



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.

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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 Australia

lian 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 m² and a 0.5 m deep vegetated pond of surface area 200 m² 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

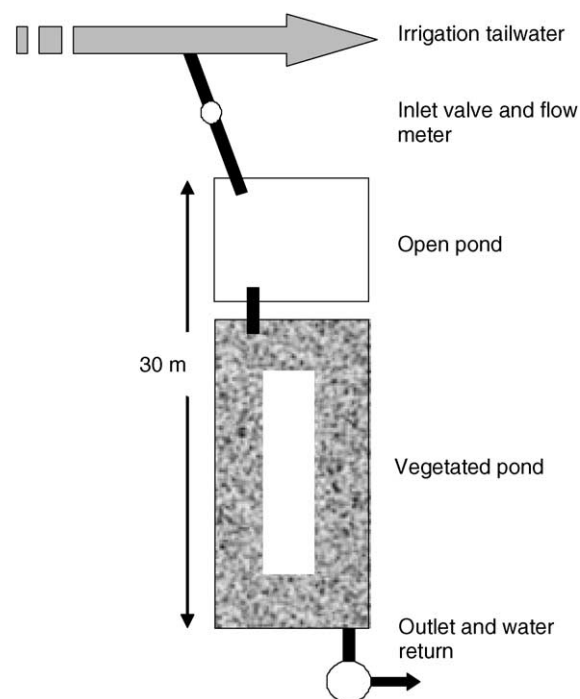


Fig. 1. Schematic diagram of the pilot-scale ponded wetland.

121 (March 2002), plant coverage was only 20% of the veg-
122 etated pond area. By the start of the second season
123 (November 2002), *B. medianus*, *T. domingensis* and *Per-*
124 *sicaria* spp. were the dominant species and coverage had
125 increased to 95% of the vegetated pond.

126 Irrigation runoff from field 24, a 30 ha field planted
127 with conventional cotton in the first season, and geneti-
128 cally modified, Roundup Ready[®] cotton in the second
129 season, was collected in a return drain that ran approx-
130 imately 120 m to a storage dam. Midway along the
131 length of this return drain was situated the inlet to the
132 constructed wetland, consisting of an 8 m length of pip-
133 ing (10 cm diameter) that diverted some, but not all, of
134 the irrigation runoff. Water from the inlet flowed first
135 into the open pond from the south-eastern corner. An
136 earthen berm separated the deep open pond from the
137 shallow vegetated pond, which were connected by a
138 rotary pipe through the berm. Another rotary siphon
139 pipe situated in the north-western corner of the vege-
140 tated pond allowed for emptying of the wetland. Water
141 leaving the wetland was returned to the storage via a
142 30 × 1 m ditch.

143 2.2. Monitoring cycle

144 At each irrigation event—approximately every
145 2 weeks for about 3 months—the wetland was filled with
146 tailwater from field 24, and the volume of water added
147 recorded from the flow meter. The water depth was also
148 recorded once the wetland had been filled. Triplicate,
149 composite water samples of the tailwater at the inlet
150 were taken throughout the filling of the pond.

151 To evaluate the extent of pesticide removal from the
152 pilot wetland, water samples were taken from both open
153 and vegetated ponds prior to each irrigation event. Dur-
154 ing the first trial season (2001–2002), duplicate water
155 samples were taken. Each sample was obtained by fully
156 filling a 1 l amber glass bottle using a grab stick then seal-
157 ing it with a Teflon[®] lined cap. During the second season
158 (2002–2003), triplicate water samples were taken from
159 each pond. In this instance, 1 l composite water samples
160 were obtained by combining four, 250 ml sub-samples
161 from random points within each pond. Also in the sec-
162 ond year, sediment samples were taken before and after
163 each irrigation event. Sediment samples were obtained
164 by taking four sub-samples taken from the top 50 mm
165 of pond bottom with a stainless steel scoop and combin-
166 ing them in an aluminium-foil sealed glass jar.

167 At the end of each incubation period following sam-
168 pling, the water level was recorded and the wetland emp-
169 tied as much as possible via the outlet siphon pipe. The
170 water level was again recorded once the wetland had
171 been emptied.

172 All water samples were refrigerated at 4 °C until pes-
173 ticide extraction, which occurred within several days of

sampling. Sediment samples were stored in sealed glass
174 jars at –20 °C until analysis. 175

2.3. Chemicals 176

Aldicarb, fluometuron and diuron standards were
177 obtained from the Australian National Analytical Refer-
178 ence Laboratory, Sydney, and were all of greater than
179 99.5% purity. Analytical reagent grade sodium sulfate
180 was obtained from Mallinckrodt. All solvents were of
181 Mallinckrodt nanograde. 182

