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Pesticide removal from cotton farm tailwater by a pilot-scale ponded wetland

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Abstract

A pilot-scale, ponded wetland consisting of an open pond and a vegetated pond in series was constructed on a cotton farm in northern New South Wales, Australia, and assessed for its potential to remove pesticides from irrigation tailwater. Ten incubation periods ranging from 7 to 13 days each were conducted over two cotton growing seasons to monitor removal of residues of four pesticides applied to the crop. Residue reductions ranging 22–53% and 32–90% were observed in the first and second seasons respectively. Average half-lives during this first season were calculated as 21.3 days for diuron, 25.4 days for fluometuron and 26.4 days for aldicarb over the entire wetland. During the second season of monitoring, pesticide half-lives were significantly reduced, with fluometuron exhibiting a half-life of 13.8 days, aldicarb 6.2 days and endosulfan 7.5 days in the open pond. Further significant reductions were observed in the vegetated pond and also following an algal bloom in the open pond, as a result of which aldicarb and endosulfan were no longer quantifiable. Partitioning onto sediment was found to be a considerable sink for the insecticide endosulfan. These results demonstrate that macrophytes and algae can reduce the persistence of pesticides in on-farm water and provide some data for modelling.

Keywords: Bioremediation; Organic pollutant; Half-life; Macrophyte; Sorption

1. Introduction

Despite a commitment to the rapid adoption of integrated pest management techniques, the cotton industry remains as one of the highest users of pesticides in Australian agriculture (Radcliffe, 2002). The herbicides diuron, fluometuron, prometryn and trifluralin are used widely for pre- and post-emergence control of weeds in fields of conventional cotton cultivars. The cyclodiene endosulfan, together with synthetic pyrethroid, organophosphate and carbamate insecticides, is applied routinely for the control of *Helicoverpa* spp., thrips and aphids.

Management of the off-farm movement of these chemicals, and potential contamination of surrounding

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ecosystems, has been addressed by the promotion of best management practices (Williams and Williams, 2000). These practices include increased care in the timing and methods of spray application to control aerial drift and the compulsory recycling of tailwater on-farm. In Australia, tailwater recycling is also necessary to gain the maximum economic benefit from a limited quantity of water allocated to farmers. Nevertheless, these practices result in the concentration of pesticides on farms, particularly in tailwater, and increase the risk of toxicity to livestock, farm workers and native plant and animal species (Sánchez-Bayo et al., 2002). Insects, amphibians and birds that are attracted by the large volumes of water on cotton farms (Sánchez-Bayo et al., 1999; Reid et al., 2003) are especially at risk. It is necessary to reduce the concentration and availability of these residues to minimise the risk for non-target species (Sánchez-Bayo et al., 2002).

Pesticide loss from aqueous systems has been well characterized and involves a combination of degradation and transport procedures. Degradation can include photolysis, chemical transformations and biological transformation (Roberts, 1998; Stangroom et al., 2000), of which microbial processes usually dominate (Vink and Van der Zee, 1997). Similarly, pesticide transport can be physicochemical or biological, but the parent compound remains unchanged; it is simply transferred from one matrix to another. Importantly, the rate of transport and breakdown of a particular pesticide depends heavily on its physicochemical properties (Stangroom et al., 2000; Crossan, 2002).

Constructed wetlands are gaining recognition as potential best management practices for the reduction of pesticide concentrations in agricultural runoff (Schulz, 2004). Generally, their success can be attributed to their diversity of function, as they improve the potential for the range of transport and degradation processes mentioned above. Most recent studies are concerned with mixed open water/vegetated constructed wetlands or fully vegetated constructed wetlands (Alvord and Kadlec, 1996; Schulz and Peall, 2001; Moore et al., 2002; Braskerud and Haarstad, 2003; Runes et al., 2003), with the aim of either quantifying pesticide removal or determining residence times needed in a particular wetland to remove a certain proportion of the chemical residue. In Australia, the scarcity of water means that any treatment of water must be rapid, with minimal loss from the system, which may occur by transpiration from aquatic macrophytes. Obstructions to water flow, the provision of refuge for weed and insect pests, and increased maintenance have also been discussed by growers as deterrents for operating vegetated wetlands on-farm.

In this study, an artificial wetland was established on a cotton farm in the Namoi River catchment near Narrabri, New South Wales, Australia. The objectives of the study were to (i) compare the rates of pesticide removal in an open (non-vegetated) and a vegetated pond, (ii) determine the fate of pesticides in the combined system, and (iii) assess the combined performance of an open and vegetated pond arranged in series in removing pesticides from tailwaters.

