Dissipation of Cotton Pesticides from Runoff Water in Glasshouse Columns

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Abstract The use of vegetated wetlands for accelerating pesticide removal from agricultural runoff is gaining acceptance as a best management practice. In this study, the dissipation of five cotton pesticides – endosulfan, chlorpyrifos, aldicarb, prometryn and diuron – was quantified in cotton field runoff water contained in glasshouse columns, under light or dark conditions. Two water samples sourced from large, non-vegetated storage dams were compared with two other water samples obtained from vegetated wetlands receiving runoff from cotton fields. All pesticides studied except chlorpyrifos dissipated significantly faster from the storage dam samples than the vegetated wetland samples. Suggested reasons include a greater number of pesticide-degrading microorganisms in the storage dam waters and/or the presence of more organic matter in the wetland samples, limiting contaminant volatilisation and hydrolysis. Exposure to light significantly reduced the rate of endosulfan removal, whereas light increased the rate of chlorpyrifos removal. Half-lives are presented for each pesticide where appropriate.

Keywords insecticide · herbicide · half-life · wetland · water · microbial · organic matter

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1 Introduction

The determination of pesticide dissipation rates from water is a necessary requirement for pesticide registration in Australia (APVMA, 2004), and data are readily available for standard conditions (Tomlin, 1997). Generally, first-order dissipation half-lives are determined from distilled or tap water. Sometimes the half-life is also separated into mechanistic removal rates such as photolysis, hydrolysis and volatilisation (APVMA, 2004). Although this gives an idea of the relative longevity of different chemicals, the procedure may not accurately describe a pesticide's persistence in natural waters, for example, river, ground or marine water. This is because dissipation varies with the pesticide and the temperature, reduction potential, chemistry and biology of the water under scrutiny (Vink, 1997). At times, different removal processes may dominate, causing the dissipation to exhibit bi-phasic or tri-phasic features. Consequently, pesticide half-lives are often presented as a range of values.

Pesticides that exhibit a relatively high environmental risk in the Australian cotton production system include the insecticides endosulfan, chlorpyrifos and aldicarb and the herbicides diuron and prometryn (Sanchez-Bayo, Baskaran, & Kennedy, 2002). Endosulfan is highly volatile and susceptible to hydrolysis in alkaline waters (Tomlin, 1997). The half-life of total endosulfan (α, β and endosulfan sulfate) is often observed to be biphasic, with a rapid initial loss of the parent compound followed by a second, slower

disappearance of the product endosulfan sulfate (Kennedy, Sanchez-Bayo, Kimber, Hugo, & Ahmad, 2001). Chlorpyrifos is also susceptible to volatilisation and alkaline chemical hydrolysis that lead to rapid removal from aqueous systems (Mazanti et al., 2003). Although apparently not as susceptible as other organophosphates, biological hydrolysis of chlorpyrifos has been observed in soil and microbial cultures (Mallick, Bharati, Banerji, Shakil, & Sethunathan, 1999). Aldicarb is rapidly biologically oxidised in aerobic environments, particularly soil, to the more toxic sulfone and sulfoxide products (Mink, Risher, & Stara, 1989). Hydrolysis to the less toxic aniline occurs under anaerobic conditions and is faster in acidic environments (Kazumi & Capone, 1995). Diuron is relatively recalcitrant, undergoing biological demethylation and hydrolysis of the urea bond to toxic halogenated anilines in soils and microbial cultures (Berger, 1998). Biological degradation is also suggested to be the major dissipation route in aqueous environments (Tomlin, 1997); however, the literature on their dissipation in surface water is sparse. Dissolved organic matter has also recently been implicated in the increased photodegradation of phenylureas (Gerecke, Canonica, Muller, Scharer, & Schwarzenbach, 2001). The s-triazine prometryn is similarly persistent, but less so than other chlorinated s-triazines such as atrazine (S. Navarro, Vela, Gimenez, & G. Navarro, 2004). This is because the methyl-thio substituent is more easily oxidised, both biologically and chemically.

The current study concerned the dissipation of these chemicals from cotton farm runoff. Irrigation tailwater and storm runoff on floodplain cotton farms usually contains a high sediment load with a significant proportion of smaller clay and colloidal particles (Silburn, 2003). Pesticide binding to these sediments can be significant (Crossan, Lee, Sharma, Kennedy, & Beckett, 2002), particularly for pesticides with a low water solubility. Pesticides strongly bound to sediments may not be bioavailable (Lee, Gan, Kim, Kabashima, & Crowley, 2004), preventing degradation and acting as a constant source for dissolution into the aqueous phase. Conversely, suspended sediments can support microbial growth (Tranvik & Jorgensen, 1995) and act to concentrate pesticides as a potential food source. Vegetated wetlands have been suggested as a best management practice for reducing pesticide loads in agricultural runoff (Bennett et al., 2005; Dabney, Moore, & Locke, 2006; Rose, Sanchez-Bayo, Crossan,

& Kennedy, 2006). The main mechanism by which this is achieved appears to be plant sorption/uptake/ degradation (Moore et al., 2006; Rose, Sanchez-Bayo, & Kennedy, 2001), but aquatic plants can also alter surface water properties, by contributing dissolved organic matter, supporting microbial growth, increasing sedimentation rates and oxygenating water (Bedford, Bouldin, & Beliveau, 1991; Braskerud, 2001).These changes can subsequently impact upon pesticide removal and degradation rates.

The main objective of this experiment was to determine indicative half-lives of three cotton insecticides and two cotton herbicides in water samples originating from cotton field runoff. These half-lives could be used for comparison with half-lives obtained under standard conditions. The factors responsible for dissipation were also investigated and any observed differences discussed with regard to the sample water characteristics. The four water samples under study included two from different cotton farm storage dams, one from a vegetated constructed wetland receiving irrigation runoff and one from a natural, semi-vegetated wetland receiving overland flow from cotton fields. The storage dam samples provided a baseline measure of pesticide dissipation under current farm practice, compared with the potential practice of using wetlands for enhanced pesticide removal.

