

## Field Dissipation and Environmental Hazard Assessment of Clomazone, Molinate, and Thiobencarb in Australian Rice Culture

WENDY C. QUAYLE,<sup>\*,†</sup> DANIELLE P. OLIVER,<sup>‡</sup> AND SHARYN ZRNA<sup>†</sup>

CSIRO Land and Water, PMB 3, Griffith, NSW, 2680 Australia, and  
 CSIRO Land and Water, PMB 2, Glen Osmond, SA, 5064 Australia

The fates of clomazone [2-(2-chlorophenyl)methyl-4,4-dimethyl-3-isoxazolidinone], molinate (S-ethyl hexahydro-1-H-azepine-1-carbothioate), and thiobencarb {S-[(4-chlorophenyl)methyl]diethylcarbamothioate} applied to rice were studied at two locations in New South Wales (Australia). Rates of dissipation (DT<sub>50</sub>) from floodwaters and soils were measured. Dissipation of the three herbicides from water and soil can be best explained by a first-order decay process. DT<sub>50</sub> values for clomazone, molinate, and thiobencarb were 7.2, 5.1, and 3.5 days, respectively, in water and 14.6, 23.9, and >46 days, respectively, in surface soil. Maximum measured concentrations of clomazone, molinate, and thiobencarb in floodwaters were 202, 1042, and 148 μg/L, respectively, taking 18.4, 26.4, and 21.4 days to dissipate to concentrations set to protect aquatic ecosystems. A hazard assessment identified clomazone as presenting a low environmental hazard while molinate and thiobencarb presented a medium environmental hazard when used at registered field rates.

**KEYWORDS:** Molinate; thiobencarb; clomazone; thiocarbamate herbicide

### INTRODUCTION

The Australian rice industry is considered to be one of the lowest users of agrochemicals while producing some of the highest yields (average 9.47 t/ha) of all rice producers in the world (1, 2). These efficiencies are achieved partly through favorable climatic conditions, including long periods of daily sunshine, and partly through the crop being grown in rotation with field crops, which usually include legumes and pasture. This type of growing system minimizes the build-up of pests and disease (2). Despite these practices, pesticide use remains significant (3). Some of these agricultural chemicals can be harmful to aquatic organisms, and contamination of drainage channels and creeks by pesticides used in rice production remains a concern in southeastern Australia (4). Clomazone [2-(2-chlorophenyl)methyl-4,4-dimethyl-3-isoxazolidinone], molinate (S-ethyl hexahydro-1-H-azepine-1-carbothioate), and thiobencarb {S-[(4-chlorophenyl)methyl]-4-[(trifluoromethyl)sulfinyl]pyrazole} are commonly applied to rice floodwaters in Australian rice growing areas for the control of broad leaf weeds, particularly barnyard grass (*Echinochloa* spp.) and dirty dora (*Cyperus difformis*).

More than 90% of Australian rice is grown in irrigated areas of New South Wales in the Murrumbidgee Irrigation Area (MIA), the Coleambally Irrigation Area (CIA), and the Murray Valley Irrigation Area (MV) with water sourced from the

Murrumbidgee and Murray Rivers. Up to about 150000 ha (depending on water availability) of rice are planted annually, producing in excess of 1 million tons of rice. This provides ~\$300 million (U.S. dollars) in annual revenue mainly through exports (1, 2).

Information in the literature is available for the persistence of thiobencarb and molinate from laboratory studies (5–8) and in controlled water management conditions (9–11). Some studies on the dissipation of thiobencarb and molinate in commercial rice fields and in agricultural drains have also been conducted (12–16). However, there are very few published studies on the behavior of clomazone in flooded rice growing conditions. Clomazone has been registered for use on rice in Australia and South American rice-producing countries for several years and only very recently in the United States. There has been one study carried out to examine its persistence and movement on paddy topsoils in laboratory experiments (17) and some investigations documented by the Californian Department of Pesticide Regulation (18). Therefore, the environmental fate of this chemical was warranted to ensure its safer use.

To minimize environmental impacts associated with herbicides, growers are required to withhold treated water on a farm for a minimum period of 21–28 days to allow time for pesticides to dissipate prior to water release into irrigation drains. However, the amount of dissipation gained by this withholding period under Australian growing conditions is not fully known. Knowing the dynamics of these chemicals and the environmental hazards that they may present, based on existing management goals, is required by the Australian rice industry. Thus, general

\* To whom correspondence should be addressed. Tel: +61-2-6960-1500. Fax: +61-2-6960-1600. E-mail: Wendy.Quayle@csiro.au.

<sup>†</sup> CSIRO Land and Water, Griffith.

<sup>‡</sup> CSIRO Land and Water, Glen Osmond.

**Table 1.** Mean Water Quality Data in Small Trial Plots and a Commercial Rice Field

parameter	units	mean	min	max	N
trial plots					
pH <sup>a</sup>		8.03	7.02	9.77	146
EC <sup>a</sup>	dS/m	0.34	0.12	0.74	146
total suspended solids <sup>b</sup>	mg/L	27	<1	268	248
temperature <sup>c</sup>	°C	21.9	8.0	36.0	2303
depth	cm	9.6	2.9	16.9	192
commercial rice field					
pH		7.8	7.35	8.34	27
EC	dS/m	0.34	0.13	0.63	27
total suspended solids	mg/L	10.6	1	32	59
temperature <sup>d</sup>	°C	18.5	6.6	30.9	2006
depth	cm	14.2	9.8	24.8	184

<sup>a</sup> EC and pH were measured using a Hanna multiprobe instrument on site.

