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Environmental Contamination and Toxicology

Movement of Bromacil and Hexazinone in a Municipal Site

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Herbicides provide a convenient means of weed control because of their effectiveness, low cost (relative to alternative strategies) and ease of application. 'Hyvar x'® and 'Velpar'® weed killers are very effective broad spectrum herbicide treatments for general weed control in non-cropland areas such as forests, industrial and right-of-way weed control areas. However, residues at the application site and even some distance away via movement through soil layers can present an environmental problem.

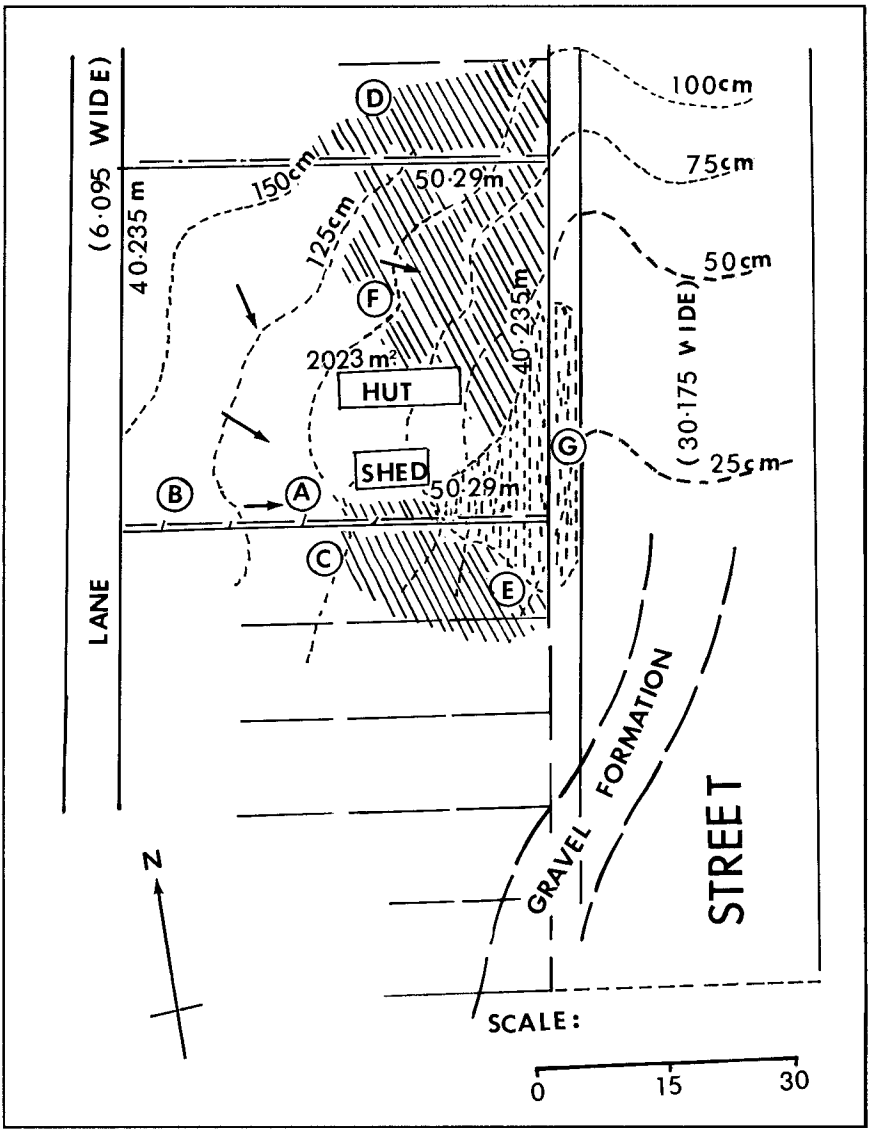
The active ingredient of 'Hyvar x'® is bromacil (5-bromo-3-sec-butyl-6-methyl uracil) and is moderately soluble in water to 0.815 g/litre at 25°C (Worthing and Walker 1983). It is considered to be moderately to highly mobile (Rhodes *et al.* 1970; Weber and Best 1972) and can persist in the soil up to 2 years in detectable amounts (Bovey *et al.* 1967).