2.4. Water extraction procedure 183

Water sub-samples (500 ml) were shaken vigorously
184 for 2 min with three volumes (100, 50, 50 ml) of dichlo-
185 romethane in a Teflon[®] separating funnel. The dichloro-
186 methane solvent was passed through sodium sulfate
187 (25 g) suspended by cotton wool in a glass filter funnel.
188 The combined extracts were collected, evaporated to
189 near dryness and exchanged three times with nanograde
190 hexane (10 ml). After the final evaporation, the volume
191 was made up to 5 ml with hexane and 1 ml removed
192 for gas chromatographic (GC) analysis. The remaining
193 4 ml was exchanged three times with methanol (10 ml).
194 After the final evaporation, the volume was made up
195 to 4 ml with 50:50 methanol/water, and filtered into a
196 4 ml glass vial through a 0.22 µm syringe filter. 197

2.5. Sediment extraction procedure 198

Twenty-five gram (wet weight) sub-samples were
199 extracted for 8 h with 60 ml of acetonitrile and again
200 for 1 h with 40 ml on a rotary shaker. The combined
201 extracts were filtered through Whatman GF/C filters,
202 evaporated to near dryness and reconstituted with
203 50 ml deionised water. These samples were cleaned up
204 on 200 mg/6 ml Strata-X[®] (modified cross-linked poly-
205 mer, Phenomenex) cartridges previously conditioned
206 with 6 ml methanol and equilibrated with 10 ml deionised
207 water, after which the sample was loaded at 1 ml min⁻¹,
208 washed with 10 ml of 10% methanol and eluted twice with
209 5 ml hexane:acetonitrile (1:1 v/v). The eluent was evapo-
210 rated to dryness and made up with 5 ml acetonitrile. A
211 1 ml aliquot was removed for GC analysis and the
212 remainder evaporated, reconstituted in 4 ml 50% acetoni-
213 trile and filtered (0.22 µm) for high performance liquid
214 chromatography (HPLC) analysis. Final concentrations
215 were determined on a dry weight basis by oven drying
216 duplicate sediment sub-samples overnight (105 °C).
217 Water content of the sediments ranged from 41% to 49%.
218

2.6. Chromatographic analyses 219

Diuron, fluometuron and aldicarb were analysed by
220 HPLC using a Shimadzu SIL-10AXL auto injector, Shi-
221

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

235 α-endosulfan, β-endosulfan and their degradation
 236 product endosulfan sulfate were analysed by gas chroma-
 237 tography at Agrisearch Analytical, Sydney, an accredited
 238 National Association of Testing Authorities (NATA) labo-
 239 ratory. Samples (1 μl) were injected into a
 240 30 m × 0.25 mm, fused silica column coated with HP-
 241 5MS (0.25 μm, Agilent) by a 7683 automatic sampler
 242 (Hewlett–Packard). Pulsed splitless injection occurred at
 243 250 °C with helium as the carrier gas (1 ml min⁻¹). The
 244 column was housed in a Hewlett–Packard 6890 GC, with
 245 the column temperature initially at 100 °C (1 min), raised
 246 to 300 °C at 10 °C min⁻¹ and held for 9 min. The GC was
 247 equipped with a Hewlett–Packard 5973 mass-selective
 248 detector held at 280 °C and operated in selected-ion moni-
 249 toring mode (SIM). The ions measured (*m/z*) and typical
 250 retention times were 339/241/272, 14.8 min, for α-endo-
 251 sulfan; 237/339/272, 16 min, for β-endosulfan; and 387/
 252 272/274, 16.8 min, for endosulfan sulfate.

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

260 2.7. Data analysis

261 For each irrigation event, the removal efficiency of
 262 each pesticide in both open and vegetated ponds was

263 estimated from the residues remaining at the end of
 264 the each incubating period, that is, the time between
 265 consecutive irrigations. Because the length of these peri-
 266 ods varied from 7 to 13 days, in order to compare the
 267 performance percent reductions of pesticides were con-
 268 verted to half-lives by the negative exponential model:

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

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

271 where x_0 is the initial pesticide concentration, x is the fi-
 272 nal pesticide concentration, t is the incubation time and
 273 k is a removal rate constant (Vink and Van der Zee,
 274 1997). The difference between treatments was analysed
 275 by unpaired Student's *t*-test with confidence limits of
 276 95%, using Genstat software.

3. Results 277

3.1. First year performance (2002) 278

279 Five incubation periods were monitored between six
 280 irrigations over a period of approximately 2 months. A
 281 number of different pesticides were applied to field
 282 pre- and post-planting of the conventional cotton culti-
 283 var (Table 2). Because none of the studied pesticides were
 284 applied after the first irrigation, the concentration of pes-
 285 ticide entering the wetland decreased in subsequent incu-
 286 bation periods (Fig. 2a). The biomass of the vegetated
 287 pond increased little throughout this first season, from
 288 coverage of less than 5% at planting time to approxi-
 289 mately 20% at the end of the cotton growing season.

290 Average pesticide removal over the entire wetland
 291 varied from 27% to 55% for diuron, 15% to 39% for aldi-
 292 carb and 0% to 34% for fluometuron. No significant dif-
 293 ference was observed between pesticide reductions in the
 294 open pond and vegetated pond over any of the incuba-
 295 tion periods for any of the pesticides ($p > 0.05$). Further-
 296 more, the half-life of diuron and aldicarb did not
 297 significantly ($p > 0.05$) change over the trial period of
 298 five incubations, despite different weather conditions
 299 (Table 2), different inlet concentrations (Table 1) and
 300 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 ($n = 5$).