<sup>b</sup> Total suspended solids were determined by vacuum filtering 200 mL of sample through preweighed GF/F filters (Whatman). The filters were dried at 80 °C overnight, cooled in a desiccator, and reweighed. <sup>c</sup> Temperature logged every half hour from 17/10/02 to 4/12/02 using a temperature probe and Campbell Datalogger.

<sup>d</sup> Temperature logged every 15 min from 17/10/01 to 3/11/01 using a temperature probe and Campbell Datalogger.

guidelines can be formulated for better management and capacity can be developed to be able to predict the behavior of other chemicals that may be used in the future (19).

## MATERIALS AND METHODS

**Trial Plot Construction.** A replicated small plot trial was set up in a rice field at a rice farm approximately 40 km from Griffith, New South Wales, southeastern Australia. The plots were constructed on soils known as transitional red brown earths or Xeralfs with surface pH<sub>w</sub> values of 5.5–6.4 and mean clay contents (<2 μm) of 36% at 0–0.1 m and 67% at 0.2–0.3 m (20, 21). A single row of 12 plots (5 m × 10 m) with earthen banks, separated by a trench (approximately 3 m wide and 1 m deep), was used in the trial. Each plot was supplied independently with water from a supply channel running parallel to the plots. The water volume in three of the plots was obtained by measuring the water depth within circular flumes enabling the water application volume to be calculated. The plots were prepared by filling them with water and then allowing the water to infiltrate naturally so that enclosing soils remained muddy, but there was no free-standing water. The plots were then refilled. This procedure was followed to obtain a reasonable estimate of water fill volume on the day of application without the water required to saturate enclosing soils. Water depths were also measured manually (two measurements/plot) by a method using rulers mounted at either end of each plot (22). After the plots had been prepared, irrigation was managed by the farmer for the duration of the trial. He also managed the flumes and siphons as needed to maintain a water depth of between 4 and 10 cm.

**Trial Plot Treatments.** Molinate, thiobencarb, and clomazone persistence were evaluated with respect to intermittent irrigation at typical application rates. The chemicals applied were all commercial formulations of Magister (containing 480 g L<sup>-1</sup> clomazone), Ordram (containing 960 g L<sup>-1</sup> molinate), and Saturn (containing 800 g L<sup>-1</sup> thiobencarb), which are emulsifiable concentrates. Chemical treatment 1 consisted of 2.0 L/ha Ordram being applied to a set of four small plots on 10/18/02 followed by 3.75 L/ha Saturn on 10/30/02. Chemical treatment 2 consisted of the application of 3.75 L/ha Ordram and 0.5 L/ha Magister on 10/18/02 to a separate set of four trial plots. Twelve carboys containing 5 L of irrigation supply water were made up with the different chemical treatments. The chemical was applied by pouring the mixture from the carboy, while walking the length of each plot in a single pass. The same procedure was repeated for four control plots using 5 L of untreated irrigation water. This approach raised the turbidity as compared with the commercial rice field in which the chemical had been applied by air (Table 1). However, it was considered a valid approach considering that in Australia, chemicals are commonly applied

to rice using the soluble chemical water injection in rice technique, which involves delivering the chemical by driving a motorbike through flooded rice bays.

**Trial Plot Sampling.** Water samples taken immediately after the application were designated as the day 0 samples. Additional samples were collected at 1, 2, 3, 4, 5, 7, 10, 12, 17, 19, 21, 23, 26, 31, 33, 38, 40, 45, and 48 days after application. Water samples for pesticide analysis were collected in 1 L amber bottles, which had been rigorously cleaned in detergent, 10% HCl, and methanol (23). At collection, the bottle was first rinsed with approximately 100 mL of sample three times and these rinses were discarded prior to the sample collection. The bottle was completely filled with sample to minimize the headspace. Samples were collected from either end of the plot, and the bottle opening was covered with aluminum foil and sealed with a screw-on lid. Samples were stored on ice in an insulated box for transport to the laboratory. Boardwalk access permitted sample collection without disturbing bottom sediments.

Two soil samples, one from opposite ends of each plot, were collected by inserting a tube (10 cm long × 5 cm diameter) into the soil. The sediment water interface was maintained using this procedure, and the tubes were propped upright during collection and transport. Soil samples were collected at the following time intervals: 4, 7, 10, 12, 17, 23, 26, 31, 33, 38, 40, 45, and 48 days after application. Previous studies seem to indicate that soil concentrations tend to increase over the first 4–8 days for thiobencarb and molinate, respectively (13). Four days after application, the first soil sampling event was chosen in order to allow soils to settle after the application of the chemicals as well as to compromise on sample analysis while still intending to capture the peak soil concentration. Estimates of heterogeneity were determined by calculating the mean soil pesticide concentration of the two samples taken from each plot and then calculating standard deviations of the mean data from the four replicate bays for each treatment.

**Physical and Chemical Analysis of Water in the Trial Plots.** Total suspended solids were analyzed according to APHA (24). Water pH and electrical conductivity (EC) were measured using a Horiba DC10 water sensor during each sampling event. The water temperature was logged in three of the plots at half hourly intervals with a Campbell Datalogger.

