

## Dissipation of the Herbicide Benzofenap (Taipan 300) in a Rice Field Ecosystem

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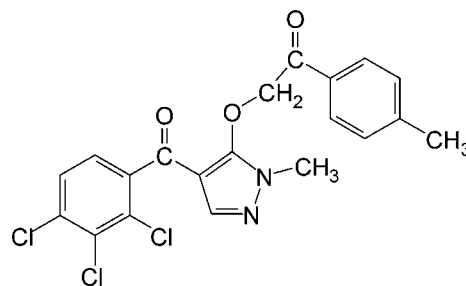
The fate of benzofenap {2-[4-(2,4-dichloro-*m*-toluoyl)-1,3-dimethylpyrazol-5-yloxy]-4'-methylacetophenone} applied to flooded rice was studied at two locations in New South Wales (Australia). Solid-phase extraction (SPE) was compared with liquid–liquid extraction (LLE) for the determination of the commercial chemical in water samples. SPE performed well as compared to LLE (84 vs 80%) in irrigation waters. However, at the lower end of the concentration range (3  $\mu\text{g/L}$ ), LLE achieved higher recoveries than SPE (72 vs 59%). Rates of dissipation ( $\text{DT}_{50}$ ) from floodwaters and soils were measured. Dissipation of the herbicide from water and soil occurred fairly erratically in both mediums and can be best explained by a first-order decay process. The  $\text{DT}_{50}$  value for benzofenap was <1 day in irrigation water due to rapid deposition of the suspension concentrate formulation. The  $\text{DT}_{50}$  in surface soil was 44 days. The maximum measured concentration of benzofenap in a rice field floodwater was 39  $\mu\text{g/L}$ , taking approximately 32 days to dissipate to <1  $\mu\text{g/L}$ .

**KEYWORDS:** Benzofenap; bensulfuron methyl; clomazone; rice herbicide

### INTRODUCTION

Benzofenap {IUPAC name, 2-[4-(2,4-dichloro-*m*-toluoyl)-1,3-dimethylpyrazol-5-yloxy]-4'-methylacetophenone; **Figure 1**} is the active ingredient in Taipan 300, a suspension concentrate (SC) formulation. Taipan 300 is a relatively new selective herbicide applied to rice (*I*) and may be used in place of bensulfuron methyl as the main form of defense against broad-leaf aquatic weeds such as Dirty Dora (*Cyperus difformis*), Starfruit (*Damasonium minus*), Arrowhead (*Sagittaria montevidensis*), and Water Plantain (*Alisma plantago-aquatica*). All of these weeds are economically important, as they can out-compete flooded rice crops and cause significant yield decline. Taipan 300 can also suppress grass weeds if application occurs soon after flooding (2). The SC formulation of benzofenap sinks to the soil surface through the floodwater. The herbicide spreads over the soil surface and forms a herbicide-treated layer.

Australian rice is mainly grown in irrigated areas of the Riverine Plain in New South Wales with water sourced from the Murrumbidgee and Murray Rivers and the Murray Aquifer System (3). The rice industry is a significant contributor to the nations' agricultural economy. Production peaked in 2000/01 at 1.625 million tons, but since 2002, drought conditions in the region have restricted irrigation water availability to growers, and production is currently around 400–600000 tons (4). This



**Figure 1.** Molecular structure of benzofenap.

provides a gross value of production of approximately A\$150 million Australian dollars (5).

Typically, pregerminated rice is aerially sown and grown under 10–15 cm of permanent water (3, 6) with weeds and insects being controlled by one further pass of an aeroplane (7, 8). Herbicides are applied as a solid stream to the floodwater surface from the aeroplane using a Bickley boom under low wind conditions. Alternative methods of chemical application include the soluble chemical injection in rice technique (SCWI-IRT), where herbicide is applied as a solid stream from a motorbike as it drives through the flooded field, and “herbigation”, where the chemical is mixed with the irrigation water as it is introduced to the field (7). The sowing and chemical application period are usually in October, with harvesting occurring in about April–May. Water levels are maintained by continually topping up of the bays. No release of water from the field occurs unless there is prolonged heavy rainfall, and

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many farms have water recycling systems where excess water may be stored.

