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Abstract: The mobility of the rice pesticides thiobencarb (S-[(4-chlorophenyl) methyl] diethylcarbamoithioate) and fipronil ([5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]pyrazole) were investigated in the glasshouse under flooded conditions using two Australian rice-growing soils. When using leakage rates of 10 mm day⁻¹, less than 20% of applied thiobencarb and fipronil remained in the water column after 10 days due to rapid transfer to the soil phase. Up to 70% and 65% of the applied thiobencarb and fipronil, respectively, were recovered from the 0-1 cm layer of soils. Only 5-7% of each pesticide was recovered from the 1-2 cm layer, and less than 2% was recovered from each 1 cm layer in the 2-10 cm region of the soils. Analysis of the water leaking from the base of the soil cores showed between 5-10% of the applied thiobencarb and between 10-20% of the applied fipronil leaching from the soil cores. The high levels of pesticide in the effluent was attributed to preferential flow of pesticide-laden water via soil macropores resulting from the wetting and drying process, worm holes and root channels.

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The mobility of thiobencarb and fipronil in two flooded rice-growing soils

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ABSTRACT

The mobility of the rice pesticides thiobencarb and fipronil were investigated in the glasshouse under flooded conditions using two Australian rice-growing soils. When using leakage rates of 10 mm day^{-1} , less than 20% of applied thiobencarb and fipronil remained in the water column after 10 days due to rapid transfer to the soil phase. Up to 70% and 65% of the applied thiobencarb and fipronil, respectively, were recovered from the 0-1 cm layer of soils. Only 5-7% of each pesticide was recovered from the 1-2 cm layer, and less than 2% was recovered from each 1 cm layer in the 2-10 cm region of the soils. Analysis of the water leaking from the base of the soil cores showed between 5-10% of the applied thiobencarb and between 10-20% of the applied fipronil leaching from the soil cores. The high levels of pesticide in the effluent was attributed to preferential flow of pesticide-laden water via soil macropores resulting from the wetting and drying process, worm holes and root channels.

KEYWORDS

sorption; degradation; diffusion; leaching; anaerobic; flooded;

INTRODUCTION

Pesticides leaching from the soil surface through the soil profile is the main mechanism of groundwater contamination,^[1] and the rate of movement through the soil matrix will depend upon the physical and chemical properties of both the soil and the pesticide. While hydrophilic pesticides may be more mobile in soil when flow occurs through the soil matrix,^[2; 3] the mobility of hydrophobic pesticides tends to increase as soil organic carbon content decreases.^[4; 5] However, water flow through the soil may be short-circuited by soil macropores which result from wetting and drying processes, worm holes and root channels.^[6; 7] Flow via these pathways, commonly known as preferential flow, may allow surface water containing contaminants to bypass the soil matrix and enter groundwater due to contaminants failing to encounter sorption sites.^[7; 8] Thus, in some instances, pesticides may penetrate soil to greater depths than predicted by transport models.^[8] Additionally, a more rapid transit of pesticide-contaminated water through the biologically active soil matrix may reduce the amount of pesticide degraded, which may also increase the risk of groundwater contamination.^[6; 9]

Pesticides may be more mobile when applied to irrigated crops, such as rice, than when applied to dryland crops due to the saturated soil potentially providing a conduit between surface and ground waters. The pesticides fipronil ([5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]pyrazole) and thiobencarb (*S*-[(4chlorophenyl)methyl] diethylcarbamothioate) are used extensively in rice production in Australia. Thiobencarb (a thiocarbamate herbicide) is used to target weeds such as barnyard grass (*Echinochloa spp*) and dirty dora (*Cyperus difformis*), while fipronil (a phenylpyrazole insecticide) is used to control bloodworm (*Chironomus tepperi*), a major insect pest in southeastern Australian rice-growing regions. Thiobencarb has been shown to be a relatively immobile herbicide as it tends to remain in the top few centimetres of soil,^[10] possibly as a consequence of higher levels of soil organic carbon.^[11; 12] In addition, slow degradation of thiobencarb has been reported to occur under flooded, anaerobic conditions.^[13; 14] Thus, penetration of thiobencarb to greater depths in the soil may occur if desorption in surface soil occurs due to its persistence under flooded conditions. Conversely, fipronil reportedly has a high mobility in non-flooded soil, with

penetration to depths of 5-10 cm in as little as 2 months,^[15] and 15 cm in non-flooded soil profile within 6 months of application.^[16]

