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The effect of vegetation on pesticide dissipation from ponded treatment wetlands: Quantification using a simple model

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ABSTRACT

Field data shows that plants accelerate pesticide dissipation from aquatic systems by increasing sedimentation, biofilm contact and photolysis. In this study, a graphical model was constructed and calibrated with site-specific and supplementary data to describe the loss of two pesticides, endosulfan and fluometuron, from a vegetated and a non-vegetated pond. In the model, the major processes responsible for endosulfan dissipation were alkaline hydrolysis and sedimentation, with the former process being reduced by vegetation and the latter enhanced. Fluometuron dissipation resulted primarily from biofilm reaction and photolysis, both of which were increased by vegetation. Here, greater photolysis under vegetation arose from faster sedimentation and increased light penetration, despite shading. Management options for employing constructed wetlands to polish pesticide-contaminated agricultural runoff are discussed. The lack of easily fulfilled sub-models and data describing the effect of aquatic vegetation on water chemistry and sedimentation is also highlighted.

1. Introduction

The use of pesticide agrochemicals requires rational selection and management to prevent toxicities to non-target organisms. Of the environmental compartments into which pesticides can partition, contamination of fresh water sources often presents the highest risk because of its ubiquitous use by organisms and high potential for direct exposure. One promising management practice for treating pesticide-contaminated runoff water at the source is the use of constructed wetlands (Reichenberger et al., 2007). Their appeal to environmental managers results from their relatively low cost, robustness and ease of integration into other land management practices (Kadlec and Knight, 1996).

Constructed wetlands have been used to treat both herbicides and insecticides under various conditions. The fate of the herbicide atrazine has been well studied in different constructed wetlands, with removal efficiencies ranging from 26 to 84% over 8–30 d residence times (Alvord and Kadlec, 1996; Moore et al., 2000; Runes et al., 2003) and aqueous half-lives of 8–14 d (Detenbeck et al, 1996), 10 d (Alvord and Kadlec, 1996) or 16–48 d (Moore et al., 2000). A similar range of removal efficiencies and/or half-lives have been observed for the herbicides metolachlor, simazine, diuron, and fluometuron (Moore et al., 2001; Stearman et al, 2003; Rose et al., 2006). Insecticides seem to be even more amenable to removal from water by constructed wetland, with chlorpyrifos exhibiting aqueous half-lives of 5–13 d (Moore et al, 2002; Sherrard et al., 2004) and endosulfan exhibiting an aqueous half life of 8 d (Rose et al., 2006) in different wetlands. Chlorpyrifos and endosulfan were reduced to undetectable levels in outlet water samples from 0.02 to 0.2 $\mu g\ l^{-1}$, respectively, in inlet water at a 0.44 ha constructed wetland in South Africa (Schulz and Peall, 2001). Importantly, the treatment of pesticide-contaminated runoff by constructed wetlands directly reduces the toxicity of runoff water to aquatic invertebrates (Schulz and Peall, 2001; Sherrard et al., 2004).

Constructed wetland performance is affected by inlet concentrations, length and hydraulic residence time (Alvord and Kadlec, 1996; Moore et al. 2000; Runes et al., 2003). There is also evidence that aquatic vegetation can accelerate pesticide removal compared to open water systems (Schulz et al., 2003; Rose et al., 2006). This reportedly occurs because of the increased capacity for plant/biofilm sorption and subsequent immobilization, breakdown or uptake of pesticides (Schulz, 2004; Bouldin et al., 2005). However, to date there has been limited effort in quantifying the effect of aquatic vegetation on other pesticide dissipation pathways from aquatic systems (Schulz, 2004). This is despite the pathways leading to the dissipation of organic contaminants such as pesticides from aquatic systems having been discussed in detail (Warren et al., 2002). More information of this type is needed to aid in the design and management of constructed wetlands; to maximise treatment rates, minimise land use and construction costs, and in the case of semi-arid environments, to minimise water loss.

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This study aimed to model the rates of major dissipation processes and project the influence of aquatic plants on these rates, in order to formulate some general recommendations regarding the use of aquatic plants in constructed wetlands for polishing pesticide-contaminated agricultural runoff. The fates of two contrasting cotton pesticides, endosulfan and fluometuron, in a pilot scale-ponded wetland consisting of a vegetated and non-vegetated pond, were used to calibrate the model.