**Commercial Rice Field—Description.** A commercial rice field located on a farm in the MIA, about 35 km southeast of Griffith, New South Wales, Australia, was monitored for molinate and thiobencarb concentrations, water depth, and chemical and physical parameters in 2001. The soil consisted of gray cracking clay that, according to EM31 and EM38 surveys, was uniform across the extent of the field. These soils are known as self-mulching gray clays or Entic Pelloxererts (20). In the top 0.1 m, the clay (<2 μm) percentage is 60%, the bulk density is 1250 kg m<sup>-3</sup>, and the long-term infiltration rate for these soils has been measured as 1–2 mm day<sup>-1</sup> (21). The field layout consisted of a laser-leveled paddock with bankless channel irrigation.

The total area of the field was 15.72 ha divided into 7 bays. Six bays were approximately 2.4 ha each with the remaining bottom bay adjacent to the drain being 1.3 ha. The slope of the field was 1:1429. A summary of the field water and pesticide management regime over the monitoring period is given in Table 2.

**Commercial Rice Field Sampling.** Water samples for pesticide, physicochemical, and total suspended solid analyses were collected in the same manner as described previously for the plot sampling. Water samples were taken from three different bays located proximal, midway, and distal from the supply water inlet at the top of the field. Each bay was sampled along the length of each bay at three locations, from approximately similar water depths (i.e., along the slope). Each water sample was analyzed for molinate and thiobencarb separately. A mean concentration of each chemical was determined for each bay, and these mean values were used to determine a mean and standard deviation for the whole field. The water depth was measured manually using rulers mounted on pegs at four positions in each bay (22).

**Pesticide Extraction. Water Samples.** Molinate, thiobencarb, and clomazone were usually extracted immediately from 200 mL aliquots of water sample. If immediate extraction was impossible, the samples were stored frozen. Analysis followed thawing at 4 °C overnight. Solid-phase extraction (SPE) using 3 mL IST ENV+ cartridges (supplied by

**Table 2.** Summary of Water and Pesticide Management in the Commercial Rice Field

date	event
05/10/2001	field filling started
12/10/2001	field "locked up", i.e., no water inflow or surface drainage
15/10/2001	field sown
17/10/2001	field aerially sprayed with 2.0 L ha <sup>-1</sup> Ordram (1.92 kg ha <sup>-1</sup> molinate) <sup>a</sup>
22/10/2001	field topped up with water
31/10/2001	field topped up with water
01/11/2001	field aerially sprayed with 3.75 L ha <sup>-1</sup> Saturn (3.0 kg ha <sup>-1</sup> thiobencarb); <sup>*</sup> field "locked up"
12/11/2001	field topped up with water
between 5/10/2001 and 25/11/2001	5.7 cm rainfall

<sup>a</sup> Lorsban also applied (a.i., 500 g L<sup>-1</sup>) but not included in this investigation.

Alltech) was employed. The cartridges contained 200 mg of divinylbenzene sorbent. Some samples contained particulate matter, but using this sample volume, blockage of the cartridges did not present a problem. The cartridges were conditioned with three cartridge volumes of acetonitrile followed by three cartridge volumes of Milli-Q water. The water sample was applied, and after passing through, the columns were dried under a gentle stream of N<sub>2</sub>. Elution was carried out passively using 4 mL of acetonitrile. The recovery efficiency of clomazone, molinate, and thiobencarb from field fortified water samples at 50 µg/L was 97 ± 4 (mean ± SD, n = 5), 101 ± 9 (mean ± SD, n = 5), and 80 ± 6% (mean ± SD, n = 5), respectively. Less than complete recoveries of thiobencarb (81–84%) by SPE extraction have been reported previously and attributed to the loss of the chemical to the plastic surfaces of the cartridges, which could not be overcome with the use of Coatasil (25).

**Soil Samples.** Soils contained within the sampling tube that were collected in the field were taken from the freezer at ~-20 °C and allowed to thaw in an upright position at 4 °C overnight. Excess surface water was removed, and the tube was able to be removed with the soil core remaining intact. An upper 2 cm slice of soil core was taken and homogenized using a spatula. An aliquot (approximately 5 g) was taken for soil water determination. A second aliquot of approximately 25 g soil was placed in a 50 mL centrifuge tube and 25 mL of 90% acetonitrile:10% water was added. The tube was shaken in an end-over-end shaker for 4 h followed by centrifugation at 3000 rpm for 35 min. The extract was filtered through 0.45 µm Teflon-coated syringe filters prior to injection onto a high-performance liquid chromatograph with diode array detection (HPLC-DAD).

Additional samples that had been collected from the control plots of the trial were spiked with 1000 µg/L of the chemicals. Excess surface water was removed, and a volume of water containing the known concentration of chemical was added to the tube to a depth of 20 mm. The tubes were left to stand in the dark for 4 days. Recovery efficiencies for field-fortified soil samples were 88 ± 11 (mean ± SD, n = 6), 72 ± 12 (mean ± SD, n = 6), and 69 ± 18% (mean ± SD, n = 6) for clomazone, molinate, and thiobencarb, respectively. The minimum detectable amount in soil was 70 µg/kg for clomazone, 200 µg/kg for molinate, and 150 µg/kg for thiobencarb.

**Pesticide Analyses.** All analyses were made using an Agilent 1100 HPLC-DAD, equipped with a quaternary pump, and an autosampler with electric sample valve. The operating conditions were as follows: isocratic solvent system composed of 70% acetonitrile and 30% water; an Agilent Zorbax SB C18 column (4.6 mm × 250 mm × 5 µm); sample volume of 20 µL; the detector wavelength for clomazone, molinate, and thiobencarb was 214 nm. Standard clomazone (98.5% purity), molinate (100% purity), and thiobencarb (99.0% purity) were obtained from Alltech. Unknown sample concentrations were compared with an external calibration curve comprising peak areas of known standard quantities for each compound having the same retention time. The retention times for clomazone, molinate, and thiobencarb were 4.5,

6.3, and 9.3 min, respectively. The minimum detectable quantity of the three pesticides in the water samples was estimated to be 0.5 µg/L (lowest standard sample/concentration factor).

