Decreased phytotoxicity of diuron applied over ash of recently burned kangaroo grass (*Themeda australis* (R.Br.) Stapf)

John Toth[A], **Paul J. Milham**[B] and **C. Jill Kaldor**[C]
[A] 4 / 10 Elizabeth Street, Parramatta, New South Wales 2150, Australia.
[B] New South Wales Agriculture, Agricultural Institute, Forest Road, Orange, New South Wales 2800, Australia.
[C] New South Wales Health, LMB 961, North Sydney, New South Wales 2059, Australia.

Summary

It is not uncommon for soil-active herbicides to be applied soon after crop residues are burned. This can reduce herbicide efficacy. To test the hypothesis that a similar effect might occur with the higher rates of herbicide used for total vegetation control, we burned a grass sward (~4000 kg dry matter ha^{-1}) that was dominated by kangaroo grass (*Themeda australis* (R.Br.) Stapf) and within six hours applied diuron (3-(3,4-dichlorophenyl)-1,1-dimethyl urea) at 32 kg a.i. ha^{-1}. There were three other treatments, namely: diuron (32 kg a.i. ha^{-1}) applied after mowing the sward and two controls, i.e. one without diuron or mowing and the other, where the sward was mowed and activated carbon broadcast at 320 kg ha^{-1}, before diuron was applied at 32 kg a.i. ha^{-1}. The latter is a *de facto* (nil diuron) mowed control. Measurements of dry matter yield during the following year showed that the burned pre-treatment had reduced the phytotoxicity of diuron; however, the effect on dry matter did not persist. The treatments affected plant populations in the sward throughout the experiment. Population responses also showed that the burned pre-treatment had reduced the phytotoxicity of diuron. The results of this study and others, indicate that the phytotoxicity of soil-active herbicides is likely to be reduced if they are applied soon after vegetation has been burned.

Introduction

Management of areas where the presence of vegetation is particularly undesirable usually involves its periodic physical removal, often followed by the application of persistent, soil-active herbicides at heavy rates that result in total vegetation control. In the absence of environmental constraints, burning is the traditional method used to remove the vegetation, because the process is quick and requires little equipment.

Burning of crop residues produces activated carbon that can adsorb herbicides and substantially reduce their biological activity (Yuen and Hilton 1962, Hilton and Yuen 1963). Furthermore, there is strong evidence that application of herbicides soon after a fire maximizes adsorption by providing the greatest possible contact between the sprayed chemical and the activated carbon in the ash (Toth *et al.* 1981). These data pertain to cropping, where the rates of herbicide applied may be as little as one tenth those used for total vegetation control. Nevertheless, appreciable losses of phytotoxicity might also occur under similar circumstances at the higher rates of herbicide application used for total vegetation control. Indeed, in an experiment designed for other purposes, we observed apparent reductions in the phytotoxicity of a number of herbicides, when they were applied at rates intended to result in total vegetation control over the ash of kangaroo grass (*Themeda australis* (R.Br.) Stapf). The kangaroo grass sward had been burned inadvertently 24–48 hours before the herbicides were applied. The herbicides included: linuron[A], diuron[B], karbutilate[C], atrazine[D], simazine[E] and bromacil[F].

The observations were subsequently supported by results which showed that the ash produced when paspalum (*Paspalum dilatatum* Poir.) was harvested and burned, adsorbed diuron from solution and reduced the phytotoxicity of diuron (8–32 kg a.i. ha^{-1}) applied over the ash during a pot trial (Toth and Milham 1975). Therefore, it is reasonable to infer that the phytotoxicity of diuron may also be reduced when the diuron is applied at a total vegetation control rate, over the ash of vegetation burned *in situ* several hours earlier. The following experiment was designed to test this inference, without attempting to quantify the amount of diuron adsorbed (if any).

Materials and methods

Site and treatments

A level site was chosen near Bringelly to the west of Sydney, in the land corridor reserved to carry the water supply for the City of Sydney. The soil at the site has a duplex profile with a light clay A-horizon 20–30 cm deep (yellow colour, pH_{Ca} 5.5), overlying a heavy clay subsoil. For at least twenty years prior to the experiment, the vegetation on the site had been burned periodically, with a typical frequency of once every five years. The sward had not been burned for at least three years before the experiment and no herbicides had been used. These conditions were conducive to the development of a uniform grass sward (~4000 kg dry matter ha^{-1}) dominated by kangaroo grass. The other main species present were paspalum and lamb's tongue (*Plantago lancelata* L).

