$ for chlorsulfuron). The herbicide doses for 85–99% control were 0·05–0·09 μg atrazine/mL for mintweed, and 0·95–1·58 ng chlorsulfuron/mL for turnip weed. These doses are equivalent to 0·04–0·07 μg atrazine/g and 0·7–1·2 ng chlorsulfuron/g, assuming a soil bulk density of 1·3 g/cm$^3$.

## Discussion

The degree and length of weed control for a given application rate of atrazine and chlorsulfuron varied greatly among different soils of southern Queensland. The examples of weed control presented in Figs 1*a* and 2*a* are for herbicide concentrations that are similar to the recommended field application rates for these weed species. Length of acceptable weed control from these applications ranged from <1 month to >4 months under moist conditions, which would have significant implications on the competitiveness of these weeds in crops. These variations were, in general, related to differences in the concentrations of plant-available residue. Mintweed was controlled (85–100%) only when the soils had ≥0·1 μg available atrazine/g (except for 1 soil), and turnip weed was controlled when soils had ≥0·8 ng available chlorsulfuron/g. These concentrations were similar to those estimated when the weeds were grown in the soil-free system.

Initial weed control was consistently greater in the grey clays than in the black earths for both herbicides. These variations in initial activity are consistent with field experience and with earlier studies in controlled environments (Walker *et al.* 1994). The greater initial activity in the grey clays was due to a greater portion of the applied dose being available for plant uptake (Figs 1*b* and 2*b*). Less of the applied herbicide was adsorbed in these soils, which was related to lower clay content and CEC, particularly Mg content (Walker *et al.* 1994).