There is very little information available on the use of Taipan 300. In the late eighties to early nineties, >90% of the Australian rice crop was treated with the herbicide Londax (bensulfuron methyl). This was unsustainable due to the development of resistance by aquatic weeds (8). Alternative herbicides were required with different modes of action to ensure good weed control. Benzofenap was identified as an alternate to bensulfuron methyl, was economically viable, and was registered for use in Australian rice in 1999 (9, 10). It is a member of group F herbicides and is an inhibitor of carotenoid synthesis. A pesticide usage study carried out in the Murrumbidgee Irrigation Area (MIA) in southwestern New South Wales in 1999 reported that 3468 kg/year of benzofenap was being used (11). Since its introduction, the adoption of benzofenap has steadily increased, and it is currently being used by up to 77% of growers in the MIA. The only other country where it is registered for use in rice is Japan, although it has been tested in other rice-producing areas such as the Far East and Southern Europe (1).

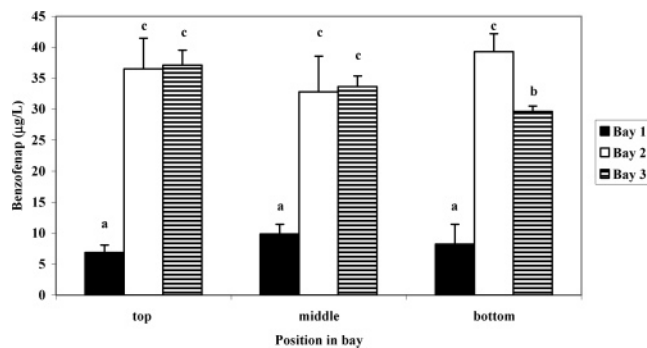
There are a number of potential pathways for the dissipation of pesticides in a rice field system. Once applied to floodwater, pesticides may be subject to a number of processes including volatilization, chemical and biological degradation, photolysis, precipitation, runoff, plant uptake, sorption and desorption to soil, and leaching through the soil profile (12).

There are no specific guideline concentrations that are used for benzofenap to ensure that it does not pose a risk to natural ecosystems. Acute and chronic toxicity tests carried out on two Australian freshwater invertebrates (final instar midge and adult aquatic snails) indicated that Taipan 300 does not represent a significant risk to these mature species at the permitted application rates (2). No acute toxicity was observed below 12 mg/L on midge larvae nor to snails at 76 mg/L. Chronic assessment could not demonstrate a significant effect on midge larvae at rates up to 0.1 mg/L, the highest rate tested. No chronic effects were observed against snails at 60 mg/L. However, greater effects may be possible in immature life cycle stages that were not tested (2). If anything, the adjuvant compounds were suggested to produce a more pronounced chronic response in these organisms than the formulation containing the active ingredient (2). Benzofenap LC<sub>50</sub> values for three fish species (including Rainbow Trout) and *Daphnia* sp. have all been reported at >10 mg/L (12). The relatively high *P*<sub>ow</sub> of the chemical and its insolubility in water may suggest a tendency to bioaccumulate, but further ecotoxicity research is required in this regard. However, no significant impact on any aquatic invertebrates has yet been demonstrated at a concentration of <10000 µg/L.

There is virtually no data available in the public domain on the extraction and analysis of benzofenap in water and soil samples, its dissipation in the aquatic environment, or its dynamics in flooded rice fields. Detailed knowledge of the environmental impact of rice growing is critical to the Australian industry and other rice-producing countries of the world to ensure sustainability. Therefore, an investigation on the environmental fate of this chemical was considered warranted.