**Statistical Analysis.** Data were analyzed by analysis of variance (ANOVA). When the pesticide concentration was below the detection limit, the value used for ANOVA was half the detection limit. Relationships between pesticide concentration and water chemistry were determined using regression analysis. All statistical analyses were determined using the commercially available software Genstat. Dissipation half-lives (DT<sub>50</sub>), the time taken for the concentration of pesticide to be reduced to 50% of its initial value, were determined from regression analyses of log mean pesticide concentration against days since application. The DT<sub>50</sub> and upper and lower 95% confidence intervals were determined from log (2)/slope of the regression.

**Environmental Hazard Assessment.** A hazard assessment was refined that is based on the concept of risk quotients (*Q*). *Q* is defined as the ratio of expected environmental concentration (EEC) to a toxicological indicator concentration (such as the median lethal concentration [LC<sub>50</sub>] for a sensitive organism (26)). The assessment involved maximum pesticide concentrations in floodwaters, dissipation rates, and "trigger values" set for different end uses, which represent management goals for water managers in Australia (Table 3). Both theoretical and field determined pesticide concentrations and dissipation rates were considered. The theoretical pesticide concentration was calculated based on registered application rates and 10 cm of uniform water depth. Where available, values used included 99, 95, and 90% trigger values for freshwater ecosystems (27), drinking water guideline values, and health values (28). In Australia, water intended for recreational or aesthetic use and for livestock and farmstead water supply should comply with "drinking water guidelines" (27). Consequently, only one hazard assessment has been made to evaluate all of these end uses (Table 3).

The assignment of high, medium, and low hazard was defined in the following way: DT<sub>50</sub> values that resulted in the dissipation of the herbicide to Australian and New Zealand Environment Conservation Council (ANZECC) 95% trigger values for freshwater ecosystems in less than 21 days (length of rice floodwater withholding period before which no release of contaminated water occurs off-farm) were assigned low risk; environmental effects to off target organisms were unlikely. For herbicides that did not dissipate to concentrations below 95% trigger values within 21 days, *Q* values were calculated. The calculations involved taking concentrations measured in the field that occurred at 21 days and dividing by the most appropriate toxicity data available. The same calculations were done using theoretical field concentration for comparison. In the case of molinate, an LC<sub>50</sub> value of 14.5 mg/L determined for *Chironomus tepperi* in river water in the presence of sediment (29) was used. For thiobencarb, a lowest observable effects level (LOEL) value of 0.1875 mg/L for *C. tepperi* (30) was used. These values are considered the most relevant available as they have been determined on *C. tepperi*, which is a pest species in Australian rice fields and a dominant community member of many Australian freshwater ecosystems including natural ecosystems that receive drainage water from rice crops. The LC<sub>50</sub> value used for molinate was determined in experimental conditions using river water (containing suspended particles) and sediment in an effort to make the environment as realistic as possible (29). Although a no observable effects level (NOEL) value for clomazone has been determined for *C. tepperi* (30), neither acute nor chronic toxicity data determined specifically on Australian freshwater ecosystems is available for clomazone. Therefore, we have used an LC<sub>50</sub> value of 5.2 mg/L quoted for *Daphnia* (31). *Q* values of <0.1 (≤10% of the LC<sub>50</sub> or LOEL value in nontarget areas, therefore, assumed that environmental effects are possible but unlikely) were assigned medium risk. Values of >0.1 were assigned high risk (>10% of the LC<sub>50</sub> or LOEL value in nontarget areas indicating that environmental effects are likely).

## RESULTS AND DISCUSSION

**Physical and Chemical Measurements.** Physical and chemical measurements of the trial plots and the commercial rice field were performed to characterize the site water (Table 1). The water quality data in both sites presented typical conditions for

**Table 3.** Environmental Hazard Assessment for Clomazone, Molinate, and Thiobencarb

		time for herbicide to dissipate to guideline levels					Q value <sup>e</sup>	hazard assessment
		days to reach						
		ANZECC <sup>a</sup> 99% trigger value	ANZECC <sup>a</sup> 95% trigger value	ANZECC <sup>a</sup> 90% trigger value	ADW <sup>b</sup> guideline value	Australian <sup>e</sup> health value		
		maximum measured field concentration ( $\mu\text{g/L}$ )						
molinate	1042	41	26.4	20.2	34.7	24.7	0.0008	medium
clomazone	202	NA	18.4 <sup>e</sup>	NA	NA	NA	0.0003	low
thiobencarb	148	27	21.4	18	NA	8.5	0.016	medium
		theoretical field concentration <sup>d</sup> ( $\mu\text{g/L}$ )						
molinate	1920	42.0	27.5	21.3	35.8	25.8	0.001	medium
clomazone	240		19				0.0004	low
thiobencarb	3000	43.5	37.9	35.2	NA	25.0	0.337	high

<sup>a</sup> Level of protection (% species). <sup>b</sup> Australian drinking water (ADW). On the basis of analytical limit of determination. On the basis of 10% of acceptable daily intake (ADI). <sup>d</sup> Application rate of 2.0 L/ha Ordram for molinate, 0.5 L/ha Magister for clomazone, and 3.75 L/ha Saturn for thiobencarb. Assuming 10 cm uniform floodwater depth and no dissipation or degradation losses. <sup>e</sup> Q value = concentration of chemical in water at 21 days after application/most relevant ecotoxicity value (LC<sub>50</sub> or LOEL).