2. Methods

2.1. Model design

The pathways describing pesticide dissipation from water bodies were combined to provide a conceptual model (Fig. 1). In this study, the model was based on the kinetic processes taking place in two pools, such that:

Total rate of pesticide change $= R_{aq} + R_{sor}$

where R_{aq} is the rate of change in the dissolved pool, and R_{sor} is the rate of change in the sorbed pool. Breaking this down further,

$$\frac{dm}{dt} = (r_{des} - r_b - r_v - r_p - r_h - r_{sor}) + (r_{sor} + r_{res} - r_{des} - r_{sed}) \qquad (1)$$

where the reaction pathways are defined in Table 1. Some pesticide fluxes were excluded, notably the degradation of sorbed residues and sediment movement pathways outlined by Warren et al. (2002), because we were concerned only with water-borne residues. The model considered net sedimentation (that is, the difference between settling and resuspension) as a removal pathway.

2.2. System boundaries and model assumptions

The model system was used to describe a ponded water storage representative of those typically found on Australian cotton farms: irrigation tailwater or rainfall runoff was returned to an uncovered dam constructed from clay soil. The initial condition used was a static body of tailwater that had just been returned to a storage dam. We assume that dissolved and bound pesticide residues equilibrated during runoff prior to returning to the storage, such that the location of the pesticide mass at the start of the model could be adequately described by a sediment partition coefficient (Silburn, 2003). These residues underwent transportation and transformation processes as described above, over a time period specified by the modeler. The modelled system did not allow for additional inputs or removal of tailwater throughout the specified time period.

The model includes a mass balance. Hydrological flux through the system including rainfall, evaporation, transpiration and deep drainage was not considered. Instead, rainfall and evaporation data were corrected for in the field calibration data. Nevertheless, if it is assumed that deep drainage and evaporation are negligible relative to the total volume of the water storage, which is reasonable over time periods of less than 1 week, this model can still be considered as a useful estimate of pesticide concentrations, as justified by Alvord and Kadlec (1996). With additional input, the model described here could be coupled to a hydrological model to refine or validate predicted concentrations without correcting actual field data.

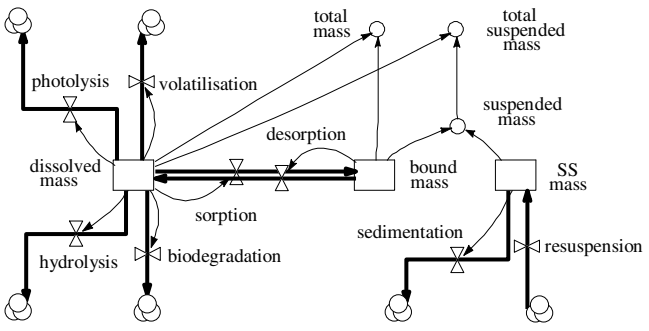

Fig. 1. Graphical display of the pesticide dissipation model in Simile. Square symbols represent compartments, thick arrows represent flows and fine arrows represent influences.

Table 1
Transformation and transportation sub-models

Flow path	Rate
Sorption	$r_s = k_s m_w$
Desorption	$r_{des} = k_{des} m_s$
Biofilm reaction	$r_b = \frac{k_a m_w S_b}{V_w}$
Photolysis	$r_p = \frac{k_p m_w S_a I_0}{V_w I_{max} k_1 e^{-k_1 z}}$
Hydrolysis	$r_h = k_h m_w$
Volatilisation	$r_v = \frac{k_v m_w S_a}{V_w}$
Sedimentation	$r_{sed} = k_{sed}$TSS

2.3. Model construction

The graphical modelling program Simile v5.0 (Simulistics Ltd., Edinburgh, UK) was used for model construction. Simile is a visual interface that requires the designation of compartments (of a substance) to which inflows and outflows can be added. Compartments were designated for dissolved pesticide mass, bound pesticide mass and suspended solid mass. Initial values for total tailwater pesticide mass and total suspended sediments (TSS) mass were user-defined, and these values were then used with a specified sediment partition coefficient to determine the initial masses of dissolved and bound pesticide. Flows out of these compartments represented the transportation and transformation processes described earlier. Importantly, adsorption–desorption did not result in pesticide loss from the system, whereas all other 'removal' flows did. All flows were dependent on compartmental masses and other variable or non-variable parameters, as shown by fine 'influence' arrows in Fig. 1. The equations and parameters defining these flows are given below and in Tables 1–3.