2. Methods

2.1. Description of the pilot-scale pond

The pilot-scale wetland system was established in September 2001, and basically consisted of a 1 m deep open pond of surface area 100 m^2 and a 0.5 m deep vegetated pond of surface area 200 m^2 in series (Fig. 1). Construction involved the excavation of the wetland ponds and installation of a depth indicator and flow meter to record water input and evaporation. An initial planting of the vegetated pond with native wetland species occurred on 1/11/01 and a second planting on 5/12/01, after which the wetland was filled with water from the nearby storage via the farm irrigation system. The species planted included knotweed (*Persicaria* spp.), water primrose (*Ludwigia peploides*), water milfoil (*Myriophyllum papillosum*), common rush (*Juncus usitatus*), clubrush (*Bolboschoenus medianus*) and cumbungi (*Typha domingensis*). At the end of the first season

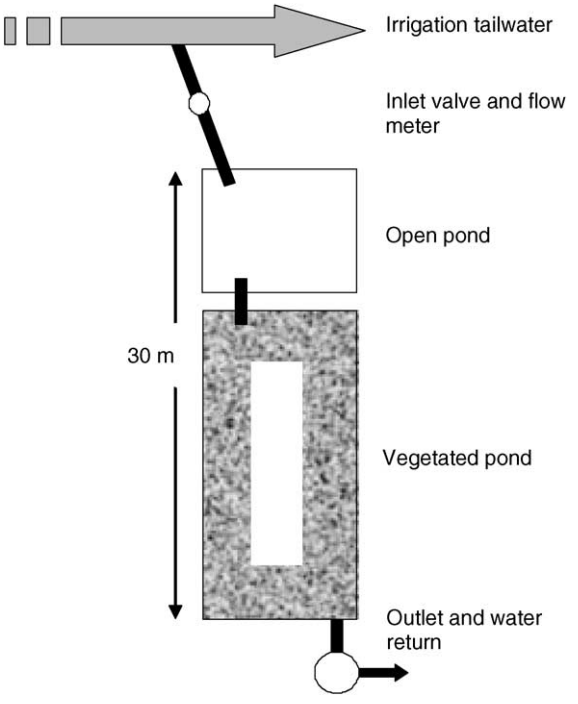

Fig. 1. Schematic diagram of the pilot-scale ponded wetland.

(March 2002), plant coverage was only 20% of the vegetated pond area. By the start of the second season (November 2002), *B. medianus*, *T. domingensis* and *Persicaria* spp. were the dominant species and coverage had increased to 95% of the vegetated pond.

Irrigation runoff from field 24, a 30 ha field planted with conventional cotton in the first season, and genetically modified, Roundup Ready® cotton in the second season, was collected in a return drain that ran approximately 120 m to a storage dam. Midway along the length of this return drain was situated the inlet to the constructed wetland, consisting of an 8 m length of piping (10 cm diameter) that diverted some, but not all, of the irrigation runoff. Water from the inlet flowed first into the open pond from the south-eastern corner. An earthen berm separated the deep open pond from the shallow vegetated pond, which were connected by a rotary pipe through the berm. Another rotary siphon pipe situated in the north-western corner of the vegetated pond allowed for emptying of the wetland. Water leaving the wetland was returned to the storage via a 30×1 m ditch.

2.2. Monitoring cycle

At each irrigation event—approximately every 2 weeks for about 3 months—the wetland was filled with tailwater from field 24, and the volume of water added recorded from the flow meter. The water depth was also recorded once the wetland had been filled. Triplicate, composite water samples of the tailwater at the inlet were taken throughout the filling of the pond.

To evaluate the extent of pesticide removal from the pilot wetland, water samples were taken from both open and vegetated ponds prior to each irrigation event. During the first trial season (2001–2002), duplicate water samples were taken. Each sample was obtained by fully filling a 1 l amber glass bottle using a grab stick then sealing it with a Teflon® lined cap. During the second season (2002–2003), triplicate water samples were taken from each pond. In this instance, 1 l composite water samples were obtained by combining four, 250 ml sub-samples from random points within each pond. Also in the second year, sediment samples were taken before and after each irrigation event. Sediment samples were obtained by taking four sub-samples taken from the top 50 mm of pond bottom with a stainless steel scoop and combining them in an aluminium-foil sealed glass jar.

At the end of each incubation period following sampling, the water level was recorded and the wetland emptied as much as possible via the outlet siphon pipe. The water level was again recorded once the wetland had been emptied.

All water samples were refrigerated at 4 °C until pesticide extraction, which occurred within several days of sampling. Sediment samples were stored in sealed glass jars at −20 °C until analysis.