Climatic data were available for the site because it was located within 2 km of official rainfall and temperature monitoring stations (Maryland and Orchard Hills). The long-term mean annual precipitation and max / min temperature are 727.7 mm and 23.0°C / 11.6°C. The corresponding data for the three years of this experiment fell within the ranges 714–930 mm and 22.5–23.5°C / 10.6–11.2°C. None of these values is extreme.

Five blocks were laid out at the site, each block consisting of four plots. The dimensions of each plot were 4 × 4 m. Within a block, plots randomly received one of four pre-treatments: mowing (to ~2 cm) with trash removed; mowing (to ~2 cm) with trash removed, followed by spreading 320 kg ha^{-1} of finely powdered activated carbon (Nuchar C 190N, practical grade, Eastman Organic Chemicals, USA); burning the sward; and, an unmowed control. Within six hours of the pre-treatments, all but the unmowed control plots were sprayed with diuron at 32 kg a.i. ha^{-1}. Within an hour of the diuron being applied, spray-irrigation was commenced on one half of each plot (subplot). A subplot on each unmowed (control) plot was also irrigated. Irrigation was continued for about 2 hours, during which about 50 mm of water was applied. Surface run-off did not result from this intensity and duration of irrigation.

Some further explanation of the treatments is pertinent. First, the sward was burned early on an October morning, when there was little breeze: conditions which consumed most of the litter mat

Footnote
[A] 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea.
[B] 3-(3,4-dichlorophenyl)-1, 1-dimethylurea.
[C] 3-[3-(N-tertbutylcarbamoyloxy) phenyl]-1,1-dimethylurea.
[D] 2-chloro-4-ethylamino 6-isopropylamino s-triazine.
[E] 2-chloro-4,6-bis (ethylamino) s-triazine.
[F] 5-bromo-3-secbutyl-6-methyl uracil.

and standing vegetation, yet minimized the risk of the fire escaping and left much of the ash *in situ*. Secondly, a rate of 32 kg diuron ha^{-1} was used because it is typical of the rates used for total vegetation control. Thirdly, the herbicide rate determined the rate of activated carbon, because a 1:10 (w:w) ratio is expected to adsorb most of the diuron (Toth and Milham 1975), i.e. create a *de facto* control. Lastly, watering-in was used to protect the diuron from photodecomposition (Sheets 1964).

Measurements and statistics

Herbicide effects on the sward were assessed on four occasions, i.e. 6, 12, 24 and 36 months after diuron application.

On the first occasion, the vegetation was cut (to ~2 cm using hand shears) from three quadrats (50 × 50 cm) on every subplot. The number of plants of each species and their dry weights (80°C), were recorded. The treatments had decreased the spatial uniformity of the sward, so for the subsequent harvests, all the vegetation on the subplots was mowed to ~2 cm and the dry weight was recorded. Harvested material was not returned to the plots. The dry weight data were subjected to repeated measurements analysis and univariate analysis. Data for the unmowed pre-treatment were omitted from the analysis for the harvests at 6 and 12 months, because the values could not validly be compared with those from the other two pre-treatments, from which the standing vegetation had been removed at the beginning of the experiment, by either mowing or burning. The number of plants of each species per subplot was transformed using the function log(number + 1) to stabilize variance before analysis (Steel and Torrie 1960). The numbers of plants were also analysed using generalized linear model methods. A Poisson error distribution was assumed and F ratios calculated from mean deviances, to allow for over-dispersion of the data.

Before the final harvest, sward density and botanical composition were assessed by using a point quadrat technique (Goodall 1952), with 200 points per subplot. Analysis of treatment effects on sward density compared the proportions of points at which there was a plant or bare ground, using generalized linear model methods. A binomial error distribution was assumed. Analysis of treatment effects on botanical composition compared the proportions of plants of each of the three principal species. Generalized linear model methods were used and a multinomial error distribution was assumed. Kangaroo grass, lamb's tongue and paspalum constituted at least 95% of the population of the sward. For the statistical analyses, other less abundant species were included in the paspalum category.