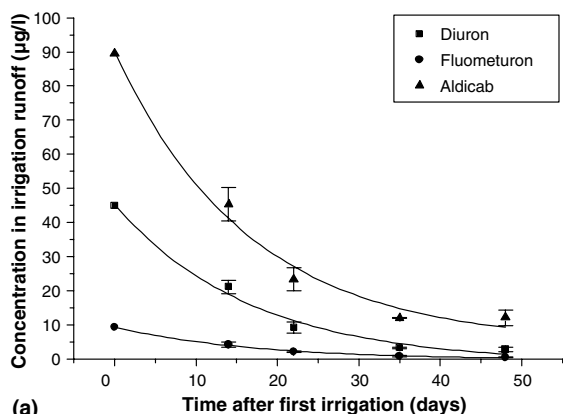
^a n.d. = Not determined.

Table 2
Environmental conditions and water quality parameters

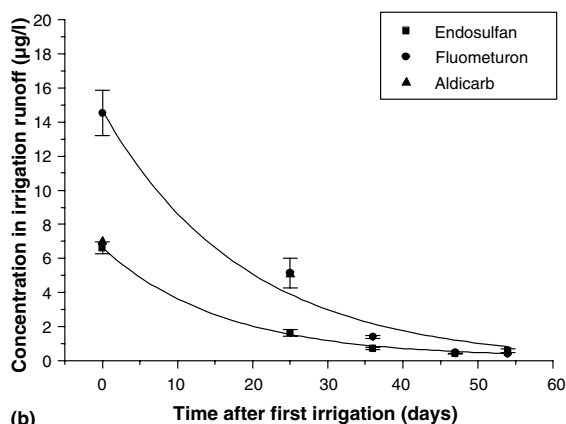
	2002 Incubations (range)	2003 Incubations (range)
Ambient temperature (°C)	10.1–39.5	9.5–41.8
Water temperature ^a (°C)	19–27	18–28
Solar radiation (MJ m ⁻² day ⁻¹)	14.7–34.0	8.7–34.0
pH	7.74–8.56	8.26–8.73
Nitrate + nitrite (mg l ⁻¹)	0.25–0.78	0.22–1.43
Ammonium (µg l ⁻¹)	54.3–143.7	78.1–247.9
Ortho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

^a Water temperature at 9.00 a.m.

^b Not determined.



(a)



(b)

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

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

305 The half-life of fluometuron was significantly differ-
306 ent ($p < 0.05$) between the first incubation in the vege-
307 tated pond, in which the concentration was found not
308 to decrease, and the fourth incubation in which the con-

centration decreased by 44%. By averaging the data for
309 the final four incubations, which were not significantly
310 different ($p > 0.05$), a half-life of 25.4 ± 8.6 days was cal-
311 culated for fluometuron.
312

3.2. Second year performance (2003)

313

Water entering the wetland during the second trial
314 period was again taken from field 24, which was planted
315 with a Roundup-Ready[®] cotton cultivar. This water had
316 already been recycled from other fields that had under-
317 gone fluometuron application, resulting in the detection
318 of this herbicide prior to irrigation of field 24. Following
319 irrigation of the latter field, aldicarb and endosulfan
320 were also detected; however, towards the end of the sea-
321 son only trace amounts of these three pesticides were
322 observed (Fig. 2b). Diuron was not applied this season
323 (see Table 2) and was not detected in the tailwaters.
324

The first incubation of the 2002/2003 cotton season
325 was disrupted by heavy rainfall, in which overland flow
326 contributed an unknown amount of pesticide to the wet-
327 land system. This is thought to have caused a large dif-
328 ference in removal efficiencies between the three
329 pesticides analysed, thus these results were omitted from
330 calculations and not shown here.
331

During the second incubation, the average half-lives
332 of fluometuron and aldicarb in the open pond
333 (13.8 ± 1.0 days and 6.2 ± 0.3 days, respectively) were
334 significantly lower ($p < 0.05$) than in the corresponding
335 incubation the previous year (Fig. 3). Interestingly, flu-
336 meturon removal was significantly greater ($p < 0.05$) in
337 the vegetated pond (58%) than in the open pond (41%)
338 during the second incubation, whereas the converse
339 was true in the third incubation, in which an algal bloom
340 occurred in the open pond. The calculated half-lives dur-
341 ing these incubations were averaged for the vegetated
342 pond (10.2 ± 1.3 days), but were split for the open pond
343 into two figures: before the algal bloom (13.8 ± 1.0) and
344 after the bloom (5.5 ± 0.4).
345

Trace amounts of aldicarb and endosulfan were
346 detected in both ponds during the third, fourth and fifth
347 incubations; however, their concentrations were reduced
348 to below levels of quantification (Table 1). This was also
349