**Table 4.** Mean DT<sub>50</sub> of Molinate, Thiobencarb, and Clomazone in Water from Treated Rice Plots and a Commercial Rice Field

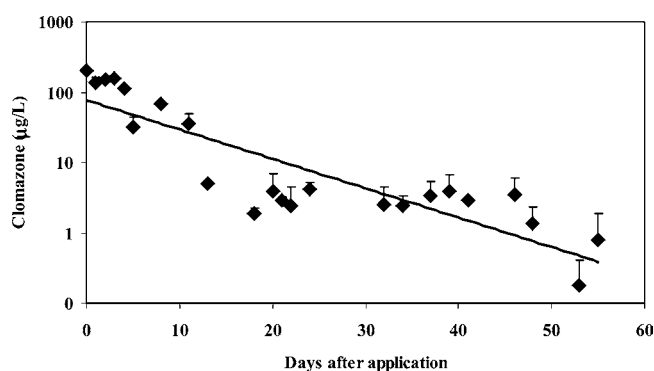
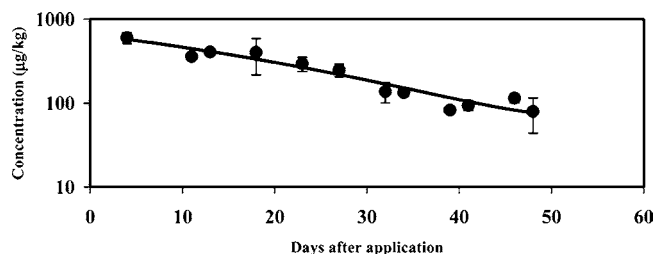
site	chemical	max initial concn ( $\mu\text{g/L}$ )	DT <sub>50</sub> <sup>a</sup> (days)	equation	R <sup>2b</sup>
trial plot	molinate (2 L/ha Ordram)	471	4.7 (5.8, 3.9)	$y = -0.06x + 2.10$	0.84
trial plot	molinate (3.75 L/ha Ordram)	1009	5.6 (8.2, 4.3)	$y = -0.05x + 2.34$	0.67
trial plot	thiobencarb (3.75 L/ha Saturn)	148	3.4 (4.1, 2.9)	$y = -0.11x + 2.16$	0.92
trial plot	clomazone (0.5 L/ha Magister)	202	7.2 (9.7, 5.8)	$y = -0.10x + 2.32$	0.90
rice field	molinate (2 L/ha Ordram)	1042	2.7 (3.1, 2.4)	$y = -0.10x + 3.17$	0.97
rice field	thiobencarb (3.75 L/ha Saturn)	105	3.6 (5.0, 2.8)	$y = -0.08x + 2.16$	0.94

<sup>a</sup> Determined from mean values from four replicates. Lower and upper 95% confidence intervals are provided in parentheses. <sup>b</sup> All R<sup>2</sup> values were significant ( $P < 0.05$ ).

rice field floodwaters in the MIA (cf. 32). The mean pH tended to be mildly alkaline (7.80–8.03) with large diel fluctuations. EC ranged from approximately 0.13 dS/m, which is similar to irrigation supply water, and increased to approximately 0.7 dS/m as a consequence of ongoing evaporation. Turbidity generally remained low (mean 0–30 mg/L) with some elevation in the trial plots immediately after chemical application caused by walking through the plot to apply the chemical.

**Dissipation in Water and Hazard Assessment—Clomazone.** Mean clomazone concentrations in water in the plots reached a maximum of 202  $\mu\text{g/L}$ , which dissipated according to a first-order equation to approximately 3  $\mu\text{g/L}$  after 19 days when 0.5 L/ha of Magister was applied (Figure 1). After 19 days, clomazone concentrations in water tended to remain fairly constant with the mean being 2.9  $\mu\text{g/L}$  at 21 days, 4.1  $\mu\text{g/L}$  at 24 days, and 3.4  $\mu\text{g/L}$  at 37 days. Using the entire data set, a DT<sub>50</sub> of 7.2 days was calculated (Table 4). A clomazone half-life in paddy waters of 5 days has been previously reported (18).

The effectiveness of floodwater withholding periods to protect off-farm receiving waters cannot be strictly assessed as there are currently no environmental protection guideline levels for clomazone in irrigation drainage waters in Australia. Considering the very high solubility of clomazone in water (1100 mg/L) and weak-moderate sorption to soil ( $K_{oc}$  150–562; 354–767; 17, 31), this chemical may be considered to have potential to contaminate creeks and channels adjacent to rice fields should

**Figure 1.** Dissipation of clomazone in rice floodwater in trial plots. Note the logarithmic scale on the y-axis. Bars show standard deviation ( $n = 4$ ).**Figure 2.** Dissipation curve for clomazone (Magister at 0.5 L/ha) in the soil of trial plots. Bars show standard deviation ( $n = 4$ ).

a release of floodwater occur. A large scale field study undertaken in the drainage canals of the MIA found clomazone concentrations ranged from 0.2 to 6.42  $\mu\text{g/L}$  (33). Nevertheless, clomazone has been consistently found to have relatively low toxicity to aquatic organisms that are indicators of ecosystem health specific to Australian freshwater environments (30, 34). The hazard assessment undertaken in this study in which we have used a nominal value of 3  $\mu\text{g/L}$  as a 95% trigger value indicated that clomazone presents a low hazard for both theoretical and measured field concentrations, which reflects the low toxicity data determined in the studies (30, 34) mentioned previously (Table 3).