Hexazinone (3-cyclohexyl 1-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione) is the active ingredient of 'Velpar'® and is water soluble (33 g/L @ 25°C) (Worthing and Walker 1983) and readily leaches in soils (Rhodes 1980). Hence, depending upon rainfall and slope, the herbicide can be transported laterally following surface applications (Harrington *et al.* 1982).

The area examined was situated at Tibooburra, a town located in the north-western region of New South Wales, Australia, (latitude 29° 26' and longitude 142° 01'). This area experiences a climate characterised by hot summers (35°C), cold winters (10°C) and low rainfall (226 mm per annum). The present report describes the movement of bromacil and hexazinone away from the target areas (namely, weed control around buildings and gas pipeline valve sites) through the upper layers of soil to affect non-target native trees (eg. *Eucalyptus* sp.) and shrubs (eg. *Melaleuca* sp. and *Callistemon* spp.) some distance away.

MATERIALS AND METHODS

The area selected for study was sampled in 1988 at seven sites (Fig. 1) after



KEY:

Area of dead trees and shrubs

Area where water pools

Direction of water flow

Figure 1. Schematic figure of sampling areas at the municipal site.

it was noticed that native trees around the sites were dying after the area was sprayed with 'Hyvar x'®. The soil properties such as field texture, pH, organic matter, phosphate, exchangeable cations and loss on drying were measured soon after sample procurement.

Table 1 (a). Soil Properties

Site	Depth (cm)	Exchangeable Cations Ca	Mg	Ca/Mg	Loss on Drying
(A)	0-15	8.7(72.0)	2.2 (18.0)	4.0	1.0
	15-30	14 (59.8)	4.7 (19.4)	3.1	9.8
	30-45	15 (66.0)	4.2 (18.9)	3.5	10.4
	45-60	15 (66.2)	3.6 (16.2)	4.1	9.0
(B)	0-15	12 (78.5)	1.8 (11.4)	6.9	1.0
	15-30	26 (87.6)	2.9 (9.7)	9.0	9.0
	30-45	23 (88.6)	2.1 (9.7)	11	9.0
	45-60	20 (88.0)	1.7 (7.8)	11	7.0
(C)	0-15	7.5(73.8)	1.3 (13.0)	5.7	2.0
	15-30	18 (75.7)	3.8 (16.4)	4.6	6.0
	30-45	21 (67.1)	5.0	4.3	8.0
	45-60	16 (72.2	3.0 (13.4)	8.0	
(D)	0-15	3.8(69.3)	0.89(16.1)	4.3	5.0
	15-30	15 (86.6)	1.6 (8.9)	9.8	9.6
	30-45	23 (81.2)	4.3 (14.9)	5.5	7.8
	45-60	17 (73.7)	5.3 (22.6)	3.3	7.0
(E)	0-15	14.9(73.8)	1.0 (15.3)	4.8	1.08
	15-30	11 (67.5)	3.3 (19.3)	3.5	12.0
	30-45	11 (56.6)	4.5 (22.1)	2.6	14.0
	45-60	18.2(75.8)	1.6 (15.0)	5.1	10.0
(F)	0-15	16 (79.3)	2.4 (12.1)	6.5	2.0
	15-30	21 (62.8)	5.4 (16.3)	3.8	5.9
	30-45	16 (64.1)	4.1 (16.3)	3.9	9.3
	45-60	21 (75.1)	2.9 (10.7)	7.0	7.0
(G)	0-15	13 (75.8)	2.6 (15.2)	5.0	2.0
	15-30	18 (71.2)	3.8 (15.4)	4.6	12.9
	30-45	15 (70.8)	2.7 (12.7)	5.6	13.0
	45-60	13 (70.8)	2.2 (11.9)	5.9	13.0

Twenty eight soils were collected from four levels at the different sites and their properties are listed in Table 1(a) and (b). The composite samples from each plot were thoroughly mixed, air dried and stored at room temperature.