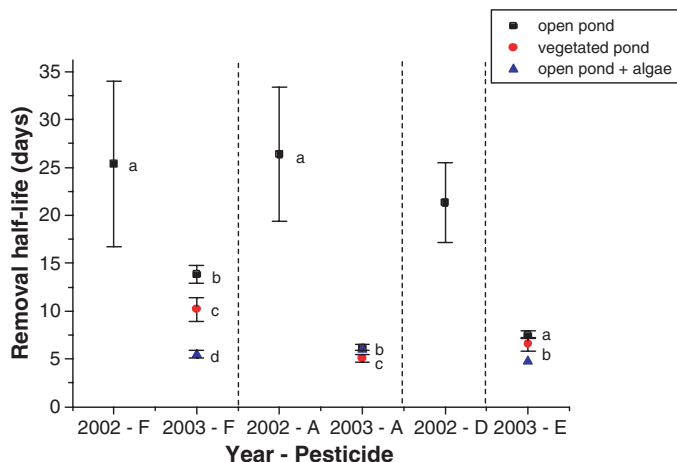


Fig. 3. Pesticide removal expressed as half-lives for fluometuron (F), aldicarb (A), diuron (D) and endosulfan (E) from irrigation tailwater. Error bars represent 95% confidence limits. Data points designated by different letters are statistically different within pesticide groupings ($p < 0.05$).

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

356 Concentration of aldicarb, fluometuron and total
 357 endosulfan (i.e. α - and β -isomers plus endosulfan sul-
 358 fate) were measured in sediment samples in the third,
 359 fourth and fifth incubations (Table 3). In addition,
 360 DDE was also detected as a residue from applications
 361 of DDT that took place in the area more than 20 years
 362 ago (Shivaramaiah et al., 2002). Results show a large
 363 variation in residue levels between incubation periods.
 364 On average, total endosulfan concentrations were
 365 reduced by 24% and 27% in the open pond and veget-
 366 ated pond respectively, with 11–61% less residue at
 367 the end of the experimental period. Residues of DDE
 368 were also reduced by an average 35% in the open pond
 369 and 18% in the vegetated pond. In contrast, fluometu-
 370 ron levels remained almost constant. Aldicarb was not pre-
 371 sent at quantifiable levels in any of the sediment samples.

372 Only the field sorption coefficient (K_d) for fluometu-
 373 ron onto sediment could be determined (0.491 kg^{-1}),
 374 since water concentrations were not quantifiable for
 375 endosulfan and DDE during these incubations (see
 376 Table 4).

377 4. Discussion

378 4.1. Justification of data transformation

379 Percent reduction was converted to an equivalent
 380 half-life for each incubation, based on assumed first-

381 order dissipation. This transformation was conducted
 382 to allow for a comparison between incubations within
 383 each trial year, which was otherwise impossible consid-
 384 ering the variation in incubation lengths (7–13 days).
 385 Because only two temporal data points were available,
 386 that is, initial time and final time, biphasic- or tripha-
 387 sic-models could not be investigated, despite evidence
 388 to suggest their possibility (Kennedy et al., 2001). Deter-
 389 mination of the true dissipation kinetic is the subject of
 390 current work.

391 It is highlighted that the half-lives presented are
 392 therefore approximations, and, as with all environmen-
 393 tal data, should be used within their limitations. Never-
 394 theless, these manipulated data maintain the trends
 395 observed with respect to differences between the open
 396 and vegetated ponds in percent reduction, which was
 397 the main aim of this study.

398 4.2. Pesticide reductions in water

399 In this study, the concentration of pesticide in tailwa-
 400 ter during both trial periods was consistent with previ-
 401 ous reports in the Australian cotton industry (Crossan,
 402 2002; Silburn et al., 2002). Decreasing amounts were
 403 found in subsequent irrigations after application as
 404 described by Kennedy et al. (2001), and similar to the
 405 exponential decrease of the insecticide tribufos observed
 406 by Potter et al. (2000) after sequential runoff events.

407 A large variability was observed for all three pesti-
 408 cides analysed in the first year, particularly fluometuron.
 409 This makes interpretation of results during this season
 410 difficult. It is likely that environmental variation was
 411 compounded due to the limited sampling regime, that
 412 is, two water samples per pond and incubation period.
 413 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
	Pyriithiobac	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	

414 of many pesticides (Burrows et al., 2002) and this is sim- 429
415 ilarly true for pH, nutrient and organic matter concen- 430
416 trations and microbial populations (Vink and Van der 431
417 Zee, 1997). The smaller variability in the second year 432
418 results using triplicate, composite samples confirmed 433
419 the benefits from a more thorough sampling scheme, 434
420 so a comprehensive sampling protocol is recommended 435
421 for future investigations of this kind. 436