2 Materials and Methods

2.1 Chemicals

Solid analytical grade pesticide standards (>99% purity) for α-endosulfan, β-endosulfan, endosulfan sulfate (Hoescht, Germany), chlorpyrifos (Dow AgroSciences, Australia), prometryn, diuron, (Syngenta, Australia) and aldicarb (Sigma-Aldrich, Germany) were either purchased or given as gifts by their manufacturers. Individual intermediate stock solutions of 1 μg ml^{-1} in 50% acetonitrile were prepared by dilution of concentrated stock (1,000 μg ml^{-1}). The intermediate stock solutions were used for preparing fresh instrumental standards every month during the experiment.

2.2 Water Samples

Water samples (5 l) were taken from four locations in the Namoi River catchment between Narrabri and

Wee Waa, New South Wales, Australia, an area extensively used for cotton production. Two water samples were obtained from cotton-farm water storage dams on the property *Mollee* (sample MS) and the property *Auscott* (sample AS). The other two samples were obtained from a constructed vegetated wetland on the *Mollee* property (sample VP) and a natural wetland area adjacent to the *Auscott* property, the Galathera Creek floodway (GC). Samples were refrigerated and stored for 1 week before use, then filtered through 1 mm gauze mesh immediately before beginning the experiment to remove debris, but not colloids. Anion concentrations, ammonium concentration and pH were determined in all water samples at the beginning of the experiment. Nitrate, nitrite, chloride, phosphate and ammonium were analysed by flow injection analysis (FIAstar 5000, Foss, Sydney) according to methods provided by the manufacturers and sulfate by ion exchange HPLC. Total suspended solids (TSS), total dissolved solids (TDS) and volatile organic carbon (VOC) were determined by standard methods of filtration, evaporation at 105°C and combustion at 450°C. Water characteristics are given in Table 1. Blank analyses of all water sources before commencement of the experiment were below limits of detection for the pesticides under study.

2.3 Glasshouse Water Columns

The experimental design included four water samples subject to light or dark conditions (imposed by covering glass measuring cylinders completely in aluminium foil). Each treatment was conducted in triplicate for a total of 24 water samples. Eight control samples containing autoclaved water, half of which were aluminium covered, were also added.

Filtered water samples (1 l) were well-mixed and distributed into glass measuring cylinders (1 l). Water samples were spiked with stock pesticide mixture in acetone to bring the target concentrations to 50 μg l^{-1} of diuron and prometryn; 10 μg l^{-1} of aldicarb; and 5 μg l^{-1} of α-endosulfan, β-endosulfan, endosulfan sulfate and chlorpyrifos. These are representative of maximum concentrations likely to be found in tailwater on Australian cotton properties where these chemicals are used (Crossan, 2002). Water columns were stirred for 1 min with a glass rod and left for 1 h to equilibrate, after which a 60 ml sample was taken and extracted as time zero. Water columns were then

covered with a glass beaker to prevent atmospheric debris and insects entering, leaving a small gap (5 mm) for air exchange, and placed in a glasshouse. Six more samples (60 ml each) were taken over the next 3 months and extracted immediately onto StrataX® (Phenomenex, Sydney) modified divinyl-benzene solid phase cartridges.

After the last sampling event (day 88), all columns were thoroughly homogenised and 200 ml was vacuum filtered through GF/C paper (Whatman International, Maidstone, UK). Filter extracts and paper were weighed (wet weight) and extracted three times (20, 10, 10 ml) with dichloromethane. Combined extracts were blown down with a gentle stream of nitrogen, exchanged for acetonitrile and prepared for HPLC and GC analysis. Filtered water was also analysed for pesticide residues.

3 Pesticide Analysis

The full methodology for pesticide analyses can be found in Rose et al. (2006). Briefly, the endosulfan isomers and metabolite and chlorpyrifos were separated by GC on a capillary column with nitrogen gas mobile phase and detected by electron capture detector. Aldicarb, diuron and prometryn were separated by HPLC on a C18 analytical column with methanol/water mobile phase and detected by UV detection.

3.1 Glasshouse Conditions

Temperature was measured by a thermocouple and radiation measured by a pyranometer CM6B (Vaisala, Helsinki). Data was logged by a datataker (Data Electronics, Australia). Water temperatures measured periodically throughout the experiment, at different times in the day, varied between columns less than ±3°C.

3.2 Data Analysis

Zero-order, first-order or second-order curves were fit to data using Origin 4.1 software (Microcal, Northampton, MA). Second-order models were of the form:

$$x = A_1 e^{-k_1 t} + A_2 e^{-k_2 t}$$

Goodness-of-fit indicated by χ^2 values was used to select the best model fit. Calculated half-lives were

Table 1 Water quality parameters

	Auscott storage (AS)	Galathera Creek (GC)	*Mollee* storage (MS)	Vegetated pond (VP)
pH	7.97 (0.15)	7.85 (0.18)	8.21 (0.19)	7.58 (0.10)
TSS (mg l^{-1})	153 (7)	117 (17)	56 (12)	15 (11)
TDS (mg l^{-1})	277 (15)	410 (11)	571 (72)	420 (10)
VOC (mg l^{-1})	96 (12)	189 (25)	125 (13)	160 (21)
$NO_3^- + NO_2^-$ (mg l^{-1})	1.6	0.55	5.0	0.04
NH_4^+ (mg l^{-1})	0.08 (0.01)	0.04 (0.01)	0.11 (0.03)	0.28 (0.02)
PO_4^{3-} (mg l^{-1})	0.07 (0.02)	0.22 (0.07)	0.19 (0.09)	0.11 (0.05)
SO_4^{2-} (mg l^{-1})	14.4	1.9	17.3	2.9
Cl^- (mg l^{-1})	60.6	18.4	59.9	74.8

Numbers in brackets indicate 95% confidence levels ($n \geq 3$)

analysed by a two-factor ANOVA to determine treatment effects (JMP 4.0, SAS Institiute, Cary, NC).