Whilst there have been no reports of preferential flow of thiobencarb or fipronil in the literature, the preferential flow of other pesticides through soil has been suggested as an important mechanism for leaching. An increase in the leaching of metsulfuron-methyl, MCPP and prochloraz was observed under flooded conditions into an aquifer as a result of preferential flow through macropores and fractures as a consequence of tree roots.^[17] Rapid saturation of worm hole linings in flooded soil by atrazine and metolachlor suggested that few sorption sites occurred in these macropores than in the soil matrix,^[18] and leaching models attributed less than 1% of total isoproturon sorption sites in the soil to being present in macropores.^[19] Preferential flow of pesticides may also increase in the presence of dissolved organic carbon (DOC) by allowing the partitioning of hydrophobic pesticides to the hydrophobic core of organic macromolecules in the DOC. Whilst no evidence has been reported for thiobencarb or fipronil, DOC-assisted leaching has been reported to influence the solubility, mobility and availability for degradation of other organic contaminants such as PAHs,^[20; 21] napropamide,^[8; 22] imidacloprid,^[23] 2,4-D, naphthalene and chlorpyrifos.^[24] Tillage of the surface soil prior to pesticide application during preparation of fields for cropping has been reported to reduce preferential flow. For example, carbofuran, alachlor and atrazine were found to leach faster and to greater depths in soil when the soils remained undisturbed prior to application than when applied to tilled soils,^[25] indicating that

mechanical disruption of these conduits prior to pesticide application may reduce leaching of pesticides through soil.

The objective of this work was to investigate the mobility of commercial formulations of the pesticides thiobencarb (Saturn™) and fipronil (Cosmos™) when applied to an environment in which reducing conditions were allowed to establish, and which was also subject to the continual downward flux of water (ie leakage). Accelerated leakage was used to determine the extent of leaching through the soil, and whether pesticide leaching occurred mainly through the soil matrix or via preferential flow through macropores after a single pesticide application. Emulsified rather than technical grade pesticides were used to allow for competition between pesticide and surfactant molecules for the soil sorption sites, as well as for the enhancement of pesticide solubility in water.

MATERIALS AND METHODS

Soil selection and characterisation

Two representative soils were chosen from rice-growing regions in the Murrumbidgee Irrigation Area (MIA) and Coleambally Irrigation Area (CIA) in New South Wales, Australia. A Birganbigil clay loam, classified as a brown chromosol,^[26] was selected from Yanco (34° 36'S, 146° 24'E) in the MIA and a Wunnamurra self-mulching clay, classified as a grey vertosol^[26] selected from Coleambally (34° 47'S, 145° 59'E) in the CIA. The properties and methods used to determine the soil properties (Table 1) have been previously reported.^[27; 28]

Characterisation of macropores

Intact soil cores were flooded to a depth of 150 mm with a solution of Coomassie Brilliant Blue (1 g L⁻¹). Cores were allowed to drain for five days after which an equal volume of

instrument grade water was applied, and allowed to drain. The cores were oven dried for two days (30 °C) and then removed from their tubes intact. Cores were inspected for staining prior to transverse sectioning into 5 mm layers for identification of flow patterns.

Experimental setup

PVC sewer pipe (100 mm ID) was cut into lengths (30 cm) and sharpened on one end. The tubes were inserted in the soil prior to irrigation in order to take intact soil cores at each of the two field sites which had not been previously exposed to either thiobencarb or fipronil. Soil cores were removed and returned to the glasshouse. Squares of fine mesh (2 cm x 2 cm) were placed in the bottom of plastic funnels (120 mm) and the funnels were filled to within 1 cm of the top with washed river sand (< 1mm). Soil cores in their PVC tubes were placed on top of the sand beds in the funnels, and the tube and funnels were joined using silicone sealant. A piece of silicone tubing (10 cm) was poked into the narrow end of each funnel and held in place with silicone sealant (Figure 1A). Tubing clamps were applied to each tube to allow regulation of leakage rates. The intact cores were flooded with irrigation water (pH 6.6 and 0.12 mS cm^{-1}) to a depth of 10 ± 0.5 cm and allowed to stand while covered with a sheet of black plastic. Sufficient cores were prepared so as to allow 4 replicates for each pesticide to be removed at each sampling. The shrink/swell capacity of both soils was assumed to be adequate to avoid the use of bentonite (or other sealant) between the soil and PVC tube at the soil water interface. Water levels were maintained using irrigation water that had been deoxygenated with nitrogen. After 5 weeks of incubation, water was drained from the base of the cores until the water depth reached 1 cm above the soil surface. Pesticides were then applied, as described in the following section. In addition, controls for each pesticide were prepared using silanised (Coatasil[√]) treated glass marbles (10 mm diameter) in place of soil to determine the amount of pesticide lost to the experimental equipment (Figure 1B).