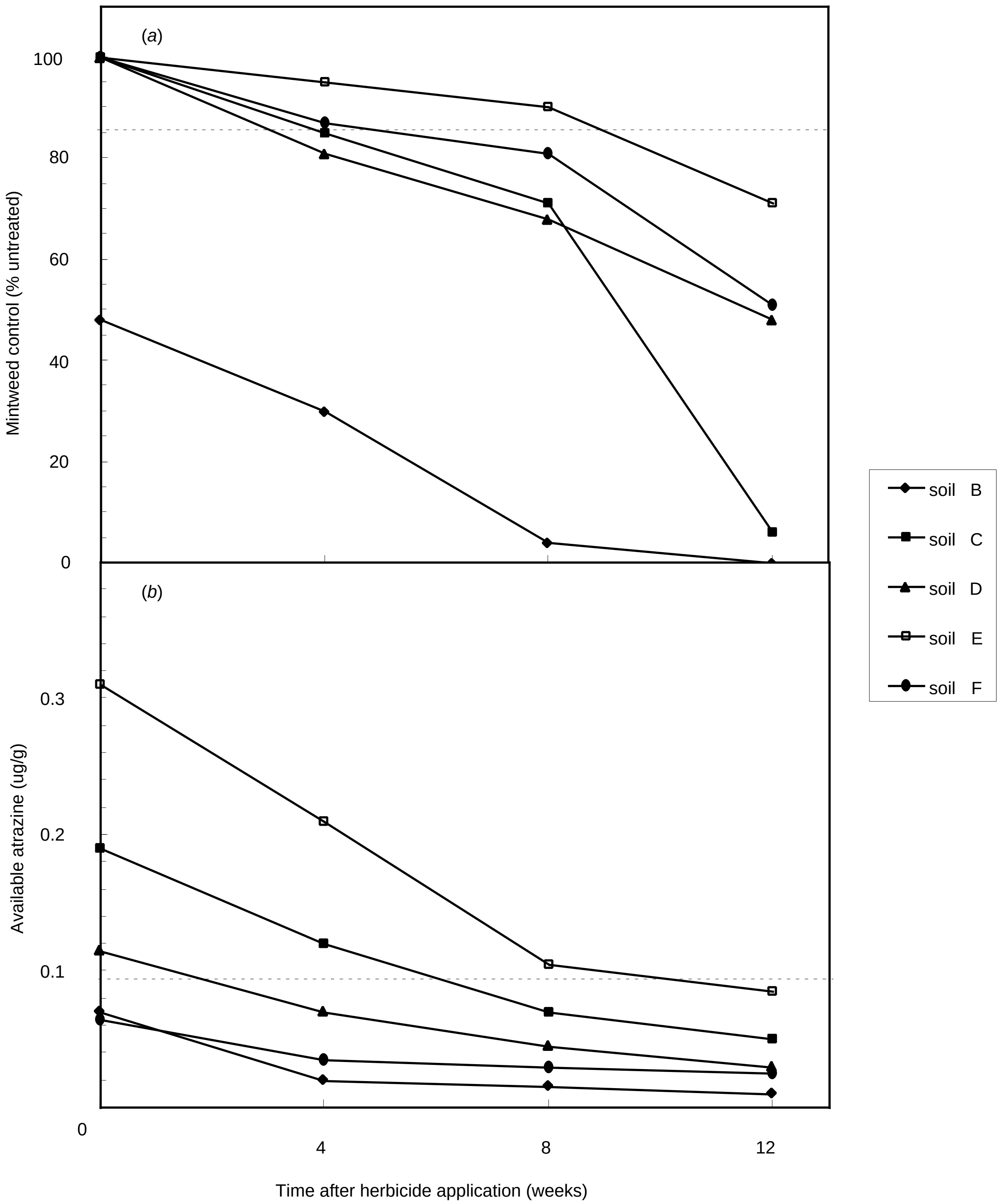


**Fig. 1.** Changes with time in ($a$) mintweed control (shoot fresh weight as % of untreated) and ($b$) available atrazine in surface 10 cm in 5 soils following an initial application of atrazine at $0 \cdot 5$ $\mu$g/g. Weeds were harvested at 4 weeks after each of 4 sowings immediately prior to the next sowing in the same pot. Available atrazine was the water-extractable portion of the residues in soils. Dotted line in ($a$) indicates 85% weed control, and in ($b$) indicates the residue level, above which mintweed was 85–100% controlled, except in Soil F.

Length of weed control was influenced by both availability and herbicide persistence. The differences in initial availability of herbicide residues between soils persisted with time. This was evident in both the measured changes in water-extractable atrazine with time (Fig. 1$b$) and the changes in weed control with