2.3. Chemicals

Aldicarb, fluometuron and diuron standards were obtained from the Australian National Analytical Reference Laboratory, Sydney, and were all of greater than 99.5% purity. Analytical reagent grade sodium sulfate was obtained from Mallinckrodt. All solvents were of Mallinckrodt nanograde.

2.4. Water extraction procedure

Water sub-samples (500 ml) were shaken vigorously for 2 min with three volumes (100, 50, 50 ml) of dichloromethane in a Teflon® separating funnel. The dichloromethane solvent was passed through sodium sulfate (25 g) suspended by cotton wool in a glass filter funnel. The combined extracts were collected, evaporated to near dryness and exchanged three times with nanograde hexane (10 ml). After the final evaporation, the volume was made up to 5 ml with hexane and 1 ml removed for gas chromatographic (GC) analysis. The remaining 4 ml was exchanged three times with methanol (10 ml). After the final evaporation, the volume was made up to 4 ml with 50:50 methanol/water, and filtered into a 4 ml glass vial through a 0.22 μm syringe filter.

2.5. Sediment extraction procedure

Twenty-five gram (wet weight) sub-samples were extracted for 8 h with 60 ml of acetonitrile and again for 1 h with 40 ml on a rotary shaker. The combined extracts were filtered through Whatman GF/C filters, evaporated to near dryness and reconstituted with 50 ml deionised water. These samples were cleaned up on 200 mg/6 ml Strata-X® (modified cross-linked polymer, Phenomenex) cartridges previously conditioned with 6 ml methanol and equilibrated with 10 ml deionised water, after which the sample was loaded at 1 ml min^{-1}, washed with 10 ml of 10% methanol and eluted twice with 5 ml hexane:acetonitrile (1:1 v/v). The eluent was evaporated to dryness and made up with 5 ml acetonitrile. A 1 ml aliquot was removed for GC analysis and the remainder evaporated, reconstituted in 4 ml 50% acetonitrile and filtered (0.22 μm) for high performance liquid chromatography (HPLC) analysis. Final concentrations were determined on a dry weight basis by oven drying duplicate sediment sub-samples overnight (105 °C). Water content of the sediments ranged from 41% to 49%.

2.6. Chromatographic analyses

Diuron, fluometuron and aldicarb were analysed by HPLC using a Shimadzu SIL-10AXL auto injector, Shi-

madzu SCL-10A system controller and an LC-10AT VP pump fitted with a Gilson UV–Vis detector. A Zorbax SB-C18 analytical column (15 cm × 4.6 mm ID, 5 μm particle size, 80 A pore size, no end-capping, Hewlett–Packard, USA) preceded by a Zorbax SB-C18 guard column was used for analyte separation. Sample injections of 100 μl were conducted and run at 1.0 ml min^{-1} for both fluometuron and diuron, and 0.7 ml min^{-1} for aldicarb. Fluometuron and diuron were run in a mobile phase of methanol:water (60:40 v/v) and detected at a wavelength of 250 nm. Aldicarb was run in a mobile phase of methanol:water (55:45 v/v) and detected at a wavelength of 265 nm.

α-endosulfan, β-endosulfan and their degradation product endosulfan sulfate were analysed by gas chromatography at Agrisearch Analytical, Sydney, an accredited National Association of Testing Authorities (NATA) laboratory. Samples (1 μl) were injected into a 30 m × 0.25 mm, fused silica column coated with HP-5MS (0.25 μm, Agilent) by a 7683 automatic sampler (Hewlett–Packard). Pulsed splitless injection occurred at 250 °C with helium as the carrier gas (1 ml min^{-1}). The column was housed in a Hewlett–Packard 6890 GC, with the column temperature initially at 100 °C (1 min), raised to 300 °C at 10 °C min^{-1} and held for 9 min. The GC was equipped with a Hewlett–Packard 5973 mass-selective detector held at 280 °C and operated in selected-ion monitoring mode (SIM). The ions measured (m/z) and typical retention times were 339/241/272, 14.8 min, for α-endosulfan; 237/339/272, 16 min, for β-endosulfan; and 387/272/274, 16.8 min, for endosulfan sulfate.

Recovery and 95% confidence data for all pesticides are shown in Table 1. Interfering peaks were not observed in matrix blanks. In all cases, compounds were quantified by comparison to external standard curves of certified analytical grade reference pesticide (National Analytical Reference Laboratories/National Measurement Institute, Sydney, Australia).