Pesticide application and sampling

Saturn[√] (EC) was initially diluted 1000 fold in acetonitrile due to its tendency to precipitate when applied to water. The acetonitrile solution (250 mL) was applied drop-wise over a 45 min period to vigorously stirred irrigation water (30 L), resulting in a thiobencarb solution of $\sim 6.5 \text{ mg L}^{-1}$. Due to the relatively low application rate of the concentrate, Cosmos[√] (SC) was serially diluted in distilled water, resulting in a fipronil solution of $\sim 20 \text{ mg L}^{-1}$. The diluted solution (50 mL) was added to vigorously stirring irrigation water (30 L), resulting in a fipronil solution of $\sim 30 \mu\text{g L}^{-1}$. Aqueous thiobencarb or fipronil solutions (700 mL) were applied to soil cores and then covered with black plastic. Water (40 mL) was released from the bottom of the cores twice a day at a rate equivalent to 10 mm of leakage per day. All water released was combined with effluent previously collected from that core in order to determine the total amount of pesticide eluted from each soil core during the lifetime of the experiment. Once the water depth reached approximately 1 cm from the soil surface (ie after 10 days), a set of four soil cores for each soil type and each pesticide were allowed to drain completely, while all other cores were topped up to a water depth of 10 cm with pesticide-free irrigation water. The fully drained cores were placed in a deep freezer ($-20 \text{ }^{\circ}\text{C}$) for subsequent extraction and analysis. Sets of four soil cores were drained and removed 17, 24 and 31 days after pesticide application, and then frozen for subsequent extraction and analysis. The remaining soil cores were topped up with irrigation water on days 17 and 24 in order to maintain a downward flux of water through the soil profile.

Analysis of soil and water

Frozen cores were defrosted overnight in their plastic tubes, and then slid out of the tube prior to being sliced transversely into 1 cm thick layers using fine steel wire. After homogenisation with a blender, sub-samples ($\sim 20 \text{ g}$) were taken and extracted using acetonitrile (30 mL) in plastic screw cap centrifuge tubes (50 mL). Whilst glass is normally

preferred for pesticide extraction, tests indicated that no appreciable loss of pesticide was observed due to the solubility of the pesticides in acetonitrile, and the relatively short contact time with the plastic. Tubes were covered in aluminium foil to minimise photodegradation and shaken (45 min, 400 oscillations min^{-1}). After centrifugation (10 min, 4000 rpm), tubes were frozen ($-20\text{ }^{\circ}\text{C}$) overnight to allow excess water to freeze and cause pesticides to partition into the acetonitrile phase. Anhydrous sodium sulfate (10 g) was added to each tube to remove the remaining water, after which the acetonitrile layer was removed and syringe filtered (GF/F 13 mm) into pre-weighed scintillation vials (22 mL). Fipronil samples were evaporated to dryness under dry nitrogen ($40\text{ }^{\circ}\text{C}$) and resuspended in ethyl acetate (0.5 mL) containing lindane internal standard (1 mg L^{-1}) for analysis by GC-ECD, whereas samples containing thiobencarb had their volume reduced by evaporation under nitrogen prior to analysis by HPLC.

Water samples were analysed directly for thiobencarb using HPLC. Fipronil and fipronil sulfide were analysed by solid-phase microextraction (SPME) GC-ECD by transferring water samples (5-15 mL) to glass scintillation vials (22 mL) which had been previously treated with Coatasil[√]. Sodium borate decahydrate buffer (5 mL, 60 g L^{-1} , pH 9) was added with enough deionised water to provide a final volume of 20 mL. Solutions were incubated ($35\text{ }^{\circ}\text{C}$) for 30 min and spiked with lindane ($50\text{ }\mu\text{L}$, 1 mg L^{-1}) in acetone. Standards were prepared by adding deionised water (15 mL) to borate buffer (5 mL) and spiking with an appropriate standard ($50\text{ }\mu\text{L}$) in acetone following incubation ($35\text{ }^{\circ}\text{C}$). A small spin bar was added to each scintillation vial, and vials were placed on a magnetic stirrer in an incubator ($35\text{ }^{\circ}\text{C}$). A polyacrylate SPME fibre (85 μm coating, Supelco) was extended into the solution for 15 min, after which, the fibre was retracted, dried and inserted into a hot GC injection port ($280\text{ }^{\circ}\text{C}$) for desorption.