## MATERIALS AND METHODS

**Characteristics of Benzofenap.** The chemical class of benzofenap is benzoylpyrazole (Figure 1). It has the following chemical properties: vapor pressure, 0.013 mPa (30 °C); solubility in water, 0.13 mg/L (25 °C); Henry's constant (calcd), 0.043 Pa m<sup>3</sup>/mol; and Log*P*<sub>ow</sub>, 4.69. The low water solubility of the chemical makes determination of an



**Figure 2.** Mean benzofenap concentration in water in different positions in the three bays sampled ( $n = 5$ ). Different letters denote means that are statistically different at the 5% level. Statistical analysis was by ANOVA determined using the commercially available software GenStat.

adsorption coefficient difficult using standard batch sorption methodology. The adsorption of benzofenap to soil has been described as “strong” (13). The proposed major decomposition pathway of benzofenap in water has been photolysis (14), and in soil, the major pathway is reduction in the alkylphenylketone group to MY71-Red, which is reversible by oxidation to the parent compound. Otherwise, benzofenap can be hydrolyzed at the ether bond to form MY71-OH (1).

**Commercial Rice Field—Description.** A commercial rice field located on a farm in the MIA, about 10 km south west of Griffith, New South Wales, Australia, was sampled for benzofenap and chemical and physical parameters in 2000. The soil consisted of transitional red brown earths, locally known as Willbriggie clay loam, that was uniform across the extent of the field. These soils when cultivated are classified as Entic Chromoxererts (15). In the top 0.1 m clay (<0.2 µM), the percentage is 34%, the bulk density is 1383 kg m<sup>-3</sup>, and the long-term infiltration rate for these soils has been measured as 0.25 mm day<sup>-1</sup> (16). The pH<sub>w</sub> (1:5; soil:water) of the surface (0–0.1 m) is neutral to alkaline (7.0–8.0; 15).

The application of the chemical was by SCWIIRT, which involved delivery of the chemical to the floodwater through a hose from a tank that was mounted on a motorbike, which was driven through flooded rice bays. The field layout consisted of five bays in a laser-leveled paddock with bankless channel irrigation. Each bay was approximately 2 ha.

**Commercial Rice Field Sampling.** Water samples were collected for pesticide, physicochemical, total suspended solids, and total dissolved solid analyses. Water samples were collected in 1 L amber bottles, which had been rigorously cleaned in detergent, 10% HCl, and methanol according to ref 17.

Water samples were taken 1 day after chemical application (October, 11, 2000) from three different bays located proximally, midway, and distally from the supply water inlet at the top of the field. Each bay was sampled through the center in a cross pattern, at five locations. Each water sample was analyzed for benzofenap. A mean concentration of the chemical was determined for each bay (Figure 2). Because of project logistical constraints, the field sampling program in 2000 did not allow the monitoring of the commercial rice field to continue. Dissipation studies were subsequently carried out in the trial plots described below.

**Trial Plot Construction.** A replicated small plot trial was set up in October 2002 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 (0–0.1 m) 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. The total organic carbon content was 0.8–2% (15, 16). Plot construction, determination of water volumes, and irrigation management have been described previously (18). 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 an irrigation water 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. Water depths were also measured manually (two measurements/plot) by a method using rulers mounted at either end of each plot. After the plots had been prepared, irrigation was managed by the farmer for the duration of the trial, as were the flumes and siphons as needed to maintain a water depth of between 4 and 10 cm.

**Trial Plot Treatments.** The treatment consisted of applying 2.0 L/ha of Taipan 300 equivalent to 600 g a.i./ha by pouring from a 5 L carboy while walking a single pass through a plot. The herbicide was applied in this way during two consecutive rice seasons in October 2002 and 2003 to a set of four, 50 m<sup>2</sup> plots. Other commonly used rice herbicides were also applied during the trial as documented previously (18).