2.4. Initial conditions

The model required the input of known values for the total pesticide concentration and TSS concentration of the tailwater under study, and a sediment-water partition coefficient (K_p) for initialisation:

$$K_p = \frac{C_s}{C_w} \qquad (2)$$

where C_s is the concentration of pesticide bound to suspended sediment ($\mu g\ kg^{-1}$) and C_w is the concentration of pesticide dissolved in water ($\mu g\ l^{-1}$). From these values, the fraction of pesticide residues in water residing in the dissolved and sediment-bound phase was calculated as,

$$\text{Fraction in water phase} = \frac{1}{(1 + SCK_p)} \qquad (3)$$

$$\text{Fraction in sediment phase} = \frac{SCK_p}{(1 + SCK_p)} \qquad (4)$$

where SC was the concentration of total suspended sediments in runoff ($kg\ l^{-1}$). In this study, a K_p was empirically obtained from existing data (Baskaran and Kennedy, 1999; Hugo, 1999), however, if a location-specific K_p is not available, an estimate could be made using literature K_{oc} values, where,

Table 2
Input parameters for fluometuron dissipation

Flow path	Parameter	Symbols	Units	Open pond calibration	Vegetated pond calibration	Data source
Photolysis	Top surface area	S_a	m^2	70	130	Field measurement
	Volume	V	m^3	58	58	Field measurement
	Depth	z	m	1	0.5	Field measurement
	Photolysis rate coefficient	k_p	h^{-1}	0.031	0.031	Estimated from Gerecke et al., 2001; Lam et al., 2003
	Maximum radiation	I_m	MJ m^{-2} h^{-1}	1.425	1.425	Field weather data
	Actual radiation	I_0	MJ m^{-2} $^{-1}$	(0.48–1.42)	(0.48–1.42) × 0.05	Field weather data
	Light attenuation coefficient	k_l	m^{-1}	25 × TSS	25 × TSS	Estimated from Heaven et al. (2005)
Biofilm reaction	Biofilm surface area	S_b	m^2	96	168	Calculated from field measurements
	Volume	V	m^3	58	58	Field measurement
	Mass transfer coefficient	k_a	m h^{-1}	9.86×10^{-4}	9.86×10^{-4}	Estimated from field data
Sorption	Adsorption rate coefficient	k_d	h^{-1}	5.08×10^{-5}	5.08×10^{-5}	Estimated from Baskaran and Kennedy (1999)
	Desorption rate coefficient	k_{des}	h^{-1}	3.39×10^{-6}	3.39×10^{-6}	Estimated from Baskaran and Kennedy (1999)
Sedimentation	Sedimentation rate coefficient	k_{sed}	h^{-1}	0.021	0.042	Estimated from field data (Fig. 3A)
	Resuspension rate	r_r	h^{-1}	4.1×10^{-3}	2.3×10^{-3}	Estimated from field data (Fig. 3A)
	Fraction of total suspended sediment	TSS	–	0.20–1.00	0.05–1.00	Calculated from field measurement

Table 3
Input parameters for endosulfan dissipation

Flow rate	Parameter	Symbols	Units	Open pond calibration	Vegetated pond calibration	Data source
Volatilisation	Top surface area	S_a	m2	70	130	Field measurement
	Windspeed	u	m s^{-1}	0–21.2	(0–21.2) × 0.1	Field weather data
	Air temperature	T	°K	9.4–39.9	9.4–39.9	Field weather data
	Henry constant	H	Pa m^3 g^{-1}	1.19×10^{-3}	1.19×10^{-3}	Peterson and Batley (1993)
	Air-side mass transfer coefficient	k_{va}	h^{-1}	$3.6 + 5 \times u^{1.2}$	$3.6 + 5 \times u^{1.2}$	Estimated from field weather data
	Water-side mass transfer coefficient	k_{vw}	h^{-1}	$0.0036 + 0.01 \times u^{1.2}$	$0.0036 + 0.01 \times u^{1.2}$	Estimated from field weather data
	Volatilisation rate coefficient	k_v	h^{-1}	$k_v = \frac{1}{\frac{1}{k_{vw}} + \frac{8.3T}{Hk_{va}}}$	$k_v = \frac{1}{\frac{1}{k_{vw}} + \frac{8.3T}{Hk_{va}}}$	Mackay (2001)
Hydrolysis	pH initial	pH	pH	8.0	7.95	Field data
	Rate of pH change	r_{pH}	pH h^{-1}	0	-1.6×10^{-3}	Estimated from field data (Fig. 3B)
	Hydrolysis rate coefficient	k_h	h^{-1}	$10^{(1.1pH-10.65)}$	$10^{(1.1pH-10.65)}$	Estimated from Peterson and Batley (1993)
Sorption	Adsorption rate coefficient	k_d	h^{-1}	5.36×10^{-4}	5.36×10^{-4}	Estimated from Hugo (1999)
	Desorption rate coefficient	k_{des}	h^{-1}	1.34×10^{-6}	1.34×10^{-6}	Estimated from Hugo (1999)
Sedimentation	Sedimentation rate coefficient	k_{sed}	h^{-1}	0.021	0.042	Estimated from field data (Fig. 2A)
	Resuspension rate	r_r	h^{-1}	4.1×10^{-3}	2.3×10^{-3}	Estimated from field data (Fig. 2A)