4 Results

4.1 Pesticide Dissipation

4.1.1 Endosulfan

Total endosulfan was best described by second-order loss in all samples except Galathera Creek, in which a first-order model fit the data better (Table 2a). α-endosulfan was more persistent than β-endosulfan in all cases, but this difference was only significant ($p < 0.05$) in half the samples (data not shown). Net endosulfate dissipation was significantly slower than that of both parent isomers ($p < 0.05$).

Half-lives of total endosulfan followed the ascending order *Mollee* storage, *Auscott* storage, vegetated pond, Galathera Creek (Table 2a). Generally, light did not influence the rate of endosulfan dissipation. Only the reduction rate of total endosulfan in vegetated pond water was significantly inhibited by light ($p < 0.05$).

4.1.2 Chlorpyrifos

Chlorpyrifos dissipation was best described by first order models in all samples except *Auscott* and *Mollee* storage water kept under dark conditions (Table 2b). In these cases, second-order fits were best. In all samples except GC, dissipation was significantly faster under light conditions. Half-lives followed the ascending order *Mollee* storage, vegetated pond, *Auscott* storage, Galathera Creek in

illuminated samples. The difference in half-lives was only significant between *Mollee* storage and *Auscott* storage/Galathera Creek ($p < 0.05$); and vegetated pond and Galathera Creek ($p < 0.05$).

4.1.3 Aldicarb

Aldicarb dissipation was best described by first order models in all samples except *Mollee* storage water under light and dark condition (Table 2c). In these cases, second-order models were best, although first-order models were still statistically viable. Light did not significantly affect degradation rates. Half-lives followed the ascending order *Auscott* storage, *Mollee* storage, vegetated pond, Galathera Creek for first-order degradation. Half-lives for *Auscott* storage and *Mollee* storage were not statistically different, but both were significantly lower than the calculated half-lives for the vegetated pond and Galathera Creek ($p < 0.05$).

4.1.4 Diuron

Diuron dissipation was could be described by first order models in all samples with statistical significance; however second-order models in light and dark *Auscott* storage samples and dark *Mollee* storage samples provided better fits (Table 2d). Light only affected *Mollee* storage samples in which illuminated columns showed accelerated dissipation (Fig. 1). Half-lives followed the ascending order *Auscott* storage, *Mollee* storage, vegetated pond, Galathera Creek for first-order degradation. As with aldicarb, *Auscott* storage and *Mollee* storage sample half-lives were not statistically different, but both were significantly lower than the vegetated pond and Galathera Creek sample half-lives ($p < 0.05$).

Table 2 Pesticide dissipation parameters estimated by curve fitting to experimental data: (a) total endosulfan, (b) chlorpyrifos, (c) aldicarb, (d) diuron, (e) prometryn

	Water sample	Treatment	Best model	χ^2	1st $t_{1/2}$	2nd $t_{1/2}$	A1/A2
(a)	AS	Light	2nd-order	0.03	1.2 (0.33)	98.6 (13.58)	0.38 (0.06)
		Dark	2nd-order	0.21	0.7 (0.65)	48.0 (8.40)	0.48 (0.09)
	GC	Light	1st-order	1.68	35.9 (10.59)		
		Dark	1st-order	2.99	24.7 (8.48)		
	MS	Light	2nd-order	0.09	0.9 (0.23)	60.2 (9.99)	0.59 (0.07)
		Dark	2nd-order	0.01	0.9 (0.08)	52.4 (1.75)	0.56 (0.02)
	VP	Light	2nd-order	0.61	4.1 (1.74)	75.5 (61.93)	0.64 (0.28)
		Dark	2nd-order	0.52	1.1 (1.09)	19.7 (1.76)	0.45 (0.08)
(b)	AS	Light	1st-order	0.13	18.9 (3.75)		
		Dark	2nd-order	0.05	2.1 (3.85)	32.8 (7.08)	0.15 (0.26)
	GC	Light	1st-order	0.13	21.0 (4.23)		
		Dark	1st-order	0.34	24.0 (7.54)		
	MS	Light	1st-order	0.07	14.1 (1.74)		
		Dark	2nd-order	0.20	2.1 (2.20)	35.5 (15.37)	0.38 (0.37)
	VP	Light	1st-order	0.12	16.8 (2.71)		
		Dark	1st-order	0.16	35.7 (8.39)		
(c)	AS	Light	1st-order	0.22	3.6 (0.44)		
		Dark	1st-order	0.54	2.8 (0.57)		
	GC	Light	1st-order	0.66	12.0 (6.62)		
		Dark	1st-order	0.90	14.0 (7.28)		
	MS	Light	2nd-order	0.01	3.3 (0.21)	23.5 (5.60)	0.83 (0.08)
		Dark	2nd-order	0.17	2.2 (0.58)	28.5 (17.82)	0.78 (0.21)
	VP	Light	1st-order	0.25	10.3 (1.88)		
		Dark	1st-order	0.71	12.6 (3.45)		
(d)	AS	Light	2nd-order	15.60	3.3 (0.75)	135.0 (256.30)	0.84 (0.17)
		Dark	2nd-order	70.99	3.2 (1.56)	111.6 (478.06)	0.87 (0.38)
	GC	Light	1st-order	88.52	20.7 (10.03)		
		Dark	1st-order	133.43	23.5 (12.24)		
	MS	Light	1st-order	41.18	4.3 (1.00)		
		Dark	2nd-order	67.86	3.3 (3.13)	55.8 (55.02)	0.54 (0.52)
	VP	Light	1st-order	77.82	38.3 (13.96)		
		Dark	1st-order	48.22	33.3 (7.60)		
(e)	AS	Light	2nd-order	162.85	2.1 (2.01)	28.5 (27.92)	0.61 (0.58)
		Dark	2nd-order	180.91	2.1 (2.09)	55.3 (49.05)	0.53 (0.44)
	GC	Light	2nd-order	79.43	4.0 (3.74)	32.1 (25.79)	0.52 (0.67)
		Dark	2nd-order	65.58	5.5 (2.90)	57.2 (63.49)	0.68 (0.46)
	MS	Light	2nd-order	107.84	2.1 (3.19)	27.2 (11.03)	0.29 (0.45)
		Dark	2nd-order	67.99	2.1 (1.14)	32.4 (12.05)	0.50 (0.26)
	VP	Light	2nd-order	17.45	4.5 (4.79)	30.6 (7.31)	0.22 (0.36)
		Dark	2nd-order	31.78	4.4 (2.20)	41.6 (17.68)	0.50 (0.32)