**Trial Plot Sampling.** Water samples taken immediately after the application were designated as the day 0 samples. Additional samples were collected 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 according to ref 17. Two water samples were taken at either end of each of the plots and composited to make up a single sample. Boardwalk access to the plots 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 placed upright during collection and transport. Soil samples were collected at the following time intervals: 1, 4, 7, 10, 12, 17, 23, 26, 31, 33, 38, 40, 45, and 48 days after application. Estimates of benzofenap concentration variation in soil were determined by calculating the mean soil pesticide concentration of the two samples taken from each plot, which were analyzed individually. Then, standard deviations of the mean data from the four replicate bays for each treatment were calculated. The standard deviations between the four replicate plots were found to be greater than the variation of the two samples within the plots.

**Physical and Chemical Analysis—Water Samples.** Total suspended solids and total dissolved solids were analyzed according to APHA (19). The 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.

**Pesticide Extraction from Water Samples—Method Validation. Technical Benzofenap.** Technical benzofenap (Dr. Ehrenstorfer) at concentrations of 10, 40, 100, 250, 1000, and 2500 µg/L in acetonitrile, were injected directly into the high-performance liquid chromatograph (HPLC). Linearity ( $R^2 > 0.99$ ) across low, mid, and high ranges was maintained.

Water samples (400 mL) including deionized water, irrigation water, and irrigation water adjusted to pH 3–4 (using 6 M HCl) were fortified with technical benzofenap to concentrations of 50 µg/L. The samples were filtered through dichloromethane-rinsed glass fiber filters (Whatman GF/F). Extraction of samples ( $n = 3$ ) was carried out by solid-phase extraction (SPE) using 3 mL IST ENV+ cartridges (Alltech) with 200 mg of divinylbenzene (DVB) sorbent set in an IST vacuum SPE manifold. The cartridges were conditioned with three cartridge volumes of acetonitrile followed by three cartridge volumes of Milli-Q water. Water samples were applied to the cartridges, which were dried under gentle vacuum. Elution was carried out passively using 2 mL of acetonitrile followed by 2 mL of dichloromethane.

Liquid–liquid extraction (LLE) of technical benzofenap was assessed by taking fortified water samples (400 mL) as described above and extracting them using dichloromethane (3 × 50 mL). Extracts were dried using sodium sulfate, evaporated to dryness using a Zymark Turbovap, and redissolved in acetonitrile. The extraction efficiency for technical benzofenap using the two extraction methods for different types of fortified waters is shown in Table 2.

**Benzofenap in the Commercial Formulation, Taipan 300.** Working standards of 10, 40, 100, 250, 1000, and 2500 µg/L in acetonitrile were injected directly to determine linearity across different ranges ( $R^2$

**Table 1.** Water Quality Data for the Commercial Rice Field

parameter	units	mean	minimum	maximum	n
conductivity	dS/m	0.29	0.22	0.34	50
pH		7.49	6.32	8.09	50
total dissolved solids	mg/L	55.3	32.8	129	41
total suspended solids	mg/L	164	95.5	244	41
chloride	mg/L	32.6	22	53	34
TOC	mg/L	15.9	10	24	7
DOC	mg/L	13.8	5.7	19	7
temperature	°C	16.7	10.0	24.3	50

**Table 2.** Extraction Efficiency of Technical Benzofenap Using SPE and LLE as Compared with Directly Injected Technical Benzofenap (No Extraction Steps)<sup>a</sup>

	fortified sample	volume extracted (mL)	extraction efficiency (%) technical benzofenap (50 µg/L)
SPE	deionized water	400	67 (15)
SPE	irrigation water <sup>b</sup>	400	57 (12)
SPE	irrigation water pH 3–4 <sup>b</sup>	400	60 (10)
LLE	irrigation water <sup>b</sup>	400	81 (5)

<sup>a</sup> The relative standard deviation (RSD) is in parentheses ( $n = 5$ ). <sup>b</sup> Irrigation water contained 8 mg/L of total suspended solids.