**Dissipation in Soil—Clomazone.** The maximum mean clomazone concentration in the soil was 602.7  $\mu\text{g/kg}$  4 days after application decreasing to 79.5  $\mu\text{g/kg}$  over 48 days of monitoring (Figure 2). The DT<sub>50</sub> for clomazone in soil was determined to be 14.6 days (Table 5). In previous reports, the soil half-life for clomazone, under a range of paddy top soils, varied from 5.7 to 22.0 days in China (17) and 38 days in California (18).

**Table 5.** Mean DT<sub>50</sub> of Molinate and Clomazone in Soil from Treated Rice Plots<sup>a</sup>

site	chemical	concentration 4 DAA (μg/kg)	DT <sub>50</sub> <sup>b</sup> (days)	equation	R <sup>2c</sup>
trial plot	molinate (2 L/ha Ordram)	790 (136)	27.2 (67.9, 17.0)	$y = -0.0643x + 2.1008$	0.55
trial plot	molinate (3.75 L/ha Ordram)	1780 (605)	20.5 (27.8, 16.2)	$y = -0.0146x + 3.3497$	0.94
trial plot	clomazone (0.5 L/ha Magister)	603 (92)	14.6 (18.4, 12.1)	$y = -0.02058x + 2.8699$	0.92

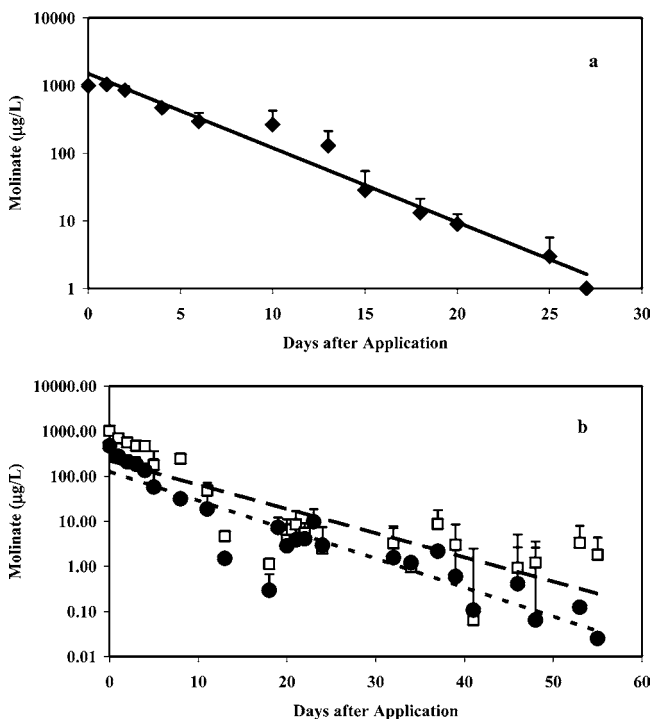
<sup>a</sup> Thiobencarb DT<sub>50</sub> could not be determined due to insignificant regression over the 48 days of monitoring. <sup>b</sup> Determined from the mean of four replicates. Lower and upper 95% confidence intervals are provided in parantheses. Initial concentrations are the mean of four replicates with standard deviations shown in parantheses. <sup>c</sup> All R<sup>2</sup> values were significant ( $P < 0.05$ ).

Anaerobic, flooded field soil conditions have been found to decrease the half-life quite significantly when compared with dissipation in aerobic soils (18). The surface soil concentrations that were determined 4 days after application equate to 65% of the initial amount of chemical that was applied.

The volume of water that each trial plot contained on the day of application was calculated in two ways: the measurement of water height in Samani flumes in three bays and manual measurement of water depth. The former gave mean volumes of 5236 L (SD 1508,  $n = 3$ ) while the latter (assuming a plot area of 50 m<sup>2</sup>) gave a mean volume of 4800 L (SD 1350,  $n = 8$ ). The concentration of clomazone in the floodwater after 4 days was approximately 83 μg/L. This equates to 0.42 g in total, assuming 5018 L of water, the mean of the values determined by the two methods for plot volume determination. This represents approximately 35% of the total chemical applied, which indicates that all of the clomazone can be accounted for in a soil and water mass balance.

#### Dissipation in Water and Hazard Assessment—Molinate.

Dissipation curves for molinate in rice floodwaters are shown in Figure 3. In the trial plots, maximum water concentrations of molinate of 471 and 1009 μg/L were found on the day of application for 2 and 3.75 L/ha Ordram, respectively (Table 4).

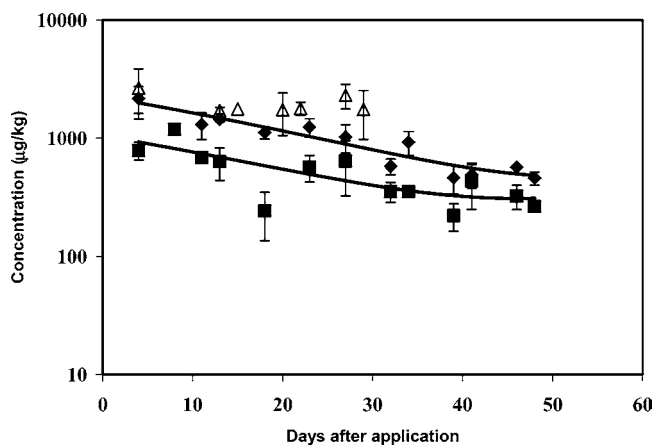


**Figure 3.** (a) Dissipation of molinate in the floodwater of a commercial rice field (Ordram at 2.0 L/ha). (b) Dissipation of molinate in the floodwater of trial plots (Ordram at 2.0 L/ha trial plot □, ---; Ordram at 3.75 L/ha trial plot ●, ---). Note the logarithmic scale on the y-axis. Bars show standard deviation ( $n = 4$ ).