Results and discussion

There was no effect of watering-in the diuron (Anon. 1972) at any harvest ($P<0.05$), probably because ~30 mm of rain fell within 72 hours of the diuron being applied. Therefore data for the watered and unwatered subplots were combined when the effects of the treatments were being statistically evaluated. Furthermore, repeated measurements analyses showed that there were no significant correlations between the quantities of dry matter harvested at 6, 12, 24 and 36 months ($P<0.05$), so the results of only the univariate analyses are presented.

The pre-treatments affected the phytotoxicity of diuron in the harvest made after six months, with the activated carbon pre-treatment producing the greatest dry weight of plant material ($P<0.05$, Table 1). This treatment is a *de facto* nil diuron mowed control: the amount of activated carbon applied should have been sufficient to almost eliminate diuron phytotoxicity by seriously depleting the concentration of diuron in the soil solution (Toth and Milham 1975, Hagon 1977). There was a tendency for the sward on the burned plots to yield more than the sward on the mowed plots (Table 1). This tendency strengthened by the harvest made after 12 months, when the yield from the burned plots exceeded the yield from the mowed plots ($P<0.05$, Table 1). This indicates that the burned pre-treatment reduced the phytotoxicity of diuron during the first year of the experiment.

At the harvest after six months, the treatments also affected plant populations, e.g. where diuron was applied following mowing or burning, the number and total weight of lamb's tongue increased relative to both the control and the *de facto* control treatments ($P<0.05$, Table 2). The number of paspalum clumps also tended to increase and each clump to weigh more (Table 2). In contrast, the plant populations in both control treatments were similar ($P<0.05$, Table 2). Therefore, the mowing component of the *de facto* control appears to have impacted little on dry matter production and plant

Table 1. Treatment effects on total dry matter production[A].

Treatments		Dry matter (kg ha^{-1})			
Pre-treatment	Diuron (kg a.i. ha^{-1})	Time after treatment (months) 6	12	24	36
Mowed	32	660 a	1425 a	1330 a	1631 a
Burned	32	796 a	2194 b	1684 a	1721 a
Mowed + activated C	32	2216 b	2769 b	1814 a	2202 a
Unmowed	0	(4465)[B]	(4563)[B]	1693 a	1921 a

[A] Values are means of five replicates and two water treatments. Within a column, values followed by a different letter are significantly different ($P<0.05$).
[B] Dry matter values for the unmowed control, for the harvests at 6 and 12 months, are larger than the other values for the same harvest, because they include much of the vegetation which was removed by the other pre-treatments, at the beginning of the experiment. The dry matter data for the unmowed control are presented for completion; although, for the preceding reason, they were excluded from the statistical analysis.

Table 2. Plant yield and population density six months after diuron treatment, assessed from quadrat harvest data[A].

Treatment		Plant species[B] 1	2	3	1	2	3
Pre-treatment	Diuron (kg a.i. ha^{-1})	Dry matter (kg ha^{-1})			Population density (100's of plants ha^{-1})		
Mowed	32	280 a	195 a	185 a	149 a	165 a	24 a
Burned	32	581 a	141 a	75 a	235 a	125 a	15 a
Mowed + activated C	32	2170 b	15 b	28 a	826 b	31 b	91 b
Unmowed	0	(3941)[C]	(156)[C]	(368)[C]	670 b	33 b	162 b

[A] Values are means of five replicates and two water treatments. Within a column, values followed by different letters are significantly different ($P<0.05$).
[B] Plant species: 1 = kangaroo grass; 2 = lamb's tongue; 3 = paspalum plus other less frequently encountered plants, including: *Vicia* spp.; *Taraxacum officinale* Weber; and, *Gnaphalium purpureum* L. The three principal species constituted at least 95% of the population of plants in the sward.
[C] Dry matter values for the unmowed control, for the harvests at 6 and 12 months, are larger than the other values for the same harvest, because they include much of the vegetation which was removed by the other pre-treatments, at the beginning of the experiment. The dry matter data for the unmowed control are presented for completion; although, for the preceding reason, they were excluded from the statistical analysis.

populations. By analogy we argue that the effects of mowing, in the mowed + diuron treatment, are also likely to have been minimal. Admittedly comparisons between treatment effects would have been stronger had the experiment included all the appropriate controls.