$$K_p = \frac{K_{oc} OC\%}{100} \quad (5)$$

with K_{oc} the organic carbon partition coefficient (L kg^{-1}) and OC% the percent organic carbon in the sediment. Following initialisation, the model used pesticide and site-specific information to determine the flows out of the compartments.

2.5. Model calibration

A ponded constructed wetland, consisting of a non-vegetated and a vegetated pond in series, was established on a cotton farm in northern New South Wales, Australia (Rose et al., 2006). Cotton field irrigation tailwater during the 2004/05 summer cotton growing season was gravity fed into the wetland until it was full (58 m^3 in each pond), after which the water was stagnant for 10 d. Measurements of pH, suspended sediment, water volume, water temperature and pesticide concentration were made immediately after filling and every 48 h after. A weather station located adjacent to the wetland took hourly measurements of wind speed, solar radiation, air temperature, humidity and rainfall.

The herbicide fluometuron and the insecticide endosulfan were used to calibrate the model because of their application at the experimental site, prevalence in the cotton industry, differing chemistry and expected removal pathways from water (Table 1), and potential to cause harm (Tomlin, 1997; Muschal and Warne, 2003). Furthermore, the behaviour of both chemicals in the cotton growing region of northern New South Wales, Australia, has been well studied and supplementary data for the calibration were readily available (Baskaran and Kennedy, 1999; Hugo, 1999; Kennedy et al., 2001; Crossan et al., 2002; Silburn, 2003; Shivaramaiah et al., 2005).

Because fluometuron does not undergo significant hydrolysis or volatilisation (Tomlin, 1997), these pathways were not considered in the fluometuron removal model. Operational flows were photolysis, biofilm reaction, sorption–desorption and sedimentation (Table 2). The total (sum of direct and indirect) photolysis rate coefficients (k_p) determined by Gerecke et al. (2001) and Lam et al. (2003) for fluometuron were averaged and used as an input for model calibration. The concentration of the major photosensitizers (dissolved organic matter, NO_3^-) in our pilot-scale wetland fell within the range of those used by these authors and thus served as the best k_p approximation obtainable. The rate of photolysis throughout the water column was scaled by a light attenuation coefficient, k_l, which described the reduction in radiation at depth due to absorption and scattering by suspended sediments. k_l was assumed to be linearly dependent on the percent TSS

remaining, such that the initial concentration of TSS (the maximum) resulted in $k = 25\ m^{-1}$; a value typically observed to be the maximum in waste stabilisation ponds (Heaven et al., 2005). A combined mass transfer/reaction coefficient previously calculated for the pilot-scale wetland ($9.86 \times 10^{-4}\ m\ h^{-1}$) was used to model biofilm reaction rates (based on data from Rose et al., 2006). Sorption data from Baskaran and Kennedy (1999) were used to estimate kinetic sorption and desorption rate constants to suspended sediments from heavy clay soils and sedimentation and resuspension rates were estimated from field data (Fig. 2A).

In contrast to fluometuron, endosulfan is relatively resistant to photolysis and biological reaction, but sorption, hydrolysis and volatilisation are important and were considered in the model. Hydrolysis rates were calculated from a first-order exponential relationship with pH that had been constructed from data related to the surface waters of NSW cotton growing regions (Peterson and Batley, 1993). The effect of aquatic plants on water pH was calculated from field trials (Fig. 2B). Volatilisation was estimated from wind speed using data at 2 m height (Mackay, 2001). Wind speed over the surface of the vegetated water was assumed to be one-tenth the speed across the open water. Sorption and desorption rate constants were derived from Hugo (1999) and sedimentation and resuspension rates were estimated from field data. For all flow pathways, rate coefficients were determined for alpha-endosulfan, beta-endosulfan and endosulfan sulfate, and then averaged by an expected environmental ratio of 3:2:5 (Hugo, 1999).