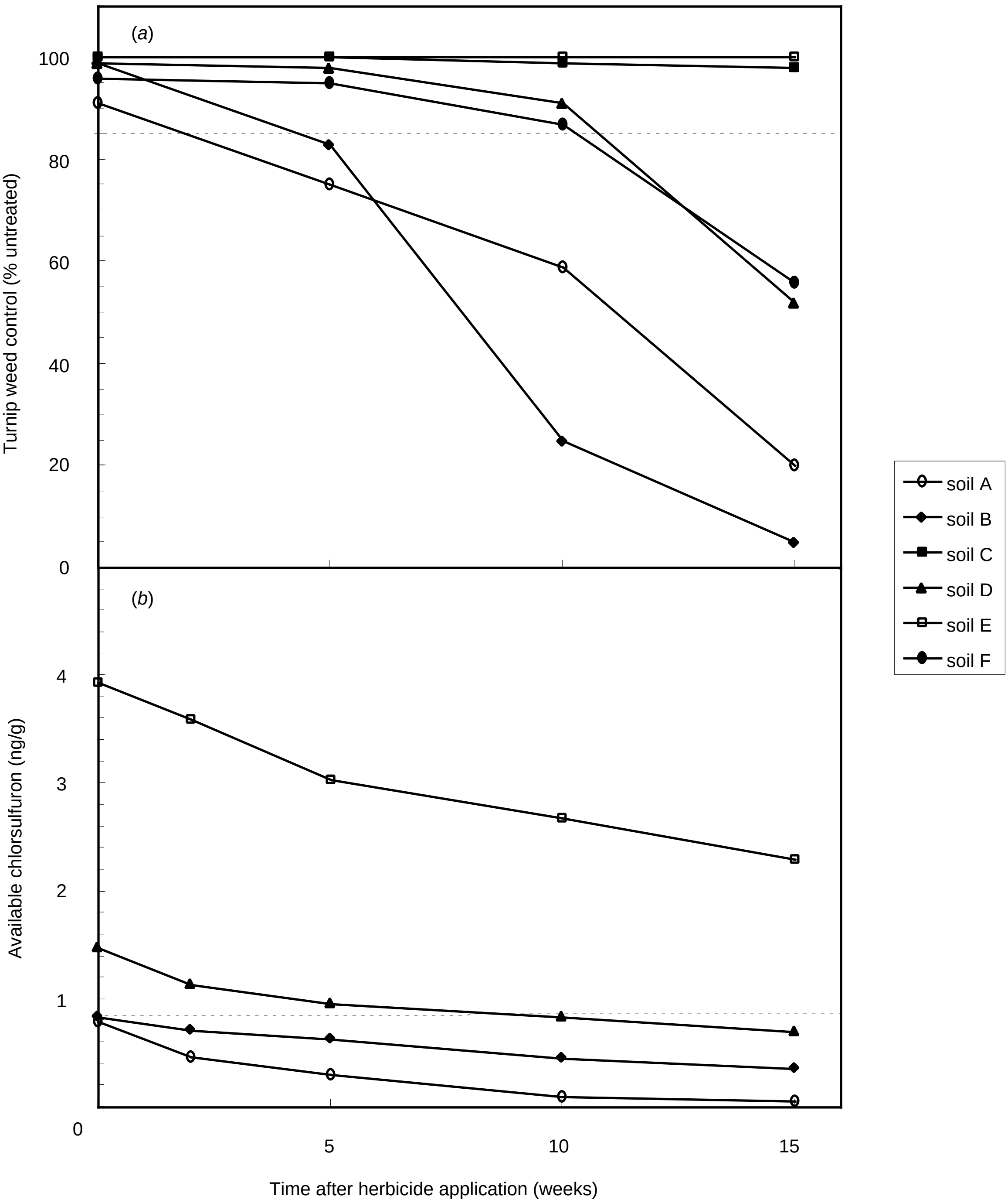


**Fig. 2.** Changes with time in (*a*) turnip weed control (shoot fresh weight as % of untreated) in 6 soils and (*b*) available chlorsulfuron in surface 10 cm in 4 soils following an initial application of chlorsulfuron at 10 ng/g. Weeds were harvested at 5 weeks after each of 4 sowings immediately prior to the next sowing in the same pot. Available portion of chlorsulfuron residues was estimated using the ratio of herbicide dose for 50% inhibition of maize root length growing in treated sand and soil. Dotted line in (*a*) indicates 85% weed control, and in (*b*) indicates the residue level above which turnip weed was 85–100% controlled.

time in black earths and grey clays with similar soil pH (Fig. 2*a*). Length of weed control with chlorsulfuron was much greater in Soils C and E (grey clays) than Soil D (black earth), all of which had a pH of approximately 8.

Soil pH was an important soil property determining atrazine and chlorsulfuron persistence. Relationships between persistence of these herbicides and pH have been recorded for other Australian soils (Holford *et al.* 1989; Walker and Blacklow 1994), and for these soils