$= >0.99$ ) and for comparison with extracted standards, normalized to the mass of benzofenap injected on-column. Three milliliter SDB-L (supplied by Phenomenex) SPE cartridges containing 200 mg of DVB solid phase were conditioned using 3 column volumes of acetonitrile followed by 3 column volumes of deionized water. A 100 mL amount of solution at commercial formulation benzofenap concentrations of 3, 10, 40, and 100 µg/L in deionized water, irrigation water, irrigation water adjusted to pH 3–4, and irrigation water containing 1% chloroform was applied to the cartridges and eluted with 4 mL of acetonitrile (Table 3). LLE for waters fortified at 3, 10, and 100 µg/L with commercial formulation benzofenap was carried out as described previously (Table 3).

**Extraction and Analysis of Benzofenap in Water Samples.** Benzofenap was extracted from frozen commercial rice field water samples that were collected in 2000 using the SPE method described as for technical benzofenap. The samples were thawed at 4 °C overnight, and 400 mL was filtered through dichloromethane-rinsed glass fiber filters (Whatman GF/F) before application to the SPE cartridges. Method validation included a study to determine the recovery of benzofenap from samples that were stored frozen vs those extracted on the same day of collection and a study that addressed the effect of filtering on the recovery of the chemical. Subsequently, it was determined that low concentrations (3 µg/L) of benzofenap were extracted more efficiently using dichloromethane by LLE (Table 3), and this method (described above) was used for extraction of water samples from the trial plots.

**Pesticide Extraction—Soil Samples.** Soils contained within the sampling tube that were collected in the field were taken from the freezer at  $\sim -20$  °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 of soil core was taken and homogenized using a spatula. A subsample (approximately 5 g) was taken for soil water determination. A second subsample of approximately 25 g soil was placed in a 50 mL centrifuge tube with 25 mL of 90% acetonitrile:10% water. 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 HPLC with diode array detection (DAD).

Additional samples of soil and water in tubes 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

**Table 3.** Extraction Efficiency of Commercial Formulation Benzofenap Using SPE as Compared with Directly Injected Commercial Formulation (No Extraction Steps)<sup>a</sup>

fortified sample		volume extracted (mL)	extraction efficiency (%) benzofenap commercial formulation, Taipan 300				concentration ( $\mu\text{g/L}$ )	mean (SD)	$R^2$
			3	10	40	100			
SPE	deionized water	100	61 (6)	103 (29)	79 (9)	66(3)	77 (12)	0.99	
SPE	irrigation water	100	59 (6)	102 (6)	91(21)		84 (11)	1	
SPE	irrigation water at pH 4	100	44 (7)	77 (22)	60 (1)		60 (10)	0.99	
SPE	irrigation water + 1% chloroform	100	53 (4)	72 (1)	69 (1)		65 (2)	0.99	
LLE	irrigation water	400	72 (14)	85 (11)		83(8)	80 (11)	0.99	

<sup>a</sup> RSD in parantheses ( $n = 3$  for all, except deionized water, where  $n = 5$ ).

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  $76 \pm 14\%$  (mean  $\pm$  SD;  $n = 5$ ) for benzofenap. The minimum detectable amount in soil was  $50 \mu\text{g/kg}$ .

**Pesticide Analyses.** All analyses were made using an Agilent 1100 HPLC-DAD, equipped with a quaternary pump and an autosampler with an 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  $\times$  250 mm  $\times$  5  $\mu\text{m}$ ); sample volume of 20  $\mu\text{L}$ ; and detector wavelength for benzofenap of 210 nm. Under these conditions, the retention time for benzofenap was 10.3 min, and the instrument detection limit was 10  $\mu\text{g/L}$  (0.0002  $\mu\text{g}$  on-column). Unknown sample concentrations were compared with an external calibration curve comprising peak areas of known standard quantities for a peak at the same retention time.