2.7. Data analysis

For each irrigation event, the removal efficiency of each pesticide in both open and vegetated ponds was estimated from the residues remaining at the end of the each incubating period, that is, the time between consecutive irrigations. Because the length of these periods varied from 7 to 13 days, in order to compare the performance percent reductions of pesticides were converted to half-lives by the negative exponential model:

$$x = x_0 e^{-kt}$$

$$t_{1/2} = 0.693/k \quad (270)$$

where x_0 is the initial pesticide concentration, x is the final pesticide concentration, t is the incubation time and k is a removal rate constant (Vink and Van der Zee, 1997). The difference between treatments was analysed by unpaired Student's t-test with confidence limits of 95%, using Genstat software.

3. Results

3.1. First year performance (2002)

Five incubation periods were monitored between six irrigations over a period of approximately 2 months. A number of different pesticides were applied to field 24 pre- and post-planting of the conventional cotton cultivar (Table 2). Because none of the studied pesticides were applied after the first irrigation, the concentration of pesticide entering the wetland decreased in subsequent incubation periods (Fig. 2a). The biomass of the vegetated pond increased little throughout this first season, from coverage of less than 5% at planting time to approximately 20% at the end of the cotton growing season.

Average pesticide removal over the entire wetland varied from 27% to 55% for diuron, 15% to 39% for aldicarb and 0% to 34% for fluometuron. No significant difference was observed between pesticide reductions in the open pond and vegetated pond over any of the incubation periods for any of the pesticides ($p > 0.05$). Furthermore, the half-life of diuron and aldicarb did not significantly ($p > 0.05$) change over the trial period of five incubations, despite different weather conditions (Table 2), different inlet concentrations (Table 1) and aging of the wetland. Consequently, the results were

Table 1
Pesticide recoveries (%) from spiked sample matrix

Pesticide	Water	Sample spike level (μg l^{-1})	Limit of quantification in sample (μg l^{-1})	Sediment	Sample spike level (μg g^{-1})	Limit of quantification in sample (μg g^{-1})
Fluometuron	96 (16.1)	10	1.0	82 (12.3)	30	4.0
Diuron	100 (5.1)	10	1.0	86 (9.1)	30	4.0
Aldicarb	113 (13.2)	10	4.0	n.d.[a]	–	–
Endosulfan	102 (7.2)	2	0.4	78 (11.4)	60	1.6

Numbers in brackets represent 95% confidence intervals ($n = 5$).
[a] n.d. = Not determined.

Table 2
Environmental conditions and water quality parameters

	2002 Incubations (range)	2003 Incubations (range)
Ambient temperature (°C)	10.1–39.5	9.5–41.8
Water temperature[a] (°C)	19–27	18–28
Solar radiation (MJ m^{-2} day^{-1})	14.7–34.0	8.7–34.0
pH	7.74–8.56	8.26–8.73
Nitrate + nitrite (mg l^{-1})	0.25–0.78	0.22–1.43
Ammonium (μg l^{-1})	54.3–143.7	78.1–247.9
Ortho phosphate (mg l^{-1})	n.d.[b]	<1

[a] Water temperature at 9.00 a.m.
[b] Not determined.

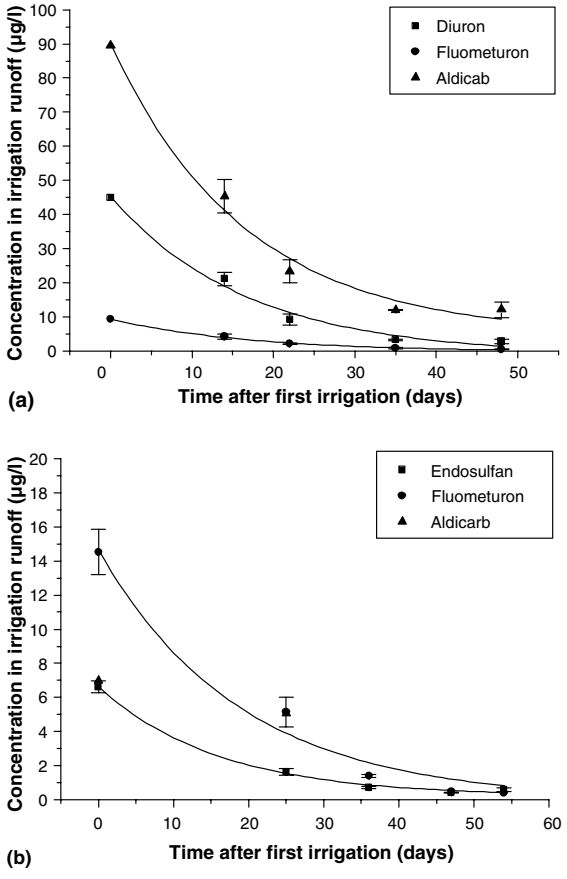

Fig. 2. Inlet concentrations of pesticides in (a) 2002 season and (b) 2003 season. Error bars represent 95% confidence limits.

averaged over both ponds and all incubations (Fig. 3). Thus, the average half-life of diuron in the combined ponds was 21.3 ± 4.2 days (95% confidence) and that of aldicarb 26.4 ± 7.0 days.