For the harvest made at 12 months, cutting of quadrats was abandoned in favour of mowing whole subplots. This change was prompted because some of the treatments had clearly decreased the uniformity of the sward. As discussed previously, this change in methodology enabled treatment effects on dry matter production to be demonstrated at 12 months, but not thereafter (P<0.05, Table 1). The subsequent failure reflects the complexity of the interactions in the sward, including: interspecific differences in tolerance of fire / mowing, recruitment from the seed bank and adaptation to nutritional impoverishment due to the ongoing removal of harvested material (Tothill 1969, Fisher 1974, Groves 1974, Hagon 1977, Boyd 1978, Stuwe 1993); and (presumed) interspecific differences in diuron tolerance and effects of the pre-treatments on the rate of decomposition of diuron (Harvey 1973). No measurements were made of interspecific differences or of diuron persistence. However, the sward had developed during a long history of burning (>20 years) before the experiment was commenced and sward composition is likely to have been stable under these conditions (Mott and Andrew 1985, Stuwe and Parsons 1997). In addition, burning of kangaroo grass depresses dry matter yield during the following two years more than mowing (Groves 1974). Since the dry matter yield on the burned + diuron plots exceeded that on the mowed + diuron plots, we argue that the yield increase is a conservative indicator of the loss of phytotoxicity caused by adsorption of diuron by the ash.

Sward density and the proportions of the three major plant species, continued to be affected by the treatments after 36 months (Table 3); although, by this time the residual concentration of diuron would have been small, because diuron has a typical half-life of 102–134 days (personal communication, DuPont 1996). The point quadrat technique showed that the mowed + diuron treatment had the highest proportion of bare ground and the two control treatments had the lowest (P<0.05). In addition, there were differences between the treatments in the relative proportions of the three major plant species (P<0.05, Table 3). Thus, in the two control treatments and in the burned pretreatment, kangaroo grass continued to dominate the sward and lamb's tongue and paspalum were less prevalent than in the mowed + diuron treatment (P<0.05, Table 3).

Decreased phytotoxicity of diuron applied at a heavy rate (32 kg a.i. ha^{-1}), over the ash of recently burned kangaroo grass in this experiment, conforms with our unpublished observations for a number of substituted urea, triazine and uracil herbicides applied at total vegetation control rates. Similar results have been obtained for a variety of soil-active herbicides applied at lower rates (Yuen and Hilton 1962, Hilton and Yuen 1963, Toth *et al.* 1981); however, it is likely that not all herbicides will be equally affected (Bovey and Miller 1969). Nonetheless, the pattern of decreased phytotoxicity of soil-active herbicides applied soon after fires is consistent and there is an accepted mechanism, for the phenomenon, *vis.* adsorption of the herbicides by activated carbon in the ash (Toth and Milham 1975). We therefore contend that the weight of evidence supports the proposition that applying residual herbicides over ash of recently burned vegetation carries with it a considerable risk of decreased phytotoxicity, for soil-active herbicides belonging to the most common chemical classes, whether they are applied at rates for selective or total vegetation control. Until this hypothesis is subjected to rigorous testing it would be prudent to apply residual herbicides either well before, or after, the vegetation is burned. Delaying the herbicide treatment by just one week after the fire should substantially decrease the risk of reduced phytotoxicity, because activated carbon rapidly deactivates on contact with soil (Helweg 1975).

Table 3. Effect of treatments on plant populations three years after diuron application[A].

Treatments		Point quadrat proportions[B]	
Pre-treatment	Diuron (kg a.i. ha^{-1})	Sward density Bare : plant	Proportion of plants Species 1: 2: 3
Mowed	32	0.64 : 0.36 a	0.66 : 0.24 : 0.10 a
Burned	32	0.55 : 0.45 ab	0.86 : 0.11 : 0.03 b
Mowed + activated C	32	0.44 : 0.56 c	0.93 : 0.05 : 0.02 b
Unmowed	0	0.49 : 0.51 bc	0.91 : 0.08 : 0.01 b

[A] Values are means of five replicates and two watering treatments. Within a column, values followed by different letters are significantly different (P< 0.05).