**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. The dissipation half-life ( $\text{DT}_{50}$ ), the time taken for the concentration of pesticide to be reduced to 50% of its initial value, was determined from regression analyses of log mean pesticide concentrations against days since application. The  $\text{DT}_{50}$  and upper and lower 95% confidence intervals were determined from  $\log(2)/\text{slope}$  of the regression.

## RESULTS AND DISCUSSION

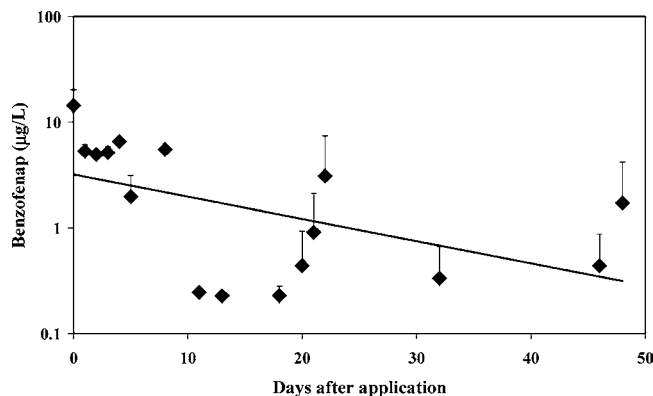
**Pesticide Extraction from Water Samples—Method Validation.** Benzofenap is difficult to analyze in water due to its low solubility (0.13 mg/L) and its SC commercial formulation, which produces a dense precipitate when it is added to water, resulting in an uneven dispersion (2). Therefore, it was deemed necessary to make an assessment of the extraction efficiency of technical benzofenap and benzofenap as the active ingredient in Taipan 300, from water samples using solid-phase cartridges and LLE. Storing the water samples frozen for several weeks prior to extraction and analysis had no effect on the recovery of technical benzofenap.

LLE provided recoveries of technical benzofenap from irrigation water of 81% as compared to approximately 57% by SPE. The recovery of the technical standard was determined from filtered as compared to nonfiltered samples applied to SPE cartridges. Recoveries in filtered samples ranged from 42 to 84% of nonfiltered samples;  $66 \pm 14$  (mean  $\pm$  SD,  $n = 5$ ). Although the concentrations were adjusted according to the mean of 66%, there was variation around this mean, and the lower recoveries reported in **Table 2** may have been caused by filtering the samples within the SPE method. Because filtering

was used to determine benzofenap concentrations from the commercial rice field floodwaters, it must be concluded that the absolute data, shown in **Figure 2**, may be somewhat conservative. The filtering step was initially considered necessary to prevent clogging of the cartridges when a sample volume of 400 mL was used. In subsequent testing of the recovery of benzofenap during the extraction of the commercial formulation Taipan 300, we omitted the filtration step and used a 100 mL sample volume. This alleviated the cartridge blocking problem while still enabling detection at sub-ppb concentrations. Sample filtering may also be the reason for the lower recovery rate of the technical standard as compared with benzofenap contained within the commercial formulation fortified samples, which were not filtered (**Tables 2 and 3**, respectively). An alternative SPE method for the extraction of benzofenap from rice field floodwaters may be one that involves the use of ascorbic acid to prevent the precipitation of iron species that can block SPE cartridges (20), although this was not evaluated here. Acidification of the fortified samples containing technical benzofenap to pH 3–4 using hydrochloric acid did not improve the extraction efficiency using solid-phase cartridges (**Table 2**).

The mean recovery of the commercial formulation across the concentration range, using SPE cartridges, was 84%. Acidifying the sample or, adding 1% chloroform, proved futile (**Table 3**). The mean recovery using LLE was 80%, although at 3  $\mu\text{g/L}$ , the lowest concentration tested, LLE achieved a higher recovery than SPE extractions (**Table 3**). Recoveries at 3  $\mu\text{g/L}$  were lower than at other concentrations for both SPE and LLE, suggesting that this was caused by systematic procedural losses rather than something that may be explained by chemical effects. Ultimately, we considered, for trace concentration determination of benzofenap in rice field water samples, that LLE remains the most reliable method.