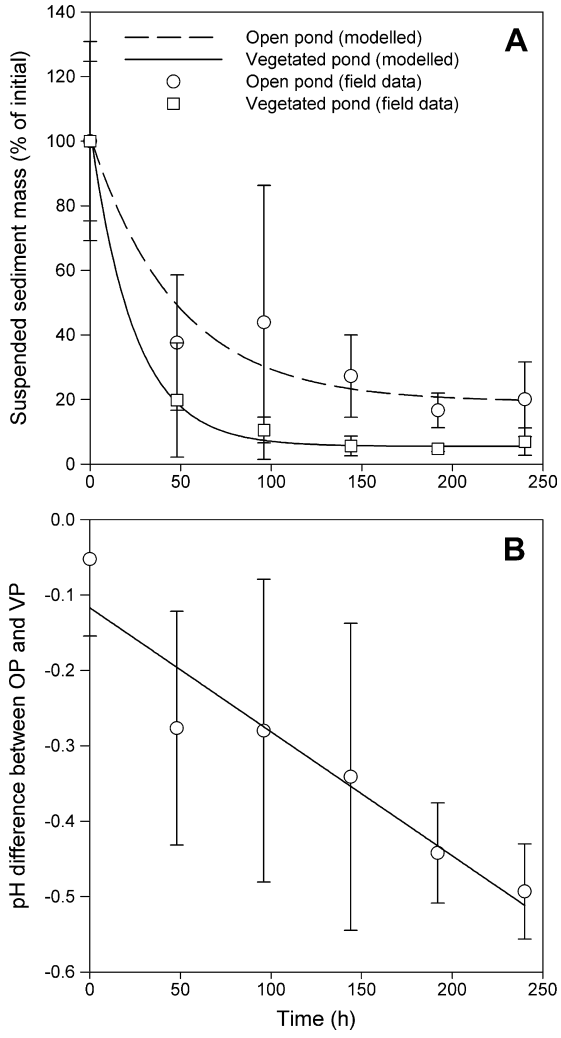

Fig. 2. (A) TSS in the open and vegetated ponds and (B) pH difference in the vegetated pond (VP) relative to the open pond (OP). Error bars represent 95% confidence levels of field data ($n = 3$).

2.6. Statistical analysis

Non-linear regression, including parameter estimation and analysis of variance at a confidence level of 95%, was performed on literature sorption, desorption and hydrolysis data to provide input for the ponded wetland model. For the ponded wetland model, linear regression of observed data against fitted results was performed. The model fit was assessed by adjusted coefficients of determination (adjusted r^2) and analysis of variance statistics, at a confidence level of 95%. All statistical procedures were carried out using SigmaPlot V9.0 (Systat Software, San Jose, USA).

3. Results

3.1. Input data

The amount of sediment in runoff entering the wetland ponds was 938 (±272) $mg\ l^{-1}$. The extent of sedimentation was greater in the vegetated pond compared to the open pond, but the high variation of suspended sediment concentrations in the open pond meant this difference was only significant between measurements taken at 144 and 192 h (Fig. 2A). Model results of the first-order sediment settling minus zero-order sediment resuspension agreed well with experimental data both for the open (adjusted $r^2 = 0.91$, $p = 0.002$) and the vegetated pond (adjusted $r^2 = 1.00$, $p < 0.001$) and estimated parameters were used in the sedimentation sub-model for both fluometuron and endosulfan dissipation (Tables 2 and 3).

The pH in the ponds at the start of the incubations was not significantly different. The pH of the open pond did not change significantly throughout the incubation, however the pH of the vegetated pond decreased significantly by 0.5 (±0.06) over 10 d. The rate of this pH reduction was estimated by linear regression (Fig. 2B; adjusted $r^2 = 0.88$, $p = 0.003$) to provide input for the hydrolysis sub-model describing endosulfan dissipation (Table 3).

3.2. Fluometuron

The initial concentration of fluometuron in water entering the wetland ponds was 5.6 (±0.4) $\mu g\ l^{-1}$. Fluometuron removal from the pilot-scale system using the model agreed well with experimental field data for both the vegetated pond (adjusted $r^2 = 0.98$; $p < 0.001$) and the open pond (adjusted $r^2 = 0.85$; $p = 0.006$) (Fig. 3A). Removal was faster in the vegetated pond than in the open pond, with only about 40% of the initial mass load remaining after 10 days compared to about 70% remaining in the open pond. In the vegetated pond, biofilm reaction was the dominant removal mechanism, with photolysis less influential because of vegetation shading the water surface. Interestingly, biofilm reaction was also the dominant removal mechanism in the open pond, with photolysis being negligible despite the full intensity of solar radiation striking the water surface (Fig. 3B). Reduced photolysis resulted from rapid absorption and scattering of light by suspended particles, which limited photolysis throughout the entire depth of the open pond. Because sorption to suspended sediments was relatively minor, actual sedimentation of sorbed fluometuron was not a major removal pathway in the ponds.