Chromatographic conditions

Quantitation of fipronil and fipronil sulfide was performed using a Carlo Erba HRGC 5300 Mega Series Gas Chromatograph with ^{63}Ni electron capture detector (GC-ECD). Analysis was performed using a J&W Scientific DB-5 capillary column (30 m x 0.25 mm id with 0.25 μm film thickness). Soil extracts were analysed using splitless injection with an injection volume of 1 μL , and a port temperature of 280 $^{\circ}\text{C}$, whilst the detector temperature was 290 $^{\circ}\text{C}$. The carrier and makeup gases were high purity nitrogen (2 mL min^{-1}) and argon containing 10% methane (20 mL min^{-1}) respectively. Data were processed using Star Chromatography Workstation software (version 6.2). The temperature program for soil extracts began at 150 $^{\circ}\text{C}$ (held for 1 min) and then increased to 260 $^{\circ}\text{C}$ (@ 15 $^{\circ}\text{C min}^{-1}$, held for 2 min) and then increased to 280 $^{\circ}\text{C}$ (@ 20 $^{\circ}\text{C min}^{-1}$ for 3 min). The program used for SPME water extracts began at 70 $^{\circ}\text{C}$ (held for 5 min for pesticide desorption), increased to 200 $^{\circ}\text{C}$ (@ 25 $^{\circ}\text{C min}^{-1}$, held for 4 min), then increased to 240 $^{\circ}\text{C}$ (@ 10 $^{\circ}\text{C min}^{-1}$, held for 5 min) and finally increased to 280 $^{\circ}\text{C}$ (@ 25 $^{\circ}\text{C min}^{-1}$, held for 2 min). Thiobencarb was quantified using a Varian 9012 HPLC equipped with 9050 variable wavelength UV/VIS detector at 220 nm. The mobile phase was 81% methanol : 19% water, with a flow rate of 1 mL min^{-1} . The stationary phase was a Phenomenex Luna C18(2) 150 mm x 4.6 mm with 5 μm particle size, and a Phenomenex C18 Security Guard pre-column with two cartridges installed. The injection volume was 50 μL and the HPLC system was run at 20 $^{\circ}\text{C}$.

RESULTS AND DISCUSSION

Recoveries of thiobencarb from water cannot be reported as direct injection HPLC was used. Likewise, recoveries for fipronil from water cannot be reported as standards for calibration had to be extracted from water via SPME using the same process as standards prior to injection into the GC. Based upon comparison with values using technical grade fipronil, the

presence of emulsifiers did not significantly impede SPME extraction of fipronil ($P>0.05$), presumably due to the presence of 50 μL acetone in all standards and samples, which resulted from the addition of a lindane internal standard. Recoveries of thiobencarb and fipronil from soil are shown in Table 2, and limits of quantification for both pesticides in soil and water is shown in Table 3.

Since the primary metabolite of fipronil under flooded reducing conditions is known to be fipronil sulfide,^[16] samples were analysed for this compound in addition to fipronil to assist in determining the extent of fipronil degradation. Conversely, thiobencarb has many metabolites under flooded conditions,^[29] some of which are only transient, and so the thiobencarb metabolites were not monitored. Despite the application rate of thiobencarb being approximately 200 times greater than that of fipronil by mass, the behaviours of both pesticides under flooded leaching conditions were quite similar. Control columns containing glass marbles instead of soil which were used to account for pesticide loss due to the apparatus, indicated losses due to processes such as adsorption and volatilisation as only $3.9\pm 0.61\%$ and $6.1\pm 0.96\%$ for fipronil and thiobencarb, respectively.

As water was allowed to percolate through the soil cores, thiobencarb, fipronil and fipronil sulfide transferred rapidly from the water column to the soil over the first 17 days. Figure 2 shows the distribution of thiobencarb in both soils, while Figures 3 and 4 show the distribution of both fipronil and fipronil sulfide in Coleambally and Yanco soils, respectively. Results are reported as μg of analyte in the total fraction rather than as a concentration in soil or water to allow direct comparison of the two phases. Additionally, due to the molecular weight difference between fipronil and fipronil sulfide, fipronil sulfide values were converted to an equivalent mass of fipronil.