The half-life of fluometuron was significantly different ($p < 0.05$) between the first incubation in the vegetated pond, in which the concentration was found not to decrease, and the fourth incubation in which the concentration decreased by 44%. By averaging the data for the final four incubations, which were not significantly different ($p > 0.05$), a half-life of 25.4 ± 8.6 days was calculated for fluometuron.

3.2. Second year performance (2003)

Water entering the wetland during the second trial period was again taken from field 24, which was planted with a Roundup-Ready® cotton cultivar. This water had already been recycled from other fields that had undergone fluometuron application, resulting in the detection of this herbicide prior to irrigation of field 24. Following irrigation of the latter field, aldicarb and endosulfan were also detected; however, towards the end of the season only trace amounts of these three pesticides were observed (Fig. 2b). Diuron was not applied this season (see Table 2) and was not detected in the tailwaters.

The first incubation of the 2002/2003 cotton season was disrupted by heavy rainfall, in which overland flow contributed an unknown amount of pesticide to the wetland system. This is thought to have caused a large difference in removal efficiencies between the three pesticides analysed, thus these results were omitted from calculations and not shown here.

During the second incubation, the average half-lives of fluometuron and aldicarb in the open pond (13.8 ± 1.0 days and 6.2 ± 0.3 days, respectively) were significantly lower ($p < 0.05$) than in the corresponding incubation the previous year (Fig. 3). Interestingly, fluometuron removal was significantly greater ($p < 0.05$) in the vegetated pond (58%) than in the open pond (41%) during the second incubation, whereas the converse was true in the third incubation, in which an algal bloom occurred in the open pond. The calculated half-lives during these incubations were averaged for the vegetated pond (10.2 ± 1.3 days), but were split for the open pond into two figures: before the algal bloom (13.8 ± 1.0) and after the bloom (5.5 ± 0.4).

Trace amounts of aldicarb and endosulfan were detected in both ponds during the third, fourth and fifth incubations; however, their concentrations were reduced to below levels of quantification (Table 1). This was also

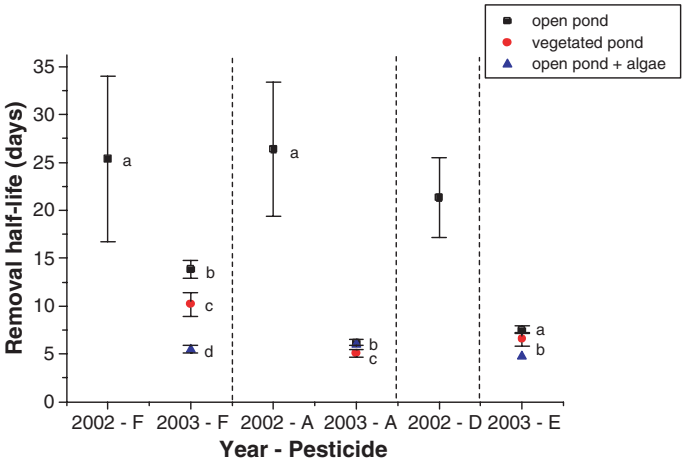

Fig. 3. Pesticide removal expressed as half-lives for fluometuron (F), aldicarb (A), diuron (D) and endosulfan (E) from irrigation tailwater. Error bars represent 95% confidence limits. Data points designated by different letters are statistically different within pesticide groupings ($p < 0.05$).

the case for fluometuron in the open pond in the fifth incubation. Fig. 3 shows a data point for the absolute maximum half-life of endosulfan and aldicarb during this period, estimated as 4.8 and 6.0 days, respectively from the limit of quantification of their analytical methods.

Concentration of aldicarb, fluometuron and total endosulfan (i.e. α- and β-isomers plus endosulfan sulfate) were measured in sediment samples in the third, fourth and fifth incubations (Table 3). In addition, DDE was also detected as a residue from applications of DDT that took place in the area more than 20 years ago (Shivaramaiah et al., 2002). Results show a large variation in residue levels between incubation periods. On average, total endosulfan concentrations were reduced by 24% and 27% in the open pond and vegetated pond respectively, with 11–61% less residue at the end of the experimental period. Residues of DDE were also reduced by an average 35% in the open pond and 18% in the vegetated pond. In contrast, fluometuron levels remained almost constant. Aldicarb was not present at quantifiable levels in any of the sediment samples.