Half–lives are given as $t_{1/2}$. Figures in brackets represent standard error as calculated by Origin 4.1

4.1.5 Prometryn

Second-order models provided the best fit for prometryn dissipation (Table 2e). However, the spread of data for all water samples meant that there was relatively high error in all model fits. The presence of light did not appear to affect dissipation from any samples. Half-lives followed the order *Auscott* storage = *Mollee* storage < vegetated pond = Galathera Creek, but the difference between the storage samples and the wetland samples was not significant because of the large variability. Nevertheless, there was significantly less prometryn remaining ($p<0.001$) in the light-treated *Auscott* storage samples
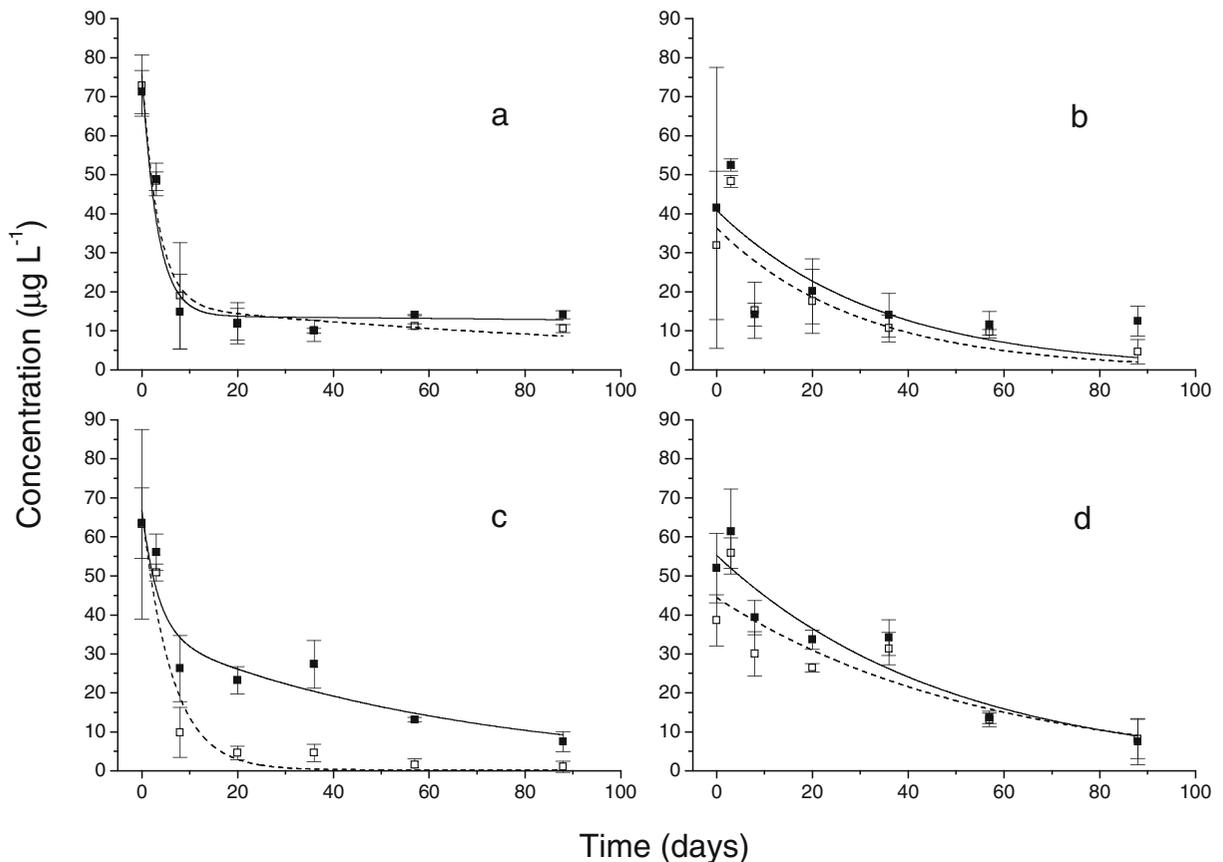
Fig. 1 Dissipation of diuron from water columns. **a** *Auscott* storage, **b** Galathera Creek, **c** *Mollee* storage, **d** Vegetated pond. *Closed symbols* and *solid line* represent dark conditions; *open symbols* and *dashed line* represent light conditions. *Error bars* represent 95% confidence intervals (*n*=3). Note the rapid dissipation of diuron from *Mollee* storage samples under light conditions

at the end of the experiment than all other samples (Fig. 2).

4.2 Effect of Water Source and Light

Results from the two-factor ANOVA's indicated a significant influence of water source for all pesticides except chlorpyrifos and a significant influence of light in the dissipation of chlorpyrifos and endosulfan (Table 3). Overall, pesticide dissipation was faster in the two storage dam waters compared to the two wetland waters. The presence of light inhibited total endosulfan dissipation and promoted chlorpyrifos dissipation.

4.3 Pesticide Sorption

Pesticide sediment/water partition coefficients were determined for all pesticides except the two parent endosulfan isomers and chlorpyrifos (Table 4). These

could not be determined because concentrations had fallen below quantifiable limits in the aqueous phase at the time of analysis.

For the insecticides, sorption was significantly higher onto suspended sediments filtered from the vegetated pond water compared to other water sources (*p*<0.05). Sorption of the herbicides was highest on *Mollee* storage suspended sediments, however this was not significantly different to other samples (*p*>0.05). Average sorption coefficients for aldicarb and total endosulfan were significantly greater than sorption coefficients for the herbicides (*p*<0.05).