Figures 2-4 show that up to 70% of the applied thiobencarb and 60% of applied fipronil accumulated in the 0-1 cm layer of each soil, with small amounts penetrating to the 1-2 cm depth (up to 7% and 12% for thiobencarb and fipronil, respectively). Thiobencarb and fipronil recovered from 1 cm soil layers between the 2 and 10 cm region of soil averaged approximately 2% of the applied amount, and did not exceed 5% for either thiobencarb or fipronil. The concentration of the fipronil tended to increase in the 0-1 cm layer up to day 17 on both soil types, while thiobencarb increased in first 1 cm layer in the Yanco soil up to day 17 with the Coleambally soil, reaching a maximum after 24 days. However, due to the variability between replicates, presumably as a consequence of the heterogeneity of the soils, there was no significant difference between the amount of thiobencarb in the 0-1 cm layer for days 10, 17, 24 and 31 on either soil ($P>0.05$). Conversely, the peak concentration of fipronil in the 0-1 cm layer of the Coleambally soil at day 17 was significantly greater than the concentration in the Yanco soil ($P<0.05$).

Batch sorption studies previously conducted^[27] indicated that the Coleambally soil had a greater sorption capacity for both fipronil and thiobencarb than the Yanco soil, however, this did not correlate with the total soil organic carbon contents of 2.2 and 2.5%, respectively. Subsequent analysis of soils indicated that while sorption of the pesticides did not correlate with total soil organic carbon, it correlated with the char (or charcoal) content of the soils. Char contents of $0.15 \pm 0.02\%$ and $0.23 \pm 0.03\%$ in the 0-1 cm layer of the Yanco and Coleambally soils, respectively, were significantly different ($P<0.05$). The char content of a soil results from the repeated burning of crop residues and its high sorption capacity has been linked to decreased efficacy of pesticides, such as thiobencarb.^[17; 30] Other soil fractions, such as clay or iron minerals were considered to have played only a minor role in the sorption of the pesticides due to the neutral, hydrophobic nature of the pesticides.

Fipronil sulfide was detected in the water applied to the soil cores, presumably as a contaminant resulting from the manufacture or long term storage of Cosmos[√]. The total amount recovered from soil and water increased during the lifetime of the experiment as a consequence of fipronil degradation. After pesticide application, water depth was decreased to 1 cm above the soil surface over a 10 day period, at which point more pesticide-free irrigation water was added to the soil cores. This had the effect of both diluting the remaining pesticide in the water column, as well as assisting leaching processes occurring in the soil bulk. An increase in pesticide concentration was observed in the 0-1 cm layer between days 10 and 17 and was attributed to the sorption of the remaining pesticide in the water column. Thus, the observed increase in soil concentration of the fipronil sulfide (and fipronil and thiobencarb) may be attributed to sorption of the remaining pesticide present in the floodwater, as it was allowed to flow through the soil core.

The rate of elution of thiobencarb and fipronil from the base of the soil cores was greater on the Yanco soil than on the Coleambally soil. Whilst batch sorption studies previously conducted^[27] indicated that while the 0-1 cm layers of each soil had greater sorption capacity for thiobencarb than did the 1-2 cm and 2-3 cm layers, the difference in sorption capacity was only slight. From these data, it is reasonable to assume that the 1-2 cm layer would adsorb any pesticide not adsorbed in the 0-1 cm layer due to leaching (ie. progressive adsorption). However, Figures 2-4 show that the effluent leakage from the bottom of each soil core contained thiobencarb or fipronil as early as 10 days after application of the pesticide to the water flooding the soil core. Thiobencarb and fipronil were also found at low concentrations at greater depths in the profile, rather than accumulating in the 1-2 cm layer once the 0-1 cm layer was theoretically saturated. The maximum concentration of each pesticide recovered from the 0-1 cm layer of soil in the experiments reported here was only 65-70% of the level of total saturation reported in previous work.^[27] These observations suggest that the distribution of thiobencarb and fipronil in the soil profile was due to preferential flow through macropores to various depths, resulting in the distribution of pesticide throughout the soil profile, or leakage around the perimeter of the core as a consequence of insufficient swelling of the

clays. In a study on macropore flow in saturated soil, reported that 96-98% of water flow was observed through macropores in the soil, with the remaining 2-4% attributed to matrix flow.^[17] These observations are supported by the rapid increase in the thiobencarb and fipronil concentrations in the 0-1 cm layer during the first 17 days, whilst the amount of pesticide distributed through the rest of the soil profile did not appear to change after the first 10 days.