Only the field sorption coefficient (K_d) for fluometuron onto sediment could be determined ($0.49\,l\,kg^{-1}$), since water concentrations were not quantifiable for endosulfan and DDE during these incubations (see Table 4).

4. Discussion

4.1. Justification of data transformation

Percent reduction was converted to an equivalent half-life for each incubation, based on assumed first-order dissipation. This transformation was conducted to allow for a comparison between incubations within each trial year, which was otherwise impossible considering the variation in incubation lengths (7–13 days). Because only two temporal data points were available, that is, initial time and final time, biphasic- or triphasic-models could not be investigated, despite evidence to suggest their possibility (Kennedy et al., 2001). Determination of the true dissipation kinetic is the subject of current work.

It is highlighted that the half-lives presented are therefore approximations, and, as with all environmental data, should be used within their limitations. Nevertheless, these manipulated data maintain the trends observed with respect to differences between the open and vegetated ponds in percent reduction, which was the main aim of this study.

4.2. Pesticide reductions in water

In this study, the concentration of pesticide in tailwater during both trial periods was consistent with previous reports in the Australian cotton industry (Crossan, 2002; Silburn et al., 2002). Decreasing amounts were found in subsequent irrigations after application as described by Kennedy et al. (2001), and similar to the exponential decrease of the insecticide tribufos observed by Potter et al. (2000) after sequential runoff events.

A large variability was observed for all three pesticides analysed in the first year, particularly fluometuron. This makes interpretation of results during this season difficult. It is likely that environmental variation was compounded due to the limited sampling regime, that is, two water samples per pond and incubation period. Temperature and radiation influence the degradation

Table 3
Pesticide application records for Field 24 in the 2002 season (top) and 2003 season (bottom)

Date	Chemical	Quantity (kg l)
25/09/2001	Trifluralin	69.6
16/10/2001	Planting	0.0
	Aldicarb	87.0
	Fluometuron	46.4
25-27/11/01	Rain	
4/12/2001	Endosulfan	30.5
	Pyrithiobac	0.9
22/12/2001	Diuron	43.5
23/12/2001	Endosulfan	30.5
	Fipronil	0.9
25/12/2001	Irrigation	
31/12/2001	Spinosad	23.2
7/01/2002	Spinosad	11.6
	Irrigation	
16/01/2002	Emamectin	13.6
17/01/2002	Irrigation	
25/01/2002	Spinosad	23.2
29/01/2002	Irrigation	
12/02/2002	Irrigation	
15/02/2002	Irrigation	
24/09/2002	Trifluralin	69.6
3/10/2002	Planting	
	Aldicarb	87.0
	Glyphosate	29.0
25/11/2002	Endosulfan	30.5
3/12/2002	Endosulfan	30.5
14/12/2003	Irrigation	
20/12/2002	Indoxacarb	23.2
29/12/2002	Emamectin	13.6
8/01/2003	Irrigation	
16/01/2003	Spinosad	11.6
19/01/2003	Irrigation	
29/01/2003	Emamectin	13.6
30/01/2003	Irrigation	
6/02/2003	Irrigation	
9/02/2003	Indoxacarb	23.2
13/02/2003	Irrigation	

of many pesticides (Burrows et al., 2002) and this is similarly true for pH, nutrient and organic matter concentrations and microbial populations (Vink and Van der Zee, 1997). The smaller variability in the second year results using triplicate, composite samples confirmed the benefits from a more thorough sampling scheme, so a comprehensive sampling protocol is recommended for future investigations of this kind.

No significant difference ($p > 0.05$) was observed between pesticide half-lives in different incubations in the first year, despite different inlet concentrations, wetland aging and plant growth. Studies by Moore et al. (2001, 2002) have similarly shown negligible effect of inlet concentration on metolachlor and chlorpyrifos removal. Atrazine, however, was observed to be approximately twice as persistent in wetlands amended with 147 $\mu g\,l^{-1}$ compared with 73 $\mu g\,l^{-1}$ (Moore et al., 2000).

Plants can increase pollutant removal, including pesticides, either directly through uptake or indirectly through associated microbiota and humic contribution (Stomp et al., 1994). In a previous glasshouse study, hydroponic cultures of *Persicaria decipiens* were able to reduce the concentrations of prometryn, fluometuron, aldicarb and endosulfan in the range 16–40% in 2 weeks (Rose et al., 2001), a time similar to the average incubation period between irrigation events in this study. However, the relatively small increase in vegetation over the first season (approximately 15%) was probably not sufficient to cause a noticeable increase in pesticide removal between incubations. The similar performance of both the open and vegetated ponds over this first season supports this view.