Initial concentrations were approximately proportional to the application rate; plots receiving the higher rate (3.75 L/ha) contained about two times that found in the lower rate (2 L/ha). The commercial rice field treated with 2 L/ha of Ordram had mean maximum molinate concentrations of 1042 μg/L. The Ordram formulation typically used by Australian growers is an emulsifiable concentrate (EC) in which the presence of a kerosene adjuvant tends to cause the chemical to disperse very rapidly throughout field waters. Nevertheless, the maximum concentration occurred 1 day after application, a characteristic similar to that described for granular formulation (12) in Californian rice growing conditions. The mean DT<sub>50</sub> for molinate in water was 4.7 and 5.6 days for the 2.0 and 3.75 L/ha trial plot treatments, respectively, and 2.7 days in the commercial rice field (Table 4). These DT<sub>50</sub> values are similar to the range of 1.6–5 days reported for previous field studies (9–13, 15).

Using the determined DT<sub>50</sub> values, the time that it took for molinate to reach 95% trigger values of 3.4 μg/L (27) was calculated to range from 26.4 (commercial rice field) to 36 days for the 3.75 L/ha treatment (trial plots). Although contaminated rice drainage waters entering agricultural drains will undergo dilution with water that is already present in the drain and further chemical dissipation will occur prior to contaminated water arriving at drainage network monitoring points, DT<sub>50</sub> values determined here suggest, that in some cases, rice drainage water withholding periods of 21–28 days may be rather short for the optimal protection of aquatic ecosystems according to regulatory guidelines (27). This is reflected in our hazard assessment where molinate was indicated to present a medium hazard. Concentrations in water drained from fields after 21 days may be higher than 95% trigger values, but  $Q$  values are  $< 0.1$ ; therefore, ecological impacts are unlikely (Table 3).

On the basis of a plot water volume of 5018 L, the amount of pesticide measured in the water 1 day after application equated to 25–28% of the total amount applied for the lower and higher rates of molinate, respectively. In the commercial rice field, using the mean water depth value (12.3 cm) that was measured when pesticide concentration was at its maximum, it was calculated that initial concentrations were 67% of the amount applied. These data seem to be lower than what may be predicted considering the soluble nature of molinate (800–970 mg/L, 31). Significant amounts of the herbicide were apparently lost through instantaneous losses in the two different field studies in that the initial measured concentrations in the water were 30–60% of the expected concentrations considering application rate and water depth. These data are extremely similar to a previous study carried out in the area (16) and in laboratory studies (29). The large proportion that was unaccounted for in this study tends to agree with the 75–85% of applied molinate that was reported to be lost from a treated rice field through volatilization to the atmosphere with  $< 10\%$  reaching the submerged soil (12). The volatilization rate is



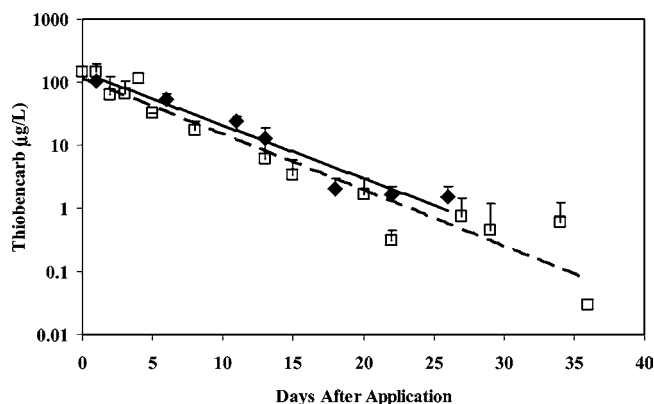
**Figure 4.** Dissipation curves in soil in the trial plots for molinate (Ordran at 3.75 L/ha,  $\blacklozenge$ ), molinate (Ordran at 2.0 L/ha,  $\blacksquare$ ), and thiobencarb (Saturn at 3.75 L/ha,  $\blacktriangle$ ; no significant relationship). Bars show standard deviation ( $n = 4$ ).

strongly dependent on field water temperature with the rate of loss occurring very rapidly at field temperatures of 28 °C (12). In this study, field water temperatures reached 36 °C (Table 1). Volatilization flux may be even higher under Australian rice growing conditions where molinate is used as an EC formulation. The high instantaneous losses of molinate that have been identified in this and other field studies suggests that there is a need in molinate management to improve the delivery of chemical to ensure losses to the atmosphere are reduced. This would enable application rates to be reduced without compromising herbicidal efficacy and minimizing environmental impact. One such approach may be to apply molinate to bare soil prior to the onset of a permanent flood regime. However, this suggestion requires further investigation.

**Dissipation in Soil—Molinate.** Concentrations of molinate in the soil were monitored in the trial plots to a depth of 2 cm. Four days after application, concentrations were 789  $\mu\text{g}/\text{kg}$  (SD = 136  $\mu\text{g}/\text{kg}$ ) for the 2 L/ha treatment and 2174  $\mu\text{g}/\text{kg}$  (SD = 605  $\mu\text{g}/\text{kg}$ ) for the 3.75 L/ha treatment (Figure 4). Similar values have been reported under Californian rice growing conditions (12, 13). Soil DT<sub>50</sub> for the 2 and 3.75 L/ha application rates of the chemical are 27 and 21 days, respectively (Table 5), showing less persistence than has been usually found in anaerobic flooded soil conditions (10, 12).