5 Discussion

5.1 Modelling and Pesticide Persistence

Pesticide dissipation kinetics were modelled using zero-, first-, or second-order exponential decay
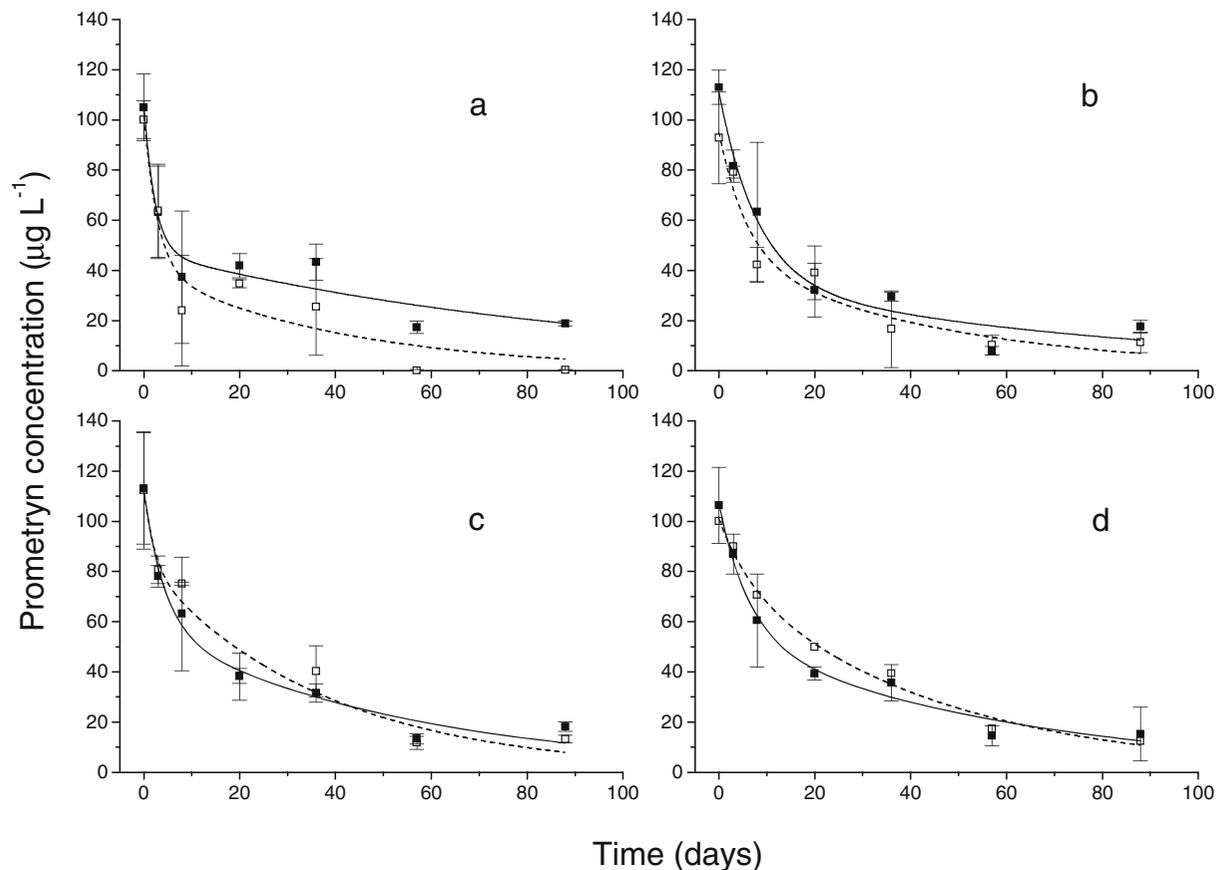
Fig. 2 Dissipation of prometryn from water columns. **a** *Auscott* storage, **b** *Galathera Creek*, **c** *Mollee* storage, **d** *Vegetated pond*. *Closed symbols* and *solid line* represent dark conditions; *open symbols* and *dashed line* represent light conditions. *Error bars* represent 95% confidence intervals (*n*=3). Note the rapid dissipation of prometryn from *Auscott* storage samples under light conditions after day 36

curves. When second-order models were employed, a constraint was placed on the first transformation rate, k_1. This value was restricted from falling below 3 days because no samples were taken between 0 and 3 days. Even though model fits with k_1 values below 3 were at times best, they could not be justified without the inclusion of more data between 0 and 3 days.

For the insecticides chlorpyrifos and aldicarb, first-order curves were generally the best fit. In contrast, the dissipation of total endosulfan (α plus β plus sulfate) displayed a second-order trend: after an initial rapid loss of parent compounds, the slower loss of endosulfate followed. However, because of limited sampling in the initial time period, it is possible that second-order loss occurred for chlorpyrifos and aldicarb but could not be elucidated. Future investigations need to employ a more thorough sampling regime within the first day of experimentation.

The herbicide diuron displayed first-order loss in the wetland samples (vegetated pond and Galathera Creek) compared to second-order loss in the storage water samples (*Mollee* storage and *Auscott* storage), whereas prometryn displayed second-order kinetics in all samples. According to literature, main routes of dissipation of both compounds are biodegradation (Roberts, 1998) and photolysis (Gerecke et al., 2001; Konstantinou, Zarkadis, & Albanis, 2001). Since photolysis by ultraviolet light was effectively negated by the glass columns, the major route of loss of these pesticides was presumably biodegradation. Thus, the presence of bi-phasic kinetics suggests an initial loss of a rapidly-degraded, bioavailable portion, followed by the dissipation of a less accessible portion. However, most other studies have only reported prometryn or diuron dissipation as a first-order process, with a wide range of half life values

Pesticide	Effect of water source	Effect of light
Total endosulfan	MS*<AS**<VP***<GC****	Dark*<light**
Chlorpyrifos	NS	light*<dark**
Aldicarb	AS*<MS*<VP**<GC**	NS
Diuron	MS*<AS*<VP**<GC**	NS
Prometryn	AS*<MS*<VP**<GC**	NS

depending on the conditions imposed (Gerecke et al., 2001; Konstantinou et al., 2001; Navarro et al., 2004).