Greater elution of thiobencarb and fipronil occurred from the base of the Yanco soil cores than from the Coleambally cores, and may be due to the differences in the sorption capacities of the soils or the stability of the macropores. In this study, macropores previously occupied by plant roots were identified in both soils and a red lining was observed on the macropore walls in the grey Coleambally soil. Analysis of this material by Atomic Absorption Spectrometry revealed the red material contained Fe, most likely due to the oxidation of soluble Fe(II) and the subsequent precipitation of Fe(III) as a result of oxygen diffusing from the roots of rice plants.^[31: 32] Given that Fe is known to act as a cementing agent between soil particles,^[33] the Fe lining of old root holes may in fact have stabilised them against collapse when the soil was flooded and the clays swelled. Whilst root holes were detected in the Yanco soil as well, a red lining could not be observed due to the soil colour; however, its presence cannot be excluded. Additionally, the greater shrink-swell capacity of the Coleambally soil compared to the Yanco soil would have resulted in greater compression of soil macropores in the Coleambally soil, leading to less preferential flow than observed for the Yanco soil.

Characterisation of soil macropores with a dye tracer indicated the presence of soil macropores, which allowed preferential flow to occur. While most of the dye tracer tended to accumulate in the top 5 mm of the soil core, small amounts of dye was found in the lower regions of the cores, indicating transport by macropore flow. The surface area by macropores in transects of the soil made up less than 0.2% of the surface area of the core, but allowed the dye to penetrate soil to depths of 5-6 cm, often along the path of hair-like roots found in the soil.

As the soil cores used in this experiment were collected intact and remained in that state for the duration of the pesticide experiments, macropores were preserved and allowed preferential flow of pesticides to occur. Since macropore flow has been predicted to reduce the influence of the chemical properties of the pesticide on the extent of leaching,^[34] the movement of less mobile compounds (eg thiobencarb) may increase due to macropore flow. Additionally, macropore flow has been reported to increase during periods of high rainfall or ponding of water,^[35] so the thiobencarb mobility may increase further when applied to soil which has been flood irrigated. Whilst DOC levels were measured in the soil prior to flooding (Table 1), the cores were drained prior to pesticide application. Thus, the influence of DOC on pesticide mobility was assumed to be negligible.

CONCLUSION

High rates of water percolating through soils may increase the extent to which applied pesticides leach through the soil profile. The mobility of the rice pesticides thiobencarb and fipronil were investigated under flooded conditions. Preferential flow of water containing pesticides through macropores in the soil resulted in the bulk soil matrix being bypassed, restricting degradation and sorption processes on pesticides transported by macropore flow.

A dye tracer was used to characterise the macropore flow, and despite its presence, accumulation of pesticides tended to occur mainly in the 0-1 cm of both soils tested, with only a small percentage of the pesticide applied to the soil surface leaching from the base of the core.

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FIGURE CAPTIONS

Figure 1 – Apparatus used for controlling the rate of soil leakage in soil (A) and in the control (B)

Figure 2 – Cumulative mass and percentage distributions of thiobencarb in flooded Coleambally soil (A) and Yanco soil (B). Results for soil layers between 3 and 9 cm were similar to those for the 1-2 and 2-3 cm fractions and have been omitted for the sake of simplicity

Figure 3 – Cumulative distribution of fipronil sulfide (A) and fipronil (B) in Coleambally soil. Results for soil layers between 3 and 9 cm were similar to those for the 1-2 and 2-3 cm fractions and have been omitted for the sake of simplicity

Figure 4 – Cumulative distribution of fipronil sulfide (A) and fipronil (B) in Yanco soil