422 No significant difference ($p > 0.05$) was observed 437
423 between pesticide half-lives in different incubations in 438
424 the first year, despite different inlet concentrations, wet- 439
425 land aging and plant growth. Studies by Moore et al. 440
426 (2001, 2002) have similarly shown negligible effect of 441
427 inlet concentration on metolachlor and chlorpyrifos 442
428 removal. Atrazine, however, was observed to be approx- 443

imately twice as persistent in wetlands amended with 429
147 $\mu\text{g l}^{-1}$ compared with 73 $\mu\text{g l}^{-1}$ (Moore et al., 2000). 430

431 Plants can increase pollutant removal, including pes- 432
433 ticides, either directly through uptake or indirectly 434
435 through associated microbiota and humic contribution 436
437 (Stomp et al., 1994). In a previous glasshouse study, 438
439 hydroponic cultures of *Persicaria decipiens* were able 440
441 to reduce the concentrations of prometryn, fluometuron, 442
443 aldicarb and endosulfan in the range 16–40% in 2 weeks 444
445 (Rose et al., 2001), a time similar to the average incuba- 446
447 tion period between irrigation events in this study. How- 448
449 ever, the relatively small increase in vegetation over the 449
450 first season (approximately 15%) was probably not suf- 451
452 ficient to cause a noticeable increase in pesticide removal 453
453 between incubations. The similar performance of both 454
454 the open and vegetated ponds over this first season sup- 455
455 ports this view. 456

457 The removal of pesticide from tailwater was greater in 458
459 the second season of operation compared to the first 459
460 year, except for the first trial in which heavy rainfall dis- 460
461 rupted results. This better performance may be explained 461
462 by an increase in organic matter providing more sites for 462
463 sorption, and/or the adaptation of microorganisms in the 463
464 winter (non-trial) period increasing the rate of degrada- 464
465 tion. Evidence for the acclimation of pesticide-degrading 465
466 bacteria has been demonstrated for both aldicarb and 466
467 endosulfan under anaerobic conditions (Khandaker 467
468 and Young, 2000; Ghadiri and Rose, 2001). Adaptation 468
469 of bacteria in the underlying sediment, which was freshly 469
470 exposed by excavation in the first season, is thus a plau- 470
471 sible scenario. In this regard, a recent review by Schulz 471
472 (2004) concludes that more research is required into the 472
473 temporal changes in wetlands to understand their vari- 473
474 able remedial performance. 474

475 Also in the second season, the performance of the 475
476 open pond and vegetated pond differed significantly in 476
477 a number of incubations. Removal of fluometuron, aldi- 477
478 carb and endosulfan from the vegetated pond was signif- 478
479 icantly greater over the second incubation period. Apart 479
480 from our previous study (Rose et al., 2001), a number of 480
481 laboratory trials have demonstrated that aquatic plants 481
482 can accelerate the removal of pesticides from water com- 482
483 pared to non-vegetated treatments by uptake and/or 483
484 enhanced rhizosphere degradation. At least two of these 484
485 have correlated herbicide uptake with water uptake/ 485
486 evapotranspiration (Wilson et al., 2000a,b). It is possible 486
487 that the higher temperature over the second trial period 487
488 (average daytime 34.4 °C) contributed to the greater 488
489 removal of fluometuron and the highly water soluble 489
490 aldicarb (water solubility of 6 g l^{-1}) from the vegetated 490
491 pond in this way. 491

492 Other studies have also shown an increased effective- 492
493 ness in pesticide removal of vegetated wetlands com- 493
494 pared with non-vegetated wetlands. Schulz et al. 494
495 (2003a) found that the concentration of an organophos- 495
496 phate insecticide, methyl parathion, in water was 496

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
<i>T3</i>						
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%
<i>T4</i>						
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%
<i>T5</i>						
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.

485 reduced to 20 µg l⁻¹ over a 20 m distance in vegetated
 486 wetland cells compared to 70 µg l⁻¹ in non-vegetated
 487 cells. Increased sorption by macrophytes, mainly *Juncus*
 488 *effusus*, and sedimentation was reported to account for
 489 the difference in removal. As a consequence, a corre-
 490 sponding reduction in toxicity to various insect species
 491 and the crustacean *Hyalella azteca* was also observed
 492 (Schulz et al., 2003b).

493 Interestingly, over the third incubation in the second
 494 year, more fluometuron was removed from the open
 495 pond (76%) compared to the second incubation (41%).
 496 Furthermore, this reduction was greater than the
 497 amount removed in the vegetated pond over the same
 498 trial periods. There was also evidence to suggest a simi-
 499 lar trend for aldicarb and endosulfan, however almost
 500 complete elimination of these insecticides during those
 501 periods prevented this trend from being quantified. A
 502 proliferation of unidentified green, filamentous algal
 503 growth was observed during the third, fourth and fifth
 504 incubations, which could explain the increased rate of
 505 removal of all three pesticides. Zablotowicz et al.
 506 (1998) studied the metabolism of fluometuron by 15
 507 algal strains and found that eight of these were capable
 508 of the *N*-demethylation of fluometuron. The most rapid
 509 transformations (by *Scenedesmus* and *Ankistrodesmus*
 510 spp.) reduced fluometuron concentrations by 50% in less
 511 than 4 days. Sethunathan et al. (2004) have also shown
 512 that a *Scenedesmus* species is capable of transforming
 513 α-endosulfan in laboratory cultures and accelerating its
 514 degradation in soil samples. Other laboratory studies
 515 have also highlighted the significance of algae in reduc-
 516 ing 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 exami-
 nation under both laboratory and field conditions.