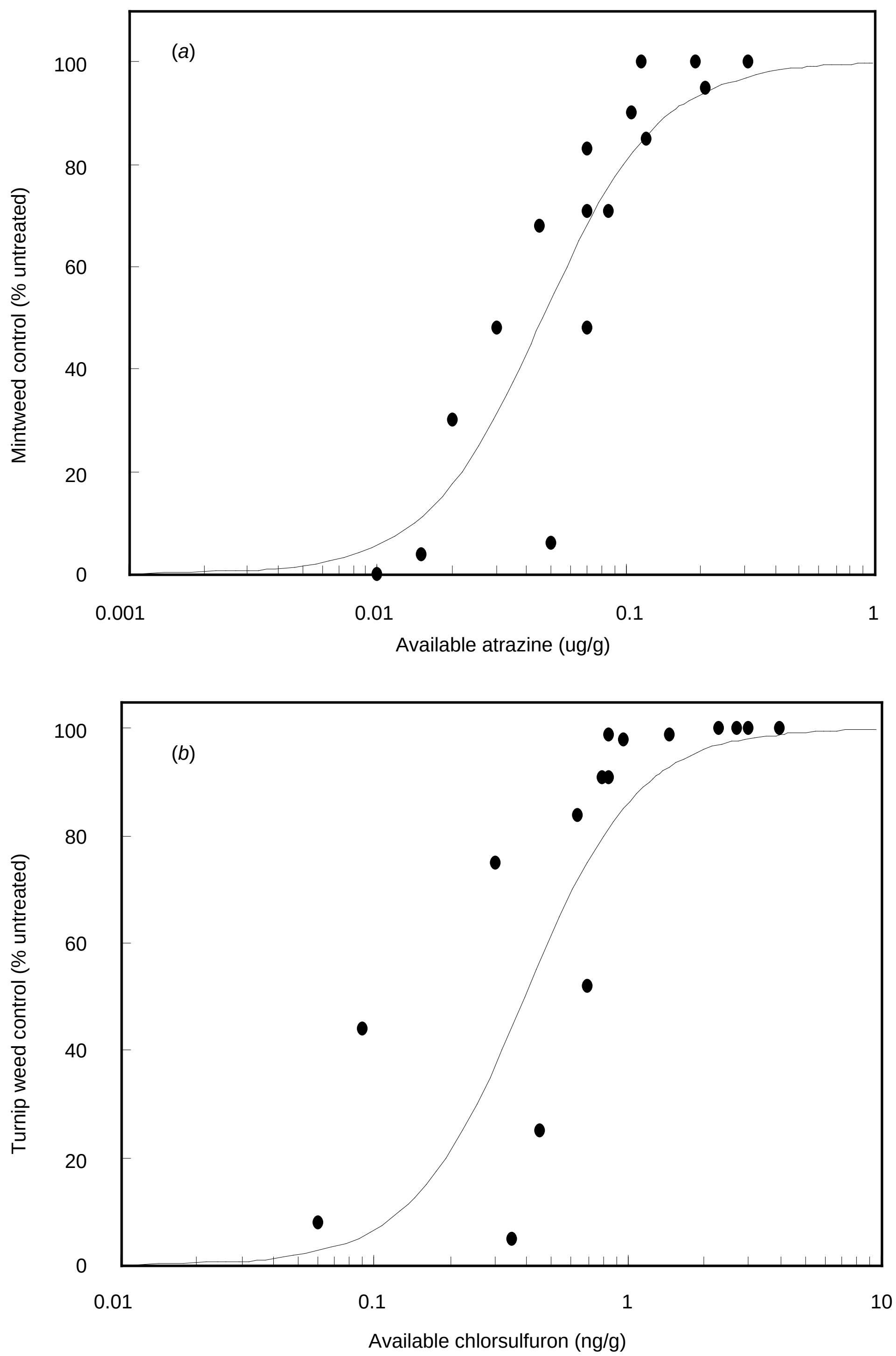


**Fig. 3.** Logistic relationships between weed control and measured or estimated available herbicide residues for (*a*) mintweed with atrazine and (*b*) turnip weed with chlorsulfuron using combined data for 4 soils.

when incubated under constant temperature (Walker *et al.* 1993). Walker *et al.* (1993) showed that soil pH and clay content together accounted for 89% of the variation in atrazine half-lives in soils of southern Queensland, whereas soil pH alone accounted for 96% of the variation in chlorsulfuron half-lives. These strong relationships between persistence and soil pH indicate that degradation is mostly by chemical hydrolysis in these soils, as also noted in other soils (Burkhard and Guth 1981).

The relationship between soil pH and atrazine persistence was greatly improved when available instead of total residues were compared. This indicates that the water-extractable portion of atrazine residues is more accessible to degradation. The half-lives of the available residues were consistently much less than those for total residues, particularly for the black earths. This was due to the decrease with time in the ratio of available to total residues. Increased adsorption of triazines with time has been noted previously in other soils (Boesten and van der Pas 1983). This has implications for predicting weed control and safety of re-cropping. It may be better to predict the persistence of the available rather than the total residues, or else the increases in adsorption need to be incorporated into a prediction model, such as the CALF model by Walker (1987).

A limitation of this study is that the available chlorsulfuron was estimated based on the initial differences between plant response in soils and a non-adsorbing medium. Chlorsulfuron may have also become progressively less available with time, resulting in overestimations of the data at the later times of sowing in Fig. 2*b*. This may explain the poorer fit of the logistic model for chlorsulfuron (Fig. 3*b*) than for atrazine (Fig. 3*a*), which is based on actual measurements of available atrazine.

In conclusion, the length of effective weed control could be estimated for different soils, at least under constant soil water conditions, if the available residues in the root-zone could be predicted and weed sensitivity was known. The concept of predicting herbicide persistence in relation to the safety of re-cropping has been discussed previously (Pestemer and Ausburg 1987; Ferris and Haigh 1992), and this approach could be extended to optimise reliable control of major weeds in different soils.

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