On the basis of a soil density of 1300  $\text{kg}/\text{m}^3$  (20), the amount of molinate in the upper 2 cm of soil over the area of each plot is 1.040 and 2.622  $\mu\text{g}$  for the lower and higher application rates, respectively. This is approximately 11% of the applied pesticide in both cases. By comparison, water concentrations after 4 days were 2–3% of the applied material. Molinate concentrations in soil horizons deeper than 2 cm were not determined.

**Dissipation in Water—Thiobencarb.** Mean thiobencarb concentrations in water in the trial plots had maximum values of 148  $\mu\text{g}/\text{L}$  on the day of application and dissipated to <1  $\mu\text{g}/\text{L}$  over 34 days of monitoring (Figure 5 and Table 4). In the commercial rice field, a maximum concentration of 105  $\mu\text{g}/\text{L}$  was determined. In other paddy fields, maximum aqueous concentrations of 576 and 380  $\mu\text{g}/\text{L}$ , which decreased below 1  $\mu\text{g}/\text{L}$  between 25 and 30 days, have been reported (13, 35). The DT<sub>50</sub> for thiobencarb in the trial plots was 3.4 and 3.6 days in the commercial rice field (Table 4). Previous half-lives for thiobencarb in rice floodwaters have been reported to be between 5 and 9 days (5, 13). Considering the maximum initial measured concentrations and the mean half-life, the time taken for thiobencarb to dissipate to 95% trigger levels of 2.8  $\mu\text{g}/\text{L}$  (27)



**Figure 5.** Dissipation of thiobencarb in rice floodwater. Thiobencarb (Saturn at 3.75 L/ha rice field  $\blacklozenge$ , —) and thiobencarb (Saturn at 3.75 L/ha trial plot  $\blacksquare$ , - - -). Note the logarithmic scale on the y-axis. Bars show standard deviation ( $n = 4$ ).

was determined to be 21 days in the commercial rice field and 16 days in the trial plots (Table 3). This suggests that the current withholding period for rice drainage water of 28 days is long enough to ensure sufficient thiobencarb dissipation so that ecological impact is minimized. A 21 day withholding period, as used in one Australian irrigation area where rice growing is common, may be too short to ensure environmental protection.

The hazard assessment assigned a medium risk to thiobencarb when the measured field concentrations were used and a high risk when theoretical concentrations were considered. Because maximum measured concentrations of thiobencarb in rice floodwater tend to be <600  $\mu\text{g}/\text{L}$  (13, 35), a medium risk is considered to be the appropriate assignment.

In the trial plot experiments, a total of 15 g of the active ingredient was applied to the water, and considering the plots contained approximately 5818 L of water, the maximum concentration measured in this study equates to 5.7% of the mass of chemical applied. In this study, only 4% of the applied thiobencarb could be accounted for in the water of the commercial rice field. Compare this with 34% in water using granular formulation thiobencarb in a previous study (13).

Thiobencarb residues in receiving waters within the irrigation area have been reported as high as 4  $\mu\text{g}/\text{L}$ , caused by catastrophic failure of rice field levee banks or over-bank flooding due to high rainfall events shortly after application. In more recent years, maximum detected levels of thiobencarb in receiving waters have been at sub-microgram/L levels. Reductions in the number of incidences of pesticide contamination in drainage channels may partly be accounted for by improved on-farm pesticide management practices. Education and awareness have increased among growers over the last 15 years, and rice farms with irrigation water recycling systems and storages are not uncommon. Another significant factor is the reduction in the total rice growing area due to water limitations for large area irrigation enterprises in Australia in recent years.

**Dissipation in Soil—Thiobencarb.** The maximum mean thiobencarb concentration in the soil from the trial plots was 2655  $\mu\text{g}/\text{kg}$ , 10 days after application. Thiobencarb did not fall below a mean value of 1700  $\mu\text{g}/\text{kg}$  for the 46 days of monitoring (Figure 4). A half-life of 100–200 days has recently been reported for two different rice growing soils in southeastern Australia (25). In other rice growing countries, thiobencarb has also been found to be degraded slowly under flooded, anaerobic soil conditions. A half-life of 100 days was determined in flooded Japanese soils, and a half-life of around 200 days was

calculated in reduced, flooded conditions in the United States (6, 11, 35, 36).

The mean mass of thiobencarb in the upper 2 cm of soil over the area of the plots was 3.45 g 10 days after application, which is 23% of the total applied, accounting for almost all of the thiobencarb in the plots after this period. In a Californian rice field 2, 4, and 6 days after application, 70% of the applied granular formulation thiobencarb was found largely in water and soil compartments (13). Thiobencarb is generally considered to have low environmental mobility and binds strongly to soil (5), and although we have not analyzed for thiobencarb in soil horizons deeper than 2 cm, it would seem unlikely that significant amounts of the chemical may have been lost by downward leaching especially in these heavy clay rice growing soils. It is more likely that the low recovery and high variability between replicates in soil thiobencarb concentrations (Figure 4) may be attributed to soil heterogeneity or sampling errors caused by the nature of the commercial formulation of thiobencarb, Saturn, which had a tendency to precipitate when applied to water.

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