FIGURES

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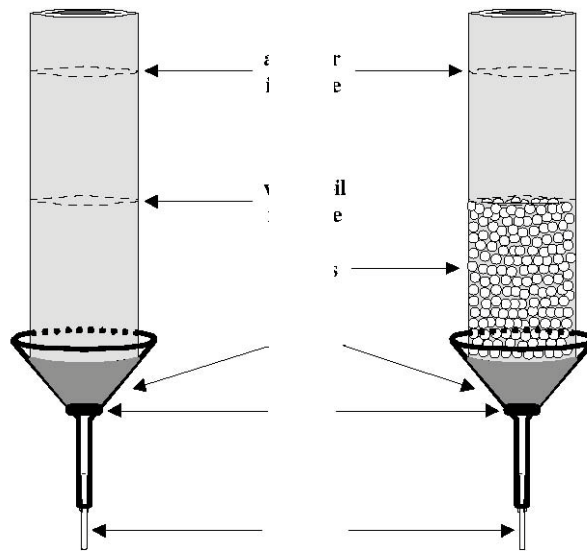
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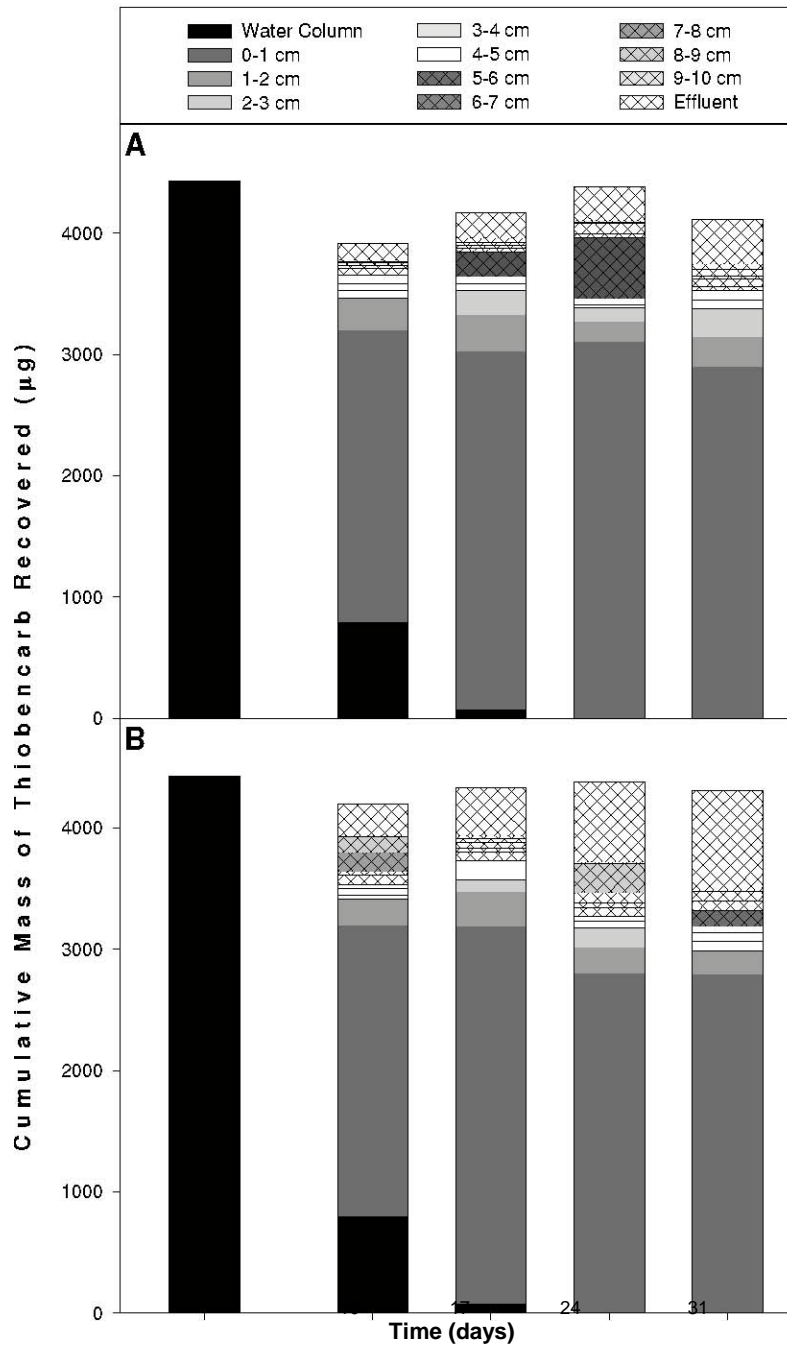


Figure 2

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Time (days)

Figure 3

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Time (days)

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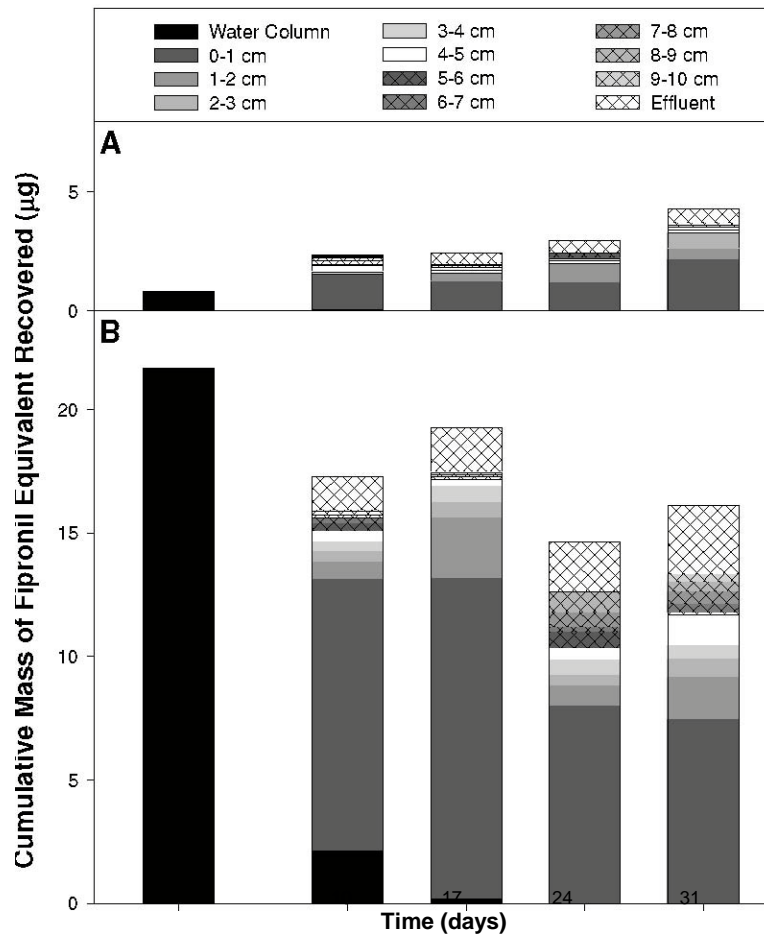