5.2 Influence of Water Source

For all pesticides except chlorpyrifos, dissipation was significantly faster from storage water samples than wetland water samples ($p<0.05$). In the case of endosulfan, dissipation in the GC wetland sample was significantly slower than the VP wetland samples ($p<0.05$). There are a number of possible reasons for these findings.

The GC wetland sample contained a high level of suspended solids. Some reports have suggested that suspended solids can enhance organic contaminant degradation by concentrating them along with bacteria and nutrients on surfaces, leading to increased biodegradation (Olmstead & Weber, 1991; Shimp & Pfaender, 1987; Tranvik & Jorgensen, 1995). In contrast, Macalady and Wolfe (1985) reported that partitioning of organophosphate esters, including chlorpyrifos, into the organic carbon of sediment suppressed abiotic, alkaline hydrolysis. More recently, Walse, Shimizu, and Ferry (2002) studied the surface catalyzed transformation of aqueous endosulfan at pH 8.15 and found that while crystalline suspensions (e.g. sea sand, TiO_2, SiO_2, laponite) accelerated hydrolysis to endosulfan diol, suspended creek sediment inhibited it. This is similar

to our observations for endosulfan, with all waters of pH 7.5–8.5. Possibly, the role of suspended solids in the breakdown of hydrolysable pesticides is a trade-off. For example, if water sample pH is conducive to alkaline hydrolysis, as in our experiment, high organic carbon sediments like those from wetland areas could inhibit breakdown. Conversely, if alkaline hydrolysis is unlikely, wetland suspended sediments may indeed increase overall dissipation by enhancing biotic degradation. This hypothesis requires testing to establish the quantitative significance of these effects.

An alternative hypothesis relates to volatilisation of the parent compound rather than degradation. According to Guerin (2001), α and β endosulfan loss from sterile filtered water is second-order (biphasic). The reasons given for this are a rapid initial loss of endosulfan via volatilisation, followed by slower chemical hydrolysis. Considering that volatilisation results from a pesticide's affinity for the gas phase relative to the aqueous phase, it is expected that by increasing the dissolved organic fraction, the affinity for the aqueous phase increases and thus volatilisation decreases. Such an occurrence was observed by Lichtenstein and Schulz (1970), who found that the addition of soil, algae or a detergent to water reduced the volatility of certain pesticides (but not others). DDT and lindane volatility from water was reduced by the addition of soil,

Water source	Endosulfan sulfate	Aldicarb	Diuron	Prometryn
AS	165 (18)	110 (48)	8 (3)	8 (2)
GC	84 (31)	306	7 (1)	13 (20)
MS	158 (42)	297 (180)	33 (37)	105 (190)
VP	611 (420)	476 (331)	11 (7)	24 (1)
Average	261 (145)	295 (116)	16 (10)	41 (45)

aldrin and dieldrin volatilisation was reduced by detergent addition, and lindane and dyfonate volatilisation was strongly reduced by the presence of algae.

5.3 Influence of Light

Dissipation of the three herbicides and the insecticide aldicarb was not affected by light. This finding is similar to that of Navarro et al. (2004), who exposed a mixture of four triazine herbicides in river, sea and groundwater samples to natural sunlight allowing UV penetration. Although illumination increased the rate of triazine degradation in sea and groundwater samples, no difference in the reduction of three triazines was observed throughout the study (130 days) between light and dark river water samples. It was suggested that energy quenching by dissolved organic matter limited photolytic degradation. This has also been reported elsewhere. In our study, UV penetration and photolysis should have been minimal because of the use of glass columns.

Chlorpyrifos dissipation increased under light conditions in all samples except those originating from Galathera Creek. The high turbidity of Galathera Creek samples may have prevented a significant difference between light and dark samples. The cause for the faster loss of chlorpyrifos under light conditions is unknown. It is likely that light conditions would exert an influence on the microbial composition of the water, increasing photoautotrophic activity by algae and cyanobacteria. Under these conditions phosphorus consumption may increase, perhaps creating a gradient to select for chlorpyrifos-degrading microorganisms. Indeed, Megharaj, Venkateswarlu, and Rao (1987) isolated five different photoautotrophs, two algae and three cyanobacteria, which could accelerate the degradation of the OP monocrotophos. Two of these, *Scenedesmus bijugatus* and *Chlorella vulgaris*, removed greater than 70% of the OP in 20 days, compared to a loss of 30% in uninoculated controls.

The proposal that the enhanced dissipation of chlorpyrifos in light samples was biologically induced is supported by the kinetics of dissipation, which show that the rate of loss from light samples only increased beyond that of dark samples after a lag period indicative of biological activity. Also, the two samples originating from *Mollee*, MS and VP, had lower concentrations of orthophosphate and displayed the greatest difference between light and dark columns, further supporting the proposed role of phosphorus.

5.4 Accelerated Dissipation

It is proposed that the accelerated dissipation of chlorpyrifos under light conditions resulted from the selection of a specific community of chlorpyrifos-degrading microorganisms. Such 'enhanced degradation' has been observed elsewhere for a number of pesticides, particularly after repeat applications in soils (Head & Cain, 1991). In our study, possible enhanced degradation was also observed for the herbicides prometryn and diuron. In *Auscott* storage samples under light conditions, prometryn was reduced from an average of 25 μg l^{-1} at day 36 to non-detectable levels at day 56. In *Mollee* storage samples under light conditions, diuron dissipation was also enhanced, but this occurred steadily as opposed to the more sudden increase in prometryn removal. A similar result was also observed for the related herbicide fluometuron in an extended study (data not shown).

The enhanced dissipation of the herbicides is specifically limited to the on-farm storages. Records obtained from the *Auscott* and *Mollee* farms indicated that prometryn has been applied annually for the last 5 years to fields contributing tailwater on *Auscott*, whereas prometryn has not been applied on the *Mollee* fields for the last 5 years. Hence a population of prometryn-degrading microorganisms may have been maintained in *Auscott* storage waters because of frequent re-exposure, compared to the other sources that have not been exposed recently. The reason for the sudden initiation of degradation after 36 days is unknown, but could be the result of a growth-lag of degrader organisms, or triggered by limited sulfur that is subsequently provided by prometryn degradation.