The removal of pesticide from tailwater was greater in the second season of operation compared to the first year, except for the first trial in which heavy rainfall disrupted results. This better performance may be explained by an increase in organic matter providing more sites for sorption, and/or the adaptation of microorganisms in the winter (non-trial) period increasing the rate of degradation. Evidence for the acclimation of pesticide-degrading bacteria has been demonstrated for both aldicarb and endosulfan under anaerobic conditions (Khandaker and Young, 2000; Ghadiri and Rose, 2001). Adaptation of bacteria in the underlying sediment, which was freshly exposed by excavation in the first season, is thus a plausible scenario. In this regard, a recent review by Schulz (2004) concludes that more research is required into the temporal changes in wetlands to understand their variable remedial performance.

Also in the second season, the performance of the open pond and vegetated pond differed significantly in a number of incubations. Removal of fluometuron, aldicarb and endosulfan from the vegetated pond was significantly greater over the second incubation period. Apart from our previous study (Rose et al., 2001), a number of laboratory trials have demonstrated that aquatic plants can accelerate the removal of pesticides from water compared to non-vegetated treatments by uptake and/or enhanced rhizosphere degradation. At least two of these have correlated herbicide uptake with water uptake/evapotranspiration (Wilson et al., 2000a,b). It is possible that the higher temperature over the second trial period (average daytime 34.4 °C) contributed to the greater removal of fluometuron and the highly water soluble aldicarb (water solubility of 6 $g\,l^{-1}$) from the vegetated pond in this way.

Other studies have also shown an increased effectiveness in pesticide removal of vegetated wetlands compared with non-vegetated wetlands. Schulz et al. (2003a) found that the concentration of an organophosphate insecticide, methyl parathion, in water was

Table 4
Pesticide concentrations in sediment (ng g^{-1} dry weight, $n = 3$) of the open pond (OP) and vegetated pond (VP) at the beginning and end of three incubation periods (T3, 11 days; T4, 7 days; and T5, 10 days) during the 2002 trial season

	Endosulfan		Fluometuron		DDE	
	OP	VP	OP	VP	OP	VP
T3						
Start	165.7 (24.6)	101.8 (24.3)	7.1 (1.7)	12.7 (3.6)	29.8 (1.9)	15.8 (5.4)
End	124.2 (19.1)	38.8 (11.0)	10.5 (3.4)	9.2 (5.3)	24.3 (3.2)	8.7 (3.3)
Reduction	25%	62%	−48%	28%	18%	45%
T4						
Start	105.8 (17.9)	134.7 (14.7)	8.2 (4.7)	4.0 (2.2)	18.5 (1.6)	15.5 (2.9)
End	61.4 (40.8)	84.8 (13.4)	5.6 (3.4)	5.5 (1.1)	12.9 (0.2)	14.7 (4.0)
Reduction	42%	37%	32%	−38%	30%	5%
T5						
Start	67.6 (14.7)	77.5 (14.5)	7.1 (4.7)	4.2 (0.8)	32.0 (8.7)	16.8 (3.6)
End	64.3 (20.3)	91.0 (16.5)	10.4 (6.3)	6.3 (4.1)	14.0 (2.6)	16.2 (2.7)
Reduction	5%	−17%	−46%	−54%	56%	4%
Average	24%	27%	−21%	−21%	35%	18%
Overall	61%	11%	−46%	50%	53%	−3%
CV	77%	149%	−218%	−203%	55%	131%

Numbers in brackets represent 95% confidence limits; CV = coefficient of variation of the overall change. Aldicarb was not detected in any of the samples.

reduced to 20 μg l^{-1} over a 20 m distance in vegetated wetland cells compared to 70 μg l^{-1} in non-vegetated cells. Increased sorption by macrophytes, mainly *Juncus effusus*, and sedimentation was reported to account for the difference in removal. As a consequence, a corresponding reduction in toxicity to various insect species and the crustacean *Hyalella azteca* was also observed (Schulz et al., 2003b).

Interestingly, over the third incubation in the second year, more fluometuron was removed from the open pond (76%) compared to the second incubation (41%). Furthermore, this reduction was greater than the amount removed in the vegetated pond over the same trial periods. There was also evidence to suggest a similar trend for aldicarb and endosulfan, however almost complete elimination of these insecticides during those periods prevented this trend from being quantified. A proliferation of unidentified green, filamentous algal growth was observed during the third, fourth and fifth incubations, which could explain the increased rate of removal of all three pesticides. Zablotowicz et al. (1998) studied the metabolism of fluometuron by 15 algal strains and found that eight of these were capable of the *N*-demethlyation of fluometuron. The most rapid transformations (by *Scenedesmus* and *Ankistrodesmus* spp.) reduced fluometuron concentrations by 50% in less than 4 days. Sethunathan et al. (2004) have also shown that a *Scenedesmus* species is capable of transforming α-endosulfan in laboratory cultures and accelerating its degradation in soil samples. Other laboratory studies have also highlighted the significance of algae in reducing the persistence of agricultural pesticides (Friesen-Pankratz et al., 2003). Our results support findings by these authors, and highlight the potential for the use of algae in the bioremediation of pesticides in aquatic environments, which therefore deserves further examination under both laboratory and field conditions.