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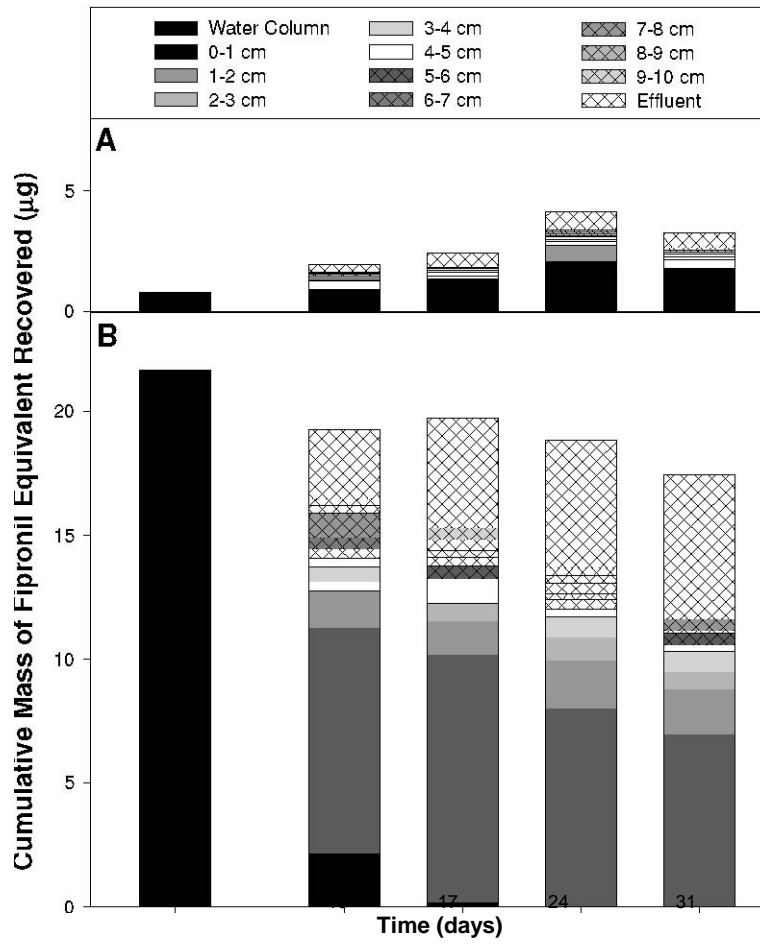


Figure 2

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Time (days)

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10 17 24 31
Time (days)

Figure 2

10 17 24 31
Time (days)

10 17 24 31
Time (days)

Figure 2

10 17 24 31
Time (days)

Figure 3

10 17 24 31
Time (days)

Figure 4

TABLES

2 Table 1 –

Soil

properties

Soil	TOC (%)	DOC (mg kg ⁻¹)	Char (%)	Bulk Density (g cm ³)	Pore Volume (%)	Total Fe (%)	Readily Reducible Fe (%)	Texture (%)		
								Sand	Silt	Clay
C	2.2	160	0.23	1.80	32	4.9	0.28	16	38	46
Y	2.5	141	0.15	1.69	36	4.8	0.48	37	33	30

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Table 2 – Percentage pesticide recovery from soil

Soil	Thiobencarb	Fipronil
Coleambally	96±3	98±4
Yanco	101±2	100±2

Table 3 – Limits of quantification of pesticides from soil and water