**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**, ref 18). The water quality was good with respect to salinity, which is typical of irrigation water throughout the region sourced from the Murrumbidgee River (18). The mean pH of the floodwaters in the rice field tended to be mildly alkaline (**Table 1**). Because the pH range of the commercial formulation is 7.5–8.5, it would seem unlikely that the field water conditions would increase the degradation rate significantly even though, under basic conditions, the compound is unstable, hydrolyzing to benzofenap-OH. The pH of the water affecting the degradation rate of the compound may become more significant in the trial plots where a maximum pH value of 9.77 was recorded. Large daily fluctuations of pH occur in ricefield floodwaters [7.35–8.34



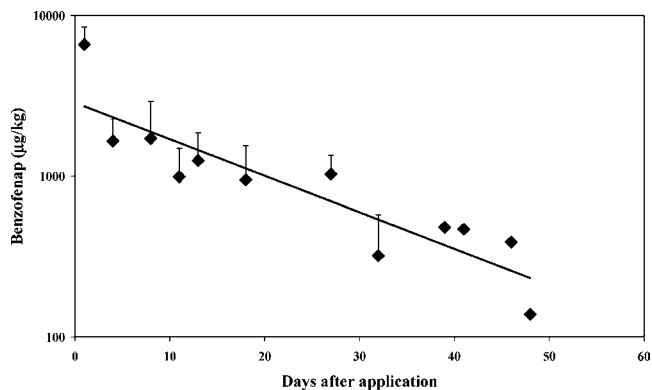
**Figure 3.** Dissipation of benzofenap (Taipan 300) in floodwater of rice grown in trial plots. Note the logarithmic scale on the  $y$ -axis. Bars show the standard deviation ( $n = 4$ ).  $R^2 = 0.4284$ ;  $p < 0.05$ .

(18)] caused by variations in the photosynthetic activity of aquatic microorganisms.

#### Concentrations of Benzofenap in a Commercial Rice Field.

The maximum field concentration of benzofenap in water, measured 1 day after application, was  $39 \mu\text{g/L}$  (SD 2.9;  $n = 5$ ). As mentioned previously, the absolute concentrations determined from the commercial rice field may be somewhat conservative due to the effect of sample filtering prior to SPE. However, because of the lack of publicly available data on the concentration of benzofenap in rice fields, it was considered worthwhile presenting the data here. This study indicated that concentrations of benzofenap were all significantly ( $p < 0.05$ ) lower in the bay nearest to where water was introduced into the field (bay 1) as compared with other bays downslope (Figure 2), as were salinity and total dissolved solids. The cause of the uneven chemical distribution may be caused by irregularities in the SCWIIRT application method. However, the sampling position within the bay nearest the supply had no significant effect on the concentration of this pesticide, suggesting that the application method provided an even distribution within bays. Alternatively, because we ascertained a very short  $\text{DT}_{50}$  for the chemical ( $< 1$  day, discussed in following text), removal of the chemical from the water column by deposition or other losses may have progressed further in the uppermost bay, which was treated earlier in the day than lower bays. Losses of the chemical by water movement from this bay to bays downslope are unlikely as the field was "locked up" with no water entering or leaving the field. The benzofenap concentration was found to have a significant relationship with total dissolved solids ( $y = 0.3x - 23.4$ ;  $R^2 = 0.4$ ;  $n = 37$ ;  $p \leq 0.05$ ) and EC ( $y = 257.5x - 46.9$ ;  $R^2 = 0.5$ ;  $n = 45$ ;  $p \leq 0.05$ ). A relatively higher concentration in the latter parameter may occur through evapoconcentration. Because it typically takes approximately 1 day to fill a rice bay, a field of 7–8 bays will take about a week to fill and stabilize. Water in bottom bays tends to have the longest residence time between the start and the end of filling. Therefore, evapoconcentration effects tend to be more significant in bays further away from the water supply as compared with upper bays (21).