3.3. Endosulfan

The initial concentration of total endosulfan in irrigation runoff entering the wetland ponds was 2.21 (±0.08) $\mu g\ l^{-1}$. Overall, the

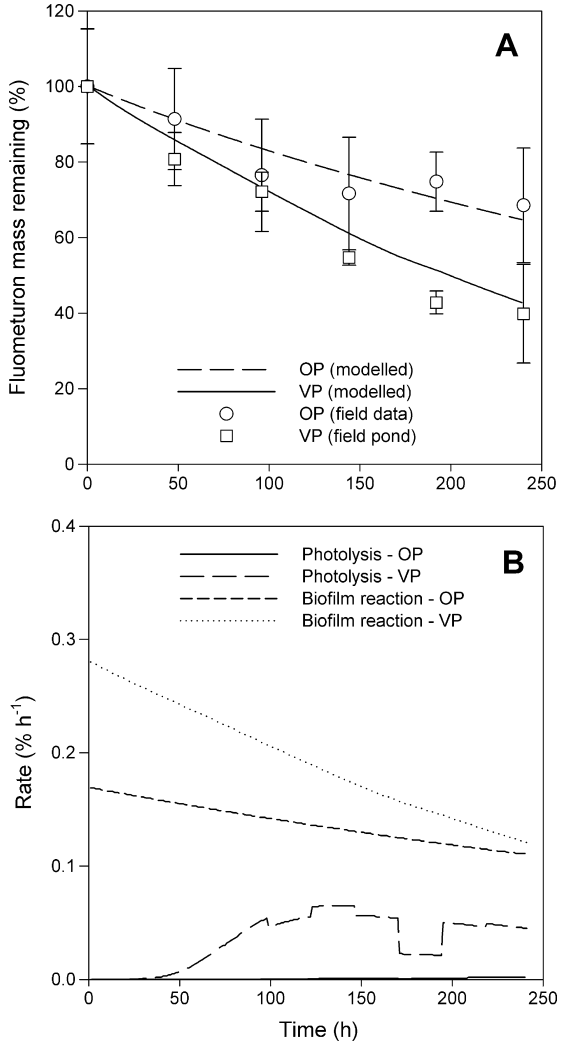

Fig. 3. Fluometuron (A) dissipation and (B) modelled removal rates from the pilot scale wetland system. Error bars represent 95% confidence levels of field data ($n = 3$).

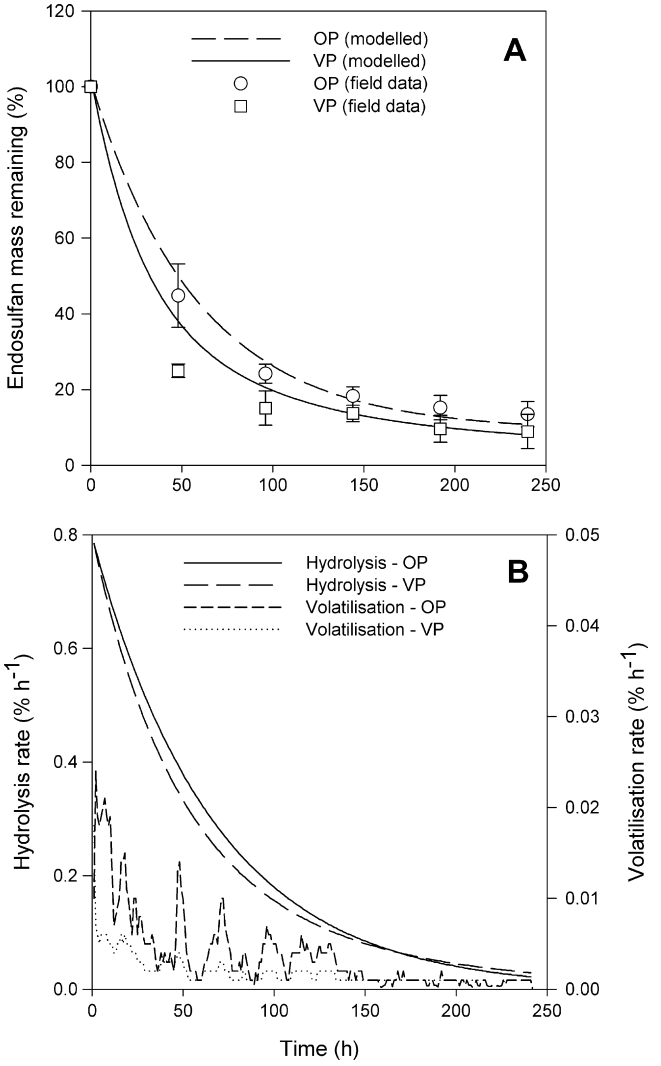

Fig. 4. Endosulfan (A) dissipation and (B) modelled removal rates from the pilot-scale wetland system. Error bars represent 95% confidence levels of field data ($n = 3$).