RESULTS AND DISCUSSION

Soil samples after initial screening, were analysed primarily for bromacil and hexazinone. Herbicide residues were found at five of the seven sites examined (Table 2). Bromacil was detected at five sites whilst hexazinone ('Velpar'®) was also found at four of the sites examined. The variable interval between sample collection and extraction may have contributed

Table 1 (b). Soil Properties

Site	Depth (cm)	Field[a] Texture	pH[b]	Organic[c] Matter	EC[d]	Phosphate[e] Bray Sorption
(A)	0-15	SCL-	7.6	1.6	1.9	39vl
	15-30	CL+	7.9	<1	4.2	131o
	30-45	CL+	8.2	<1	5.3	<31o
	45-60	SL+	8.3	<1	4.8	<3vl
(B)	0-15	SCL	7.6	2.3	12	48vl
	15-30	CL	7.9	<1	26	31o
	30-45	LC̲cS	8.1	<1	23	<31o
	45-60	LcC̲S	8.3	<1	20	<3vl
(C)	0-15	LS	8.0	2.1	0.22	55vl
	15-30	LC	8.1	<1	0.15	11vl
	30-45	LC	8.3	<1	0.81	611o
	45-60	LC	8.3	<1	2.9	<31o
(D)	0-15	SL	7.3	<1	0.13	23vl
	15-30	CL	7.9	<1	0.20	9vl
	30-45	LC	7.9	<1	0.27	31o
	45-60	LC	8.1	<1	0.85	31o
(E)	0-15	SL	7.2	1.2	0.28	68v
	15-30	LC	8.1	<1	0.23	14vl
	30-45	LC	8.1	<1	1.4	19vl
	45-60	LC̲c	8.2	<1	1.5	<3v
(F)	0-15	LC	8.0	1.1	3.1	61o
	15-30	LC	8.1	<1	3.8	91o
	30-45	LC	8.2	<1	3.6	<31o
	45-60	SCL	8.2	<1	4.1	<31o
(G)	0-15	LC-	8.0	<1	0.27	25vl
	15-30	LC	7.9	<1	0.31	5lo
	30-45	LC	8.3	<1	0.47	<31o
	45-60	LC	8.4	<1	0.50	<31o

[a] **Field Textures:**
LS - loamy sand -: slight lighter
SL - sandy loam +: slightly heavier
SCL - sandy clay loam
LC̲cS - light clay with sand content

[b] pH̲ of a 1:5 v/v soil suspension in 0.01M $CaCl_2$ at 25°C

[c] Organic matter content (dag/Kg) of oven dry soil, calculated from organic carbon content by dividing by 0.57

[d] Electrical conductivity (ds/m) % 1:5 m/v soil suspension in water at 25°C

[e] Phosphate sorption rating -vl: very low; lo: low

[f] Exchangeable cation concentrations (cmol(+)/Kg and, in parentheses, as a percentage of the total.

Table 2. Residual concentrations of bromacil and hexazinone at a municipal site in ppm.

Site	Depth (cm)	Pesticide Residues (mg/kg) Bromacil	Hexazinone
(A)	0-15	0.77	ND
	15-30	1.25	0.27
	30-45	ND	<0.1
	45-60	ND	ND
(B)	0-15	1.20	ND
	15-30	ND	ND
	30-45	ND	ND
	45-60	ND	ND
(C)[u]	0-15	1.75	0.24
	15-30	<0.2	<0.1
	30-45	ND	ND
	45-60	ND	ND
(D)[u]	0-15	ND	ND
	15-30	ND	<0.1
	30-45	ND	ND
	45-60	ND	ND
(E)[u]	0-15	ND	ND
	15-30	ND	<0.1
	30-45	ND	ND
	45-60	ND	ND
(F)	0-15	3.38	1.15
	15-30	<0.2	<0.1
	30-45	ND	ND
	45-60	ND	ND
(G)	0-15	1.10	ND
	15-30	ND	0.26
	30-45	ND	<0.1
	45-60	ND	ND

ND = Not detected [u] = Untreated area * = dry basis

some error. Because this interval could not be controlled, some hexazinone and bromacil may have escaped detection, though this is not known.

The detection of hexazinone was unexpected as 'Hyvar x'® (bromacil) was said to have been the only herbicide used for weed control around the buildings and pipeline valve sites for some years.