**Dissipation of Benzofenap in Water.** The mean maximum benzofenap concentration in the water in the trial plots was  $14 \mu\text{g/L}$  (SD = 5.8;  $n = 4$ ), which dissipated irregularly to  $< 1 \mu\text{g/L}$  after 32 days (Figure 3). Sporadic detections of the chemical of up to  $1 \mu\text{g/L}$  recorded for up to 53 days after application may be explained as sampling bias that occurred due to shallow water (10–20 mm depth) at some sampling events. It is possible that during these times, deposited or sediment-associated



**Figure 4.** Dissipation of benzofenap (Taipan 300 at 2.0 L/ha) in the soil of trial plots. Note the logarithmic scale on the  $y$ -axis. Bars show the standard deviation ( $n = 4$ ).  $R^2 = 0.4729$ ;  $p < 0.05$ .

chemicals were sampled in addition to chemicals that were truly dissolved in the water column. Taking this into consideration, we calculated a  $\text{DT}_{50}$  of  $< 1$  day from data collected for 41 days after application, which showed first-order decay (Figure 3). A benzofenap half-life in water has been previously reported to be 7 days with an important degradation pathway being via photolysis (14). The role of photolysis as a dissipation pathway for the chemical in the SC would seem relatively minor due to its rapid precipitation onto the soil where photodecomposition is probably a fairly insignificant dissipation pathway (22).

**Dissipation of Benzofenap in Soil.** A mean concentration of  $6595 \mu\text{g/kg}$  (SD, 1870;  $n = 4$ ) was determined 1 day after application. Benzofenap soil concentrations declined, if somewhat erratically, over 48 days to  $138 \mu\text{g/kg}$  (SD, 255;  $n = 4$ ; Figure 4). According to a 2 L/ha application rate (300 g/L a.i.), a total of 3.0 g of a.i. was applied to each bay. Assuming a soil density of  $1300 \text{ kg/m}^3$  and samples consisting of a 2 cm depth interval,  $6595 \mu\text{g/kg}$  equates to 2.86 times the possible maximum concentration, should 100% of applied herbicide be found in the soil. Such high initial concentrations and the large standard deviations for each data point in the sample set indicate the uneven distribution of the chemical in the soil surface and a sampling strategy that did not overcome this variation. The variation is likely caused by the method of chemical application, its low solubility in water, and rapid rate of deposition after application.

The trial plots data suggest that in field situations, where the method of application involves a solid stream of herbicide being poured into a flooded bay either from an airplane or using a Bickley boom or motorbike (SCWIIRT), soil heterogeneity may occur. This could result in some soil being loaded with pesticide at 3–4 times recommended application rates, which may have implications for sediment toxicity assessment for rice field ecosystems.

Using the maximum initial concentration of  $6595 \mu\text{g/kg}$ , dissipating to  $138 \mu\text{g/kg}$  over 48 days, the  $\text{DT}_{50}$  for benzofenap in these rice growing soils was 44 days. This compares with previous reports of 38 days in paddy field soil (1, 20). The surface soil (0–2 cm) concentrations that were determined 4 days after application equate to 71.5% of the initial amount of chemical that was applied. The volume of water that each trial plot contained on the day of application was approximately 5018 L. The concentration of benzofenap in the water 4 days after application was  $3.7 \mu\text{g/L}$ . This represents  $< 1\%$  of the total chemical applied. The proportions of chemical determined in the soil and water, 4 days after application, suggest that the most dominant fate pathway for benzofenap, in this herbicide,

is soil association. The nature of this association, whether it is physically adsorbed to soil components or merely deposited on the surface within its SC formulation, has not been determined.

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