A limitation of this study was the inability of our
 analytical techniques to monitor concentrations of deg-
 radation products, particularly those of aldicarb. Aldi-
 carb 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 sat-
 urated sediment (Kazumi and Capone, 1995). Instead,
 hydrolysis to less toxic, non-carbamate degradates pre-
 dominates (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-

547 tions of total endosulfan (39–166 $\mu\text{g kg}^{-1}$ dry weight)
548 and fluometuron (4–11 $\mu\text{g kg}^{-1}$) in sediments of the
549 open and vegetated ponds were not significantly differ-
550 ent (see Table 3), which suggests that these pesticides
551 are associated with smaller colloids that remain sus-
552 pended long enough to equilibrate in both ponds, and
553 then eventually settle.

554 According to Wu et al. (2003), the binding of pesti-
555 cides to different size fractions has been receiving
556 increasing attention, particularly the finer particles
557 because of their large specific surface area, high stability
558 in suspension and their potential role in facilitating
559 transport of contaminants. These authors found that
560 >20% of the fungicide propiconazole ($\log K_{ow} = 3.72$)
561 was associated with particles of size <2.0 μm , even
562 though this fraction accounted for less than 8% of the
563 sediment mass. Crossan et al. (2002) also found that
564 more than 80% of diuron and endosulfan in runoff from
565 Australian cotton soils is associated with suspended par-
566 ticles less than 65 μm in size.

567 The rapid reduction of endosulfan in the aqueous
568 phase prevented the determination of its partitioning
569 coefficient, but its high levels in sediments suggests the
570 sedimentation process plays an important role in its
571 removal from the water phase (Kennedy et al., 2001).
572 This was also the case for DDE, which was not detected
573 in any aqueous samples, including inlet water, but was
574 found at levels between 9 and 32 $\mu\text{g kg}^{-1}$ in sediments.
575 Although the use of DDT in Australia was discontinued
576 over 20 years ago, its breakdown product DDE is still
577 frequently detected in soils and biota of the northern
578 river valleys of New South Wales (Sánchez-Bayo et al.,
579 1999; Shivaramaiah et al., 2002). In contrast, the unde-
580 tectable levels of aldicarb in sediments prevented deter-
581 mination of its sorption coefficient.

582 The calculated partitioning coefficient for fluometu-
583 ron onto sediment ($K_d = 0.49 \pm 0.18 \text{ l kg}^{-1}$) is in close
584 agreement with available laboratory data. Baskaran
585 and Kennedy (1999) found a K_d of $0.48 \pm 0.21 \text{ l kg}^{-1}$
586 for fluometuron onto soil from the same region. Such
587 a result indicates that this laboratory data would be use-
588 ful for predicting pesticide sorption behaviour in the
589 field. While sorption characteristics for endosulfan are
590 available (Parkpian et al., 1998), those of aldicarb and
591 DDE are required to solve pesticide transport and
592 removal models. Pesticide sorption data onto macro-
593 phytes and biofilms would also be desirable for vege-
594 tated wetland modelling, as described by Alvord and
595 Kadlec (1996).

596 5. Conclusions

597 This study has given a preliminary insight into pesti-
598 cide transport and removal efficiency in constructed wet-
599 lands on cotton farms. It is recommended that such

wetlands are comprised of both open water and vege- 600
tated zones, to increase the potential for complementary 601
chemical, photolytic, microbial and plant-mediated pes- 602
ticide breakdown. Further work is necessary to examine 603
the potential for algae in pesticide remediation of irriga- 604
tion tailwaters on farm, and the determination of mod- 605
elling parameters for wetland sizing and design. 606

607 Because of the scarcity of water in Australia, recy- 608
cling schemes will play an increasing role in ensuring 609
economic and environmental sustainability of irrigated 610
agriculture. The success of constructed wetlands for 611
treatment of pesticide-contaminated water elsewhere 612
makes them attractive. Nevertheless, local assessment 613
is still required to document regional variability, address 614
concerns of landholders and, if discovered to be suitable, 615
accelerate their adoption as a best management practice 616
on farm.