model results suitably described the loss of water-borne endosulfan observed in the field data for the open pond (adjusted $r^2 = 0.98$; $p < 0.001$) and the vegetated pond (adjusted $r^2 = 0.97$; $p < 0.001$). However, the model underestimated the initial rate of endosulfan loss in the vegetated pond, and overestimated endosulfan loss later in the open pond incubation (Fig. 4A). In both systems, over 80% of the endosulfan was removed in the first 4 days. According to the model, the rapid initial loss was brought about by hydrolysis of dissolved pesticide (Fig. 4B) and sedimentation in the vegetated pond (Fig. 2A). Although the rate of hydrolysis was faster in the open pond because of the higher pH, the amount of water-borne endosulfan hydrolysed in the open pond was lower because a higher proportion existed as bound residues, which were resistant to hydrolysis in this model. Volatilisation played only a minor role in endosulfan loss from both ponds.

4. Discussion

The application of modelling to illustrate pesticide loss from a ponded aquatic system was investigated with particular emphasis on the effect of aquatic plants. Because of the wide variety of pesticides and the characteristic complexities of environmental systems such as wetlands, theoretical models describing their interactions are scarce. In the case of the cotton-growing systems of northern NSW, the availability of site-specific data for pesticide transportation and transformation parameters allowed us to construct a compartmental model based on empirical estimates of individual pesticide dissipation pathways.

Although the model performed well for our two case studies, there were deficiencies with respect to its overall design. Transportation and transformation rates are temperature dependent, a fact which our model did not incorporate. This was somewhat circumvented by using site-specific rate constants determined under 'average' temperature conditions found in Australian cotton-growing regions. In doing so, the model lost resolution so that day-to-day fluctuations in temperature could not be accounted for. The model will always require site-specific rate constants for different locations. Another limitation of this model is its inability to account for pesticide that is already sorbed within the system (for example, from treatment of prior irrigation tailwater). This should be easily overcome by modifying the model initialisation procedure.

A more specific problem was the underestimation of early and overestimation of late endosulfan loss. This results from limitations in the sedimentation and sorption sub-models. Here, sedimentation was lumped as total sediment loss whereas in reality sediment loss is dependent on sediment size, removing larger particles faster than smaller particles. Because pesticides have affinity

for smaller particles on a mass/mass basis (Crossan et al., 2002; Wu et al., 2003), the loss of sediment will not necessarily equate to a similar loss of endosulfan as assumed in this model. Also, endosulfan associated with colloids in natural waters appears to be more resistant to hydrolysis than dissolved endosulfan (Walse et al., 2002), which would explain the tail observed in the field data.

Other empirical models that describe the fate of organic contaminants in aquatic systems exist in the literature. Mass transfer to biofilms on the wetland bottom is the rate-limiting removal step for atrazine, a herbicide of similar water solubility to fluometuron, according to Alvord and Kadlec (1996). They calculated mass transfer coefficients of 10–15 m per year for atrazine in a slow flow wetland, similar to transfer coefficients for BOD and nutrients reported elsewhere. Model output based on biofilm reaction as the only route of atrazine removal was in close agreement with field data in their study. In our study we used an average mass transfer coefficient of 11 m per year for fluometuron in the ponded wetland, within the range of values given above. However, because fluometuron is susceptible to photolytic degradation, unlike atrazine, inclusion of this pathway increased the model accuracy to our field data.

Warren et al. (2002) presented a more general multi-tiered approach, based on the fugacity concept (Mackay, 2001), in a system with increasing complexity. Different model versions were given for addressing equilibrium or non-equilibrium situations, steady-state or dynamic conditions and either single or multiple segments. A similar approach was taken to that outlined here for the kinetic characterisation, with the overall dissipation of organic contaminants separated into a maximum of 17 different flows. Some of the flows suggested by Warren et al. (2002) that were not used here include hydraulic flow, rain dissolution and atmospheric particle deposition. Warren et al. (2002) also emphasise the importance of sediment transport pathways, with six of the flows associated with sediment behaviour.