[B] Proportion of 200 points where ground was bare or occupied by a plant (sward density) and, for the positions occupied by plants, the proportion of sites occupied by one of the three principal species: 1= kangaroo grass; 2= lamb's tongue; 3= paspalum plus other less abundant species. Kangaroo grass, lamb's tongue and paspalum constituted at least 95% of the population of the sward.

Acknowledgments
We thank: ICI Australia Ltd. for supplying the diuron (an 80% a.i. powder formulation); Sydney Water for making a secure field site available; the Australian Bureau of Meteorology, NSW Regional Office, for rainfall and temperature records; Russell Silk for field assistance and, Richard Medd for helpful suggestions about the presentation of the data. The research was funded by NSW Agriculture.

References

Anon. (1972). Product Information Bulletin No. PM 117. ICI Australia Ltd., Rural Chemicals Division, Melbourne, Australia.

Bovey, R.W. and Miller, F.R. (1969). Effect of activated carbon on the phytotoxicity of herbicides in a tropical soil. *Weed Science*, 17, 189-92.

Boyd, M. (1978). Pasture recovery after bushfires. *Journal of Agriculture* 76, 128-31.

Fisher, H.J. (1974). Effect of nitrogen fertiliser on a kangaroo grass (*Themeda australis*) grassland. *Australian Journal of Experimental Agriculture and Animal Husbandry* 14, 526-32.

Goodall, D.W. (1952). Some considerations in the use of point quadrats for the analysis of vegetation. *Australian Journal of Scientific Research, Series B* 5, 1-41.

Groves, R.H. (1974). Growth of *Themeda australis* grassland in response to firing and mowing. Field Station Record 13, 1-7.

Harvey, R.G. (1973). Influence of cropping and activated carbon on persistence of atrazine in sand. *Weed Science* 21, 204-6.

Hagon, M.W. (1977). Effects of competition, herbicides and activated carbon on establishment of Australian grasses. *Weed Research* 17, 297-301.

Helweg, A. (1975). Degradation of ^{14}C-maleic hydrazide in soil as influenced by adsorption on activated carbon. *Weed Research* 15, 129-33.

Hilton, H.W. and Yuen, Q.H. (1963). Adsorption of several pre-emergence herbicides by Hawaiian sugarcane soils. *Journal of Agricultural and Food Chemistry* 11, 230-4.

Mott, J.J. and Andrew, M.H. (1985). Effect of fire on the grass understorey of Australian savannas. Technical memorandum, CSIRO Institute of Biological Resources, Division of Land and Water Resources, No. 85-2, pp. 77-91.

Sheets, T.J. (1964). Metabolism of α-chloro-N,N-diallylacetamide and

2-chloroallyl-N,N-diethyldithiocarbamate by plants. *Agricultural and Food Chemistry* 12, 30-3.

Steel, R.G.D. and Torrie, J.H. (1960). 'Principles and Procedures of Statistics'. (McGraw-Hill Book Co., New York).

Stuwe, J. (1993). The role of fire in ground flora ecology. *Victorian Naturalist* 110, 93-5.

Stuwe, J. and Parsons, R.F. (1977). *Themeda australis* grasslands on the Basaltic Plains, Victoria: floristics and management effects. *Australian Journal of Ecology* 2, 467-76.

Toth, J. and Milham, P.J. (1975). Activated-carbon and ash-carbon effects on the adsorption and phytotoxicity of diuron. *Weed Research* 15, 171-6.

Toth, J., Milham, P.J. and Raison, J.M. (1981). Ash from rice stubble inactivates thiobencarb and molinate. *Weed Research* 21, 113-7.

Tothill, J.C. (1969). Soil temperatures and seed burial in relation to the performance of *Heteropogon contortus* and *Themeda australis* in burnt native woodland pastures in eastern Queensland. *Australian Journal of Botany* 17, 269-75.

Yuen, Q.H. and Hilton, H.W. (1962). The adsorption of monuron and diuron by Hawaiian sugarcane soils. *Journal of Agricultural and Food Chemistry* 10, 386-92.