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References 626

- 627 Alvord, H.H., Kadlec, R.H., 1996. Atrazine fate and transport
628 in the Des Plaines wetlands. *Ecol. Model.* 90, 97–107.
- 629 Baskaran, S., Kennedy, I.R., 1999. Sorption and desorption
630 kinetics of diuron, fluometuron, prometryn and pyriithiobac
631 sodium in soils. *J. Environ. Sci. Health B* 34, 943–963.
- 632 Braskerud, B.C., Haarstad, K., 2003. Screening the retention of
633 thirteen pesticides in a small constructed wetland. *Water*
634 *Sci. Technol.* 48, 267–274.
- 635 Burrows, H.D., Canle, L.M., Santaballa, J.A., Steenken, S.,
636 2002. Reaction pathways and mechanisms of photodegrada-
637 tion of pesticides. *J. Photochem. Photobiol. B* 67, 71–108.
- 638 Crossan, A.N., 2002. Remediation of pesticides on cotton
639 farms: studies of the environmental distribution, transport
640 and fate of five pesticides, PhD thesis. The University of
641 Sydney, New South Wales, Australia.
- 642 Crossan, A.N., Lee, N., Sharma, R., Kennedy, I.R., Beckett,
643 R., 2002. Assessment of the distribution of pesticides on soil
644 particle fractions in simulated irrigation run-off using
645 centrifugal SPLITT fractionation and ELISA. *Anal. Chim.*
646 *Acta* 468, 199–208.
- 647 Friesen-Pankratz, B., Doebel, C., Farenhorst, A., Goldsbor-
648 ough, L.G., 2003. Interactions between algae (*Selenastrum*
649 *capricornutum*) and pesticides: implications for managing
650 constructed wetlands for pesticide removal. *J. Environ. Sci.*
651 *Health—Part B* 38, 147–155.