Despite our model's shortcomings, valuable information regarding the effect of aquatic plants on pesticide removal from water was obtained. The model supports the view that sedimentation plays an undervalued role in the removal process of different contaminants. Moreover, and this is less explicit in the literature, sedimentation has both a direct and an indirect influence on pesticide dissipation, both of which benefit from aquatic vegetation. The self-cleansing of aqueous systems can be relatively rapid if fine sediments and colloids are removed from the system before water is returned to farm water storage or sensitive environmental areas, via photolysis, hydrolysis and volatilisation of dissolved pesticide. For chemicals that are recalcitrant to these pathways, dissipation can be enhanced by promoting biofilm reactions. Design features such as aquatic vegetation, corrugations in the wetland bottom, small islands, and sub-surface flow gravel beds can all increase the potential reactive biofilm surface area. The concept of increasing the surface area/volume ratio is also applicable to surface-flow wetlands to enhance volatilisation and phototransformation rates.

In undertaking this modelling exercise, some gaps in our current knowledge were also uncovered. Foremost is our inability to predict the potential for plants to stimulate sedimentation and suppress sediment resuspension. Some studies have shown that vegetation reduces TSS beyond that of open systems (Hosokawa and Furukawa, 1994; Karathanasis et al., 2003), whilst others have shown that there is no effect (Tanner et al., 1995; Thomas et al., 1995). The work of Braskerud (2001, 2002) and Braskerud and Haarstad (2003) has highlighted our lack of understanding in this area. Braskerud emphasised that total sedimentation can be increased by increasing wetland surface area and decreasing depth, but shallow wetlands are more susceptible to resuspension in high flow events (Braskerud, 2002). Braskerud concluded that sedimentation rates in wetlands were not increased by vegetation, but instead resuspension rates were decreased. Unfortunately, most of this work included little quantitative information on the sedimentation *process*. In our study, total sediment loss was suitably described by a first-order settling process minus a zero-order resuspension process; but despite the good model fit it is unknown whether this describes the physical reality. If it does, or even closely approximates it, then our results suggest that vegetation both increases sediment settling and decreases resuspension (see parameters in Table 2), in contrast to Braskerud's conclusion.

Other quantitative sedimentation models investigated by Braskerud (2002), including those of Chen (1975), Haan et al. (1994) and Kadlec and Knight (1996), were under predictive. More recently, Stephan et al. (2005) and Schmid et al. (2005) found that emergent structures decreased sedimentation by increasing vertical water mixing. However, these results disagree with flow-through studies that show increased removal of TSS by submerged vegetation (Sand-Jensen, 1998), possibly because the filtration and flocculation effects of plants were not accounted for in the former report. Furthermore, Stephan et al. (2005) demonstrated a clear effect of wind shear in promoting suspended sediments, but did not attempt to resolve the impact of emergent vegetation in reducing wind shear. The variance in measured TSS concentrations in our results for the open pond system compared to the vegetated pond shows that wind shear indeed plays a crucial role.

There are also limitations in our understanding of how the pesticide dissipation pathways respond to environmental conditions and water quality aspects. Differences in local climates, pH, microbial communities, metal reaction centres and organic residues may prevent models like this from being easily transferred from one site to another. Because aquatic vegetation directly influences all of these characteristics, the situation becomes even more complex. The aim of our current research is to collate data from field experiments involving constructed wetlands for treating pesticide-contaminated runoff, and refine the model using sensitivity and uncertainty analysis. It is anticipated that this will provide some more site-specific recommendations for the design and operation of constructed wetlands for this purpose.

5. Conclusions

A graphical model describing pesticide loss from ponded aquatic systems was designed and tested. The model requires input parameters for kinetic rate constants of the major dissipation pathways, including mass transfer to biofilms, photolysis, hydrolysis and volatilisation. The model was successfully calibrated to field data. The results show that aquatic plants enhance sedimentation, thus directly contributing to removal of sediment-bound pesticide whilst also promoting light penetration and photolysis of the dissolved pesticides studied. Accurate estimates of pesticide sorption to sediments and subsequent settling of sediments were found to be essential for good predictions. The results clearly indicated a role for the use of both vegetated and non-vegetated wetland areas to increase the dissipation and removal of pesticides from agricultural runoff. A number of gaps in our understanding of the factors driving pesticide dissipation in vegetated systems, including sediment behaviour and the influence of other water quality parameters are also highlighted.

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