A limitation of this study was the inability of our analytical techniques to monitor concentrations of degradation products, particularly those of aldicarb. Aldicarb has been shown to undergo rapid oxidation in soil and water to the equally toxic products aldicarb sulfoxide and aldicarb sulfone (Jones and Estes, 1995). This is reportedly faster under acidic conditions at pH less than 5.5 (Tomlin, 1997). However, recent research has shown that these oxidative pathways may not be as prevalent as previously thought, particularly under anoxic conditions in water (Wilson et al., 2005) and saturated sediment (Kazumi and Capone, 1995). Instead, hydrolysis to less toxic, non-carbamate degradates predominates (Kazumi and Capone, 1995). It is speculated that accumulation of the toxic oxidative metabolites is therefore unlikely to occur in the alkaline ponded system described here, but future efforts should at least monitor dissolved oxygen concentrations, or if possible, aldicarb sulfone and sulfoxide residues.

4.3. Pesticide partitioning onto sediment

Pesticide concentrations were measured in sediments throughout the second season only. Despite the deeper open pond being designed to slow water velocity and remove the bulk of sediment-associated pesticide prior to the vegetated pond, this did not occur. Concentra-

tions of total endosulfan (39–166 μg kg^{-1} dry weight) and fluometuron (4–11 μg kg^{-1}) in sediments of the open and vegetated ponds were not significantly different (see Table 3), which suggests that these pesticides are associated with smaller colloids that remain suspended long enough to equilibrate in both ponds, and then eventually settle.

According to Wu et al. (2003), the binding of pesticides to different size fractions has been receiving increasing attention, particularly the finer particles because of their large specific surface area, high stability in suspension and their potential role in facilitating transport of contaminants. These authors found that >20% of the fungicide propiconazole ($\log K_{ow} = 3.72$) was associated with particles of size <2.0 μm, even though this fraction accounted for less than 8% of the sediment mass. Crossan et al. (2002) also found that more than 80% of diuron and endosulfan in runoff from Australian cotton soils is associated with suspended particles less than 65 μm in size.

The rapid reduction of endosulfan in the aqueous phase prevented the determination of its partitioning coefficient, but its high levels in sediments suggests the sedimentation process plays an important role in its removal from the water phase (Kennedy et al., 2001). This was also the case for DDE, which was not detected in any aqueous samples, including inlet water, but was found at levels between 9 and 32 μg kg^{-1} in sediments. Although the use of DDT in Australia was discontinued over 20 years ago, its breakdown product DDE is still frequently detected in soils and biota of the northern river valleys of New South Wales (Sánchez-Bayo et al., 1999; Shivaramaiah et al., 2002). In contrast, the undetectable levels of aldicarb in sediments prevented determination of its sorption coefficient.

The calculated partitioning coefficient for fluometuron onto sediment ($K_d = 0.49 \pm 0.18$ l kg^{-1}) is in close agreement with available laboratory data. Baskaran and Kennedy (1999) found a K_d of 0.48 ± 0.2 l kg^{-1} for fluometuron onto soil from the same region. Such a result indicates that this laboratory data would be useful for predicting pesticide sorption behaviour in the field. While sorption characteristics for endosulfan are available (Parkpian et al., 1998), those of aldicarb and DDE are required to solve pesticide transport and removal models. Pesticide sorption data onto macrophytes and biofilms would also be desirable for vegetated wetland modelling, as described by Alvord and Kadlec (1996).

5. Conclusions

This study has given a preliminary insight into pesticide transport and removal efficiency in constructed wetlands on cotton farms. It is recommended that such wetlands are comprised of both open water and vegetated zones, to increase the potential for complementary chemical, photolytic, microbial and plant-mediated pesticide breakdown. Further work is necessary to examine the potential for algae in pesticide remediation of irrigation tailwaters on farm, and the determination of modelling parameters for wetland sizing and design.

Because of the scarcity of water in Australia, recycling schemes will play and increasing role in ensuring economic and environmental sustainability of irrigated agriculture. The success of constructed wetlands for treatment of pesticide-contaminated water elsewhere makes them attractive. Nevertheless, local assessment is still required to document regional variability, address concerns of landholders and, if discovered to be suitable, accelerate their adoption as a best management practice on farm.

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