- 652 Ghadiri, H., Rose, C.W., 2001. Degradation of endosulfan in a
653 clay soil from cotton farms of western Queensland. *J.*
654 *Environ. Manage.* 62, 155–169.
- 655 Jones, R.L., Estes, T.L., 1995. Summary of aldicarb monitoring
656 and research programs in the USA. *J. Contam. Hydrol.* 18,
657 107–140.
- 658 Kazumi, J., Capone, D.G., 1995. Microbial aldicarb transfor-
659 mation in aquifer, lake, and salt-marsh sediments. *Appl.*
660 *Environ. Microb.* 61, 2820–2829.
- 661 Kennedy, I.R., Sánchez-Bayo, F., Kimber, S.W., Hugo, L.,
662 Ahmad, N., 2001. Off-site movement of endosulfan from
663 irrigated cotton in New South Wales. *J. Environ. Qual.* 30,
664 683–696.
- 665 Khandaker, N.R., Young, J.C., 2000. Effect of culture accli-
666 mation on the kinetics of aldicarb insecticide degradation
667 under methanogenic conditions. *J. Agr. Food Chem.* 48,
668 1411–1416.
- 669 Moore, M.T., Rodgers, J.H., Cooper, C.M., Smith, S., 2000.
670 Constructed wetlands for mitigation of atrazine-associated
671 agricultural runoff. *Environ. Pollut.* 110, 393–399.
- 672 Moore, M.T., Rodgers, J.H., Smith, S., Cooper, C.M., 2001.
673 Mitigation of metolachlor-associated agricultural runoff
674 using constructed wetlands in Mississippi, USA. *Agric.*
675 *Ecosyst. Environ.* 84, 169–176.
- 676 Moore, M.T., Schulz, R., Cooper, C.M., Smith, S., Rodgers,
677 J.H., 2002. Mitigation of chlorpyrifos runoff using con-
678 structed wetlands. *Chemosphere* 46, 827–835.
- 679 Parkpian, P., Anurakpongsatorn, P., Pakkong, P., Patrick Jr.,
680 W.H., 1998. Adsorption, desorption and degradation of α -
681 endosulfan in tropical soils of Thailand. *J. Environ. Sci.*
682 *Health B* 33, 211–233.
- 683 Potter, T.L., Marti, L., Bellflower, S., Truman, C.C., 2000.
684 Multiresidue analysis of cotton defoliant, herbicide, and
685 insecticide residues in water by solid-phase extraction and
686 GC-NPD, GC-MS, and HPLC-diode array detection. *J.*
687 *Agric. Food Chem.* 48, 4013–4108.
- 688 Radcliffe, J.C., 2002. Pesticide use in Australia. Australian
689 Academy of Technological Sciences and Engineering,
690 Parkville, Victoria, Australia.
- 691 Reid, N., O'Shea, G., Silberbauer, L., 2003. A Review of
692 Biodiversity Research in the Australian Cotton Industry.
693 Australian Cotton Research and Development Corpora-
694 tion, Armidale, Australia.
- 695 Roberts, T.R. (Ed.), 1998. *Metabolic Pathways of Agrochemi-
696 cals.* The Royal Society of Chemistry, Cambridge, UK.
- 697 Rose, M., Sánchez-Bayo, F., Kennedy, I.R., 2001. Phytoreme-
698 diation of pesticide residues by wetland plants. *Abs. 2nd*
699 *Nat. Wetlands Conf., South Stradbroke Island, Queens-
700 land, Australia, 14–16 November, p. 104.*
- 701 Runes, H.B., Jenkins, J.J., Moore, A., Bottomley, P.J., Wilson,
702 B.D., 2003. Treatment of atrazine in nursery irrigation
703 runoff by a constructed wetland. *Water Res.* 37, 539–550.
- 704 Sánchez-Bayo, F., Ward, R., Beasley, H., 1999. A new
705 technique to measure bird's dietary exposure to pesticides.
706 *Anal. Chim. Acta* 399, 173–183.
- 707 Sánchez-Bayo, F., Baskaran, S., Kennedy, I.R., 2002. Ecolog-
708 ical relative risk (EcoRR): another approach for risk
709 assessment of pesticides. *Agric. Ecosyst. Environ.* 91, 37–57.
- 710 Schulz, R., 2004. Field studies on exposure, effects, and risk
711 mitigation of aquatic nonpoint-source insecticide pollution:
712 a review. *J. Environ. Qual.* 33, 419–448.
- Schulz, R., Peall, S.K.C., 2001. Effectiveness of a constructed
713 wetland for retention of nonpoint-source pesticide pollution
714 in the Lourens River Catchment, South Africa. *Environ.*
715 *Sci. Technol.* 35, 422–426.
- Schulz, R., Moore, M.T., Bennett, E.R., Farris, J.L., Smith Jr.,
717 S., Cooper, C.M., 2003a. Methyl parathion toxicity in
718 vegetated and nonvegetated wetland mesocosms. *Environ.*
719 *Toxicol. Chem.* 22, 1262–1268.
- Schulz, R., Moore, M.T., Bennett, E.R., Milam, C.D., Bouldin,
721 J.L., Farris, J.L., Smith Jr., S., Cooper, C.M., 2003b. Acute
722 toxicity of methyl-parathion in wetland mesocosms: assess-
723 ing the influence of aquatic plants using laboratory testing
724 with *Hyalella azteca*. *Arch. Environ. Contam. Toxicol.* 45,
725 331–336.
- Sethunathan, N., Megharaj, M., Chen, Z.L., Williams, B.D.,
727 Lewis, G., Naidu, R., 2004. Algal degradation of a known
728 endocrine disrupting insecticide, α -endosulfan, and its
729 metabolite, endosulfan sulfate, in liquid medium and soil.
730 *J. Agric. Food Chem.* 52, 3030–3035.
- Shivaramaiah, H.M., Odeh, I.O., Kennedy, I.R., Skerritt, J.H.,
732 2002. Mapping the distribution of DDT residues as DDE in
733 the soils of the irrigated regions of northern New South
734 Wales, Australia using ELISA and GIS. *J. Agric. Food*
735 *Chem.* 50, 5360–5367.
- Silburn, D.M., Simpson, B.M., Hargreaves, P.A., 2002. Man-
737 agement practices for control of runoff losses from cotton
738 furrows under storm rainfall. II. Transport of pesticides in
739 runoff. *Aus. J. Soil Res.* 40, 21–44.
- Stangroom, S.J.C., Collins, C.D., Lester, J.N., 2000. Abiotic
741 behaviour of organic micropollutants in soils and the
742 aquatic environment. A review: II. Transformations. *Envi-
743 ron. Technol.* 21, 865–882.
- Stomp, A.M., Han, K.H., Wilbert, S., Gordon, M.P., Cunn-
745 ingham, S.D., 1994. Genetic strategies for enhancing phy-
746 toremediation. *Ann. New York Acad. Sci.* 721, 481–491.
- Tomlin, C.D.S. (Ed.), 1997. *The Pesticide Manual*, 11th ed. The
748 British Crop Protection Council, Surrey, UK.
- Vink, J.P.M., Van der Zee, S.E.A.T.M., 1997. Pesticide
750 biotransformation in surface waters: multivariate analyses
751 of environmental factors at field sites. *Water Res.* 31, 2858–
752 2868.
- Williams, A., Williams, J., 2000. *Australian Cotton Industry Best*
754 *Management Practices Manual*, second ed. Cotton Research
755 and Development Corporation, Narrabri, Australia.
- Wilson, P.C., Whitwell, T., Klaine, S.J., 2000a. Metalaxyl and
757 simazine toxicity to and uptake by *Typha latifolia*. *Arch.*
758 *Environ. Contam. Toxicol.* 39, 282–288.
- Wilson, P.C., Whitwell, T., Klaine, S.J., 2000b. Phytotoxicity,
760 uptake, and distribution of C-14-simazine in *Acorus grame-
761 nius* and *Pontederia cordata*. *Weed Sci.* 48, 701–709.
- Wilson, P.C., Foos, J.F., Jones, R.L., 2005. Pulsed losses and
763 degradation of aldicarb in a South Florida agricultural
764 watershed. *Arch. Environ. Contam. Toxicol.* 48, 24–31.
- Wu, Q., Riise, G., Kretzschmar, R., 2003. Size distribution of
766 organic matter and associated propiconazole in agricultural
767 runoff material. *J. Environ. Qual.* 32, 2200–2206.
- Zablotowicz, R.M.S., Schrader, K.K., Locke, M.A., 1998.
769 Algal transformation of fluometuron and atrazine by *N*-
770 dealkylation. *J. Environ. Sci. Health B* 33, 511–528.
- 771
772