Diuron and/or fluometuron have been applied to both *Auscott* and *Mollee* fields annually for the last 5 years, however fast dissipation rates were only observed in *Mollee* storage samples. It is not known why this occurred, but it is possible that a high number of degrader organisms were already present in *Mollee* storage water from the previous season. Advances in molecular techniques mean that

it may soon be possible to quantify populations of degrader organisms, enabling hypotheses such as these to be verified or falsified and such research is suggested.

5.5 Pesticide Sorption

Sediment-water partition coefficients were successfully determined for all pesticides except the two parent endosulfan isomers and chlorpyrifos. Coefficients for these compounds could not be calculated because concentrations were below quantifiable limits in the aqueous phase, indicating high affinity for sediment. This affinity is regularly reported for both insecticides (Silburn, 2003) and occurs because of their low water solubility. Endosulfan sulfate is slightly more soluble than the parent endosulfan isomers but still displayed a relatively high average partition coefficient of 261 (±145). Hugo (1999) calculated a K_D of 42 for endosulfate onto a clay soil from the same region (*Auscott*, Narrabri).

In contrast, the herbicides and aldicarb are more water-soluble. As such, the herbicides displayed partition coefficients an order of magnitude lower than endosulfan sulfate. Interestingly, the partition coefficients calculated for fluometuron and diuron in *Mollee* storage samples were high compared to other samples. This resulted from very low aqueous concentrations, suggesting that the accelerated dissipation occurred by degradation of dissolved residues rather than bound residues.

Aldicarb displayed a sediment partition coefficient much higher (average of 295) than soil sorption literature values, which range from 10 to 30 (Rao, Mansell, Baldwin, & Laurent, 1993; Wauchope, Buttler, Hornsby, Augustijn-Beckers, & Burt, 1992). Interestingly, Vink (1997) reported a K_{OC} value for aldicarb sorption to sediment that was 10 times greater than the K_{OC} value for aldicarb sorption to soil, which is similar to our result. Thus, aged, saturated sediments may have an increased capacity for aldicarb sorption. Also, Guo, Wagenet, and Jury (1999) showed that aldicarb degrades up to 65 times faster when dissolved in the soil solution compared to degradation whilst sorbed to sediment. Because our K_D values were calculated after incubation for 88 days, it is possible that the degradation of dissolved aldicarb in our water columns exceeded that of sorbed aldicarb, leading to an exaggerated sorption coefficient.

6 Conclusions

The hypothesis that pesticide dissipation would be significantly enhanced in water obtained from wetlands compared to storage dam water per se (that is, discounting the presence of macrophytes) was disproved in this study. The suggested reasons for this unexpected result include:

1. Levels of suspended sediments and dissolved organic matter that were inhibitory to volatilisation and hydrolysis of susceptible pesticides. Studies have demonstrated that suspended mineral sediments can catalyse alkaline hydrolysis, but organic matter reduces this effect. Both storage-water samples contained moderate amounts of suspended solids but with lower organic matter than wetland samples. The natural wetland water was found to be high in suspended sediments, but also higher in organic matter. Water from the constructed wetland was lower in suspended sediments, but most of this was organic rather than mineral.

2. The history of regular exposure to high levels of cotton chemicals. Galathera Creek natural wetland is adjacent to a cotton property but would only receive runoff periodically during high flows in which pesticides would be dilute. The constructed wetland (VP) has only been in operation for four growing seasons, during which it has received inputs of endosulfan, aldicarb, fluometuron and diuron, but not chlorpyrifos or prometryn. In comparison, both storage dams have been in operation for more than 10 years, regularly receiving inputs of the pesticides examined in this study and other structurally similar pesticides. This is likely to have caused adaptation within the microbial communities residing in sediments and overlying water enabling faster breakdown of these chemicals.

References

APVMA (2004). *Manual of requirements and guidelines for agricultural applications*. Canberra, Australia: Australian Pesticides and Veterinary Medicines Association.

Bedford, B. L., Bouldin, B. R., & Beliveau, B. D. (1991). Net oxygen and carbon dioxide balances in solution bathing roots of wetland plants. *Journal of Ecology, 79*, 943–959.

Bennett, E. R., Moore, M. T., Cooper, C. M., Smith, S., Shields, F. D., Drouillard, K. G., et al. (2005). Vegetated agricultural drainage ditches for the mitigation of pyrethroid-associated runoff. *Environmental Toxicology and Chemistry, 24*, 2121–2127.

Berger, B. M. (1998). Parameters influencing biotransformation rates of phenylurea herbicides by soil microorganisms. *Pesticide Biochemistry and Physiology, 60*, 71–82.

Braskerud, B. C. (2001). The influence of vegetation on sedimentation and resuspension of soil particles in small constructed wetlands. *Journal of Environmental Quality, 30*, 1447–1457.

Crossan, A. N. (2002). Remediation of pesticides on cotton farms: Studies of the environmental distribution, transport and fate of five pesticides. PhD thesis, The University of Sydney.

Crossan, A. N., Lee, N., Sharma, R., Kennedy, I. R., & Beckett, R. (2002). Assessment of the distribution of pesticides on soil particle fractions in simulated irrigation run-off using centrifugal SPLITT fractionation and ELISA. *Analytica et Chimica Acta, 468*, 199–208.

Dabney, S. M., Moore, M. T., & Locke, M. A. (2006). Integrated management of in-field, edge-of-field, and after-field buffers. *Journal of the American Water Resources Association, 42*, 15–24.

Gerecke, A. C., Canonica, S., Muller, S. R., Scharer, M., & Schwarzenbach, R. P. (2001). Quantification of dissolved natural organic matter (DOM) mediated phototransformation of phenylurea herbicides in lakes. *Environmental Science and Technology, 35*, 3915–3923.

Guerin, T. F. (2001). Abiological loss of endosulfan and related chlorinated organic compounds from aqueous systems in the presence and absence of oxygen. *Environmental Pollution, 115*, 219–230.