Herbicide residues were extracted from soil samples with methanol/water (2:1, v/v) in conical flasks. Samples of 20 g were initially moistened with

30 mL water, followed by 60 mL methanol and placed onto an orbital mixer for 1 hour. The sample mixtures were then filtered (Whatman #1 filters) into graduated measuring cylinders and volumes of filtrates noted. A 50 mL aliquot of each filtrate was then transferred into a 250 mL round bottom flask and the organic solvent removed on a rotary evaporator. The residual aqueous fractions were then treated with 15 mL aliquots of saturated sodium chloride solution and extracted with three 100 mL portions of dichloromethane. The extracts were then passed through a filter containing anhydrous sodium sulphate (ca 30 g) into 500 mL round bottom flasks. Extracts were evaporated to dryness on a water bath at 30-40°C with a rotary evaporator, the residues were then redissolved in 10.0 mL of methanol and screened initially by high-performance liquid chromatography (HPLC). Recoveries of greater than 90% were obtained from soils fortified with hexazinone and bromacil at levels of 0.5 ppm and 1.0 ppm.

A Waters Associates liquid chromatograph fitted with a Model 6000A solvent delivery system and interfaced with a M450 detector was used. The chromatography column was a Spherisorb ODS 5 (25 cm x 4 mm id). The mobile phase consisted of methanol/water (65:35) and the flow rate set at 1.0 mL/min. All samples were analysed by HPLC at a general monitoring wavelength of 254 mm (attentuated @ 0.02 aufs). Samples in which bromacil was detected, were subsequently analysed at 280 nm (a more sensitive wavelength for bromacil).

Confirmatory and check analyses were carried out on a Varian gas chromatograph model 3700 equipped with an electron capture detector containing a Ni63 (8mCi) ionization source and a thermionic specific detector (rubidium silicate bead) for bromacil and hexazinone residues respectively. The chromatographic column was 1.8 m x 4 mmid Pyrex glass packed with 10% OV-17 an acid washed Chromsorb W 80/100 mesh. The carrier gas was nitrogen, which was dried by passing through a molecular sieve. The flow rate was 30 mL/min. Attentuation was 128, with injector, column and detector at 230°C, 210°C and 290°C respectively. A herbicide mixture of analytical grade bromacil, metribuzin, simazine, hexazinone, diuron, propazine and linurone was used as a soil residues screening standard. The herbicide residues in the soil layers were calculated as parts per million (ppm).

Hexazinone readily leaches to lower depths because of its higher water solubility and leaching is an important means of dissipation from soil (Rahman 1981; Rhodes 1980). The patterns of dead native flora at the site (Fig. 1) also suggests some lateral movement of hexazinone. The die-back of the trees and shrubs, *Eucalyptus* sp. in particular, was noticeable following heavy rainfall for this area which resulted in surface water flow and water ponding. The rainfall for 1987 was 372.8 mm per annum (146.8 mm above the average) with 126 mm falling between October 1987 and March 1988.

The native flora in the Tibooburra area is of the dry sclerophyll type and adapted to the poor soil types which are typical for the region (ref. Table 1.) These sclerophyll adaptations are suited to the semi-arid climate of the area and as such are very efficient in moisture absorption and usage. Because of this, 'Velpar'® (hexazinone) is known to be very toxic to *Eucalyptus* and many other native species eg. *Melaleuca* sp. and Callistemon sp. (NSW *Forestry Commission* 1988 *Private communication*). However, blue berries for example, are tolerant to hexazinone at rates that give selective control of many weed species associated with this crop (Jensen and Kimball 1985).

The highest recommended rate for non cropland use of hexazinone in the USA is 12 kg active ingredient/ha (Beste 1983). This rate of application is equivalent to 48 kg/ha of 'Velpar'®. At this rate of treatment, hexazinone has affected vegetation beyond the site of application (up to 100 metres off-site) because of its mobility in soils and surface run-off (Feng 1987). Hence this herbicide has the potential to destroy native non-target vegetation some distance away from the point of application.

This study illustrates the consequences of applying a mobile herbicide, whether by accident or intentionally, which can move away from target areas to affect or destroy xerophytic native species.

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