Guo, L., Wagenet, R. J., & Jury, W. A. (1999). Adsorption effects on kinetics of aldicarb degradation: Equilibrium model and application to incubation and transport experiments. *Soil Science Society of America Journal, 63*, 1637–1644.

Head, I. M., & Cain, R. B. (1991). Enhanced pesticide degradation in soil – Microbiology and genetics. *Pesticide Outlook, 2*, 13–16.

Hugo, L. (1999). Physico-chemical methods for the containment of potential chemical contaminants on cotton farms. PhD thesis, The University of Sydney.

Kazumi, J., & Capone, D. G. (1995). Microbial aldicarb transformation in aquifer, lake, and salt-marsh sediments. *Applied and Environmental Microbiology, 61*, 2820–2829.

Kennedy, I. R., Sanchez-Bayo, F., Kimber, S. W., Hugo, L., & Ahmad, N. (2001). Off-site movement of endosulfan from irrigated cotton in New South Wales. *Journal of Environmental Quality, 30*, 683–696.

Konstantinou, I. K., Zarkadis, A. K., & Albanis, T. A. (2001). Photodegradation of selected herbicides in various natural waters and soils under environmental conditions. *Journal of Environmental Quality, 30*, 121–130.

Lee, S., Gan, J. Y., Kim, J. S., Kabashima, J. N., & Crowley, D. E. (2004). Microbial transformation of pyrethroid insecticides in aqueous and sediment phases. *Environmental Toxicology and Chemisty, 23*, 1–6.

Lichtenstein, E. P., & Schulz, K. R. (1970). Volatilization of insecticides from various substrates. *Journal of Agricultural and Food Chemistry, 18*, 814–818.

Macalady, D. L., & Wolfe, N. L. (1985). Effects of sediment sorption and abiotic hydrolyses. I. organophosphorothioate esters. *Journal of Agricultural and Food Chemistry, 33*, 167–173.

Mallick, K., Bharati, K., Banerji, A., Shakil, N. A., & Sethunathan, N. (1999). Bacterial degradation of chlorpyrifos in pure cultures and in soil. *Bulletin of Environmental Contamination and Toxicology, 62*, 48–54.

Mazanti, L., Rice, C., Bialek, K., Sparling, D., Stevenson, C., Johnson, W. E., et al. (2003). Aqueous-phase disappearance of atrazine, metolachlor, and chlorpyrifos in laboratory aquaria and outdoor macrocosms. *Archives of Environmental Contamination and Toxicology, 44*, 67–76.

Megharaj, M., Venkateswarlu, K., & Rao, A. S. (1987). Metabolism of monocrotophos and quinalphos by algae isolated from soil. *Bulletin of Environmental Contamination and Toxicology, 39*, 251–256.

Mink, F. L., Risher, J. F., & Stara, J. F. (1989). The environmental dynamics of the carbamate insecticide aldicarb in soil and water. *Environmental Pollution, 61*, 127–155.

Moore, M. T., Bennett, E. R., Cooper, C. M., Smith, S., Farris, J. L., Drouillard, K. G., et al. (2006). Influence of vegetation in mitigation of methyl parathion runoff. *Environmental Pollution, 142*, 288–294.

Navarro, S., Vela, N., Gimenez, A. J., & Navarro, G. (2004). Persistence of four s-triazine herbicides in river, sea and groundwater samples exposed to sunlight and darkness under laboratory conditions. *Science of the Total Environment, 329*, 87–97.

Olmstead, K. P., & Weber, W. J. (1991). Interactions between microorganisms and activated carbon in water and waste treatment operations. *Chemical Engineering Communications, 108*, 113–125.

Rao, P. S. C., Mansell, R. S., Baldwin, L. B., & Laurent, M. F. (1993). *Pesticides and their behavior in soil and water*. Florida Cooperative Extension Service, University of Florida, USA.

Roberts, T. R. (Ed.) (1998). *Metabolic pathways of agrochemicals*. Cambridge: The Royal Society of Chemistry.

Rose, M. T., Sanchez-Bayo, F., Crossan, A. N., & Kennedy, I. R. (2006). Pesticide removal from cotton farm tailwater by a pilot-scale ponded wetland. *Chemosphere, 63*, 1849–1858.

Rose, M. T., Sanchez-Bayo, F., & Kennedy, I. R. (2001). Phytoremediation of pesticide residues by wetland plants. Paper presented at the 2nd National Wetlands Conference, South Stradbroke Island, Queensland, Australia November.

Sanchez-Bayo, F., Baskaran, S., & Kennedy, I. R. (2002). Ecological relative risk (EcoRR): Another approach for

risk assessment of pesticides in agriculture. *Agriculture, Ecosystems and Environment, 91*, 37–57.

Shimp, R. J., & Pfaender, F. K. (1987). Effect of adaptation to phenol on biodegradation of monosubstituted phenols by aquatic microbial communities. *Applied Environmental Microbiology, 53*, 1496–1499.

Silburn, D. M. (2003). Characterising pesticide runoff from soil on cotton farms using a rainfall simulator. PhD thesis, The University of Sydney.

Tomlin, C. D. S. (Ed.) (1997). The pesticide manual. Farnham, UK: The British Crop Protection Council.

Tranvik, L. J., & Jorgensen, N. O. G. (1995). Colloidal and dissolved organic matter in lake water-carbohydrate and amino acid composition, and ability to support bacterial growth. *Biogeochemistry, 30*, 77–97.

Vink, J. P. (1997). Pesticide biotransformation and fate in heterogeneous environments. PhD thesis, Wageningen University.

Walse, S. S., Shimizu, K. D., & Ferry, J. L. (2002). Surface-catalyzed transformations of aqueous endosulfan. *Environmental Science and Technology, 36*, 4846–4853.

Wauchope, R. D., Buttler, T. M., Hornsby, A. G., Augustijn-Beckers, P. M., & Burt, J. P. (1992). The SCS/ARS/CES pesticide properties database for environmental decision making. *Reviews of Environmental Contamination and Toxicology, 123*, 1–164.