

# Preliminary Modeling of Pesticide Fate in Drainage Channels Using the RIVWQ Model

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## EXTENDED ABSTRACT

Contamination of drainage channels and creeks with pesticides used in agriculture is of major concern in south eastern Australia. In this study the stream pesticide model RIVWQ version 2.02 was assessed for its applicability to simulate pesticide fate in drainage channels. The model was successfully calibrated against field data collected on flows and pesticide concentrations for a drainage channel from a small catchment of five farms in the Murrumbidgee Irrigation Area of south western New South Wales. Using the calibrated model the effects of different pesticide loading scenarios from farm fields on channel water quality were analysed.

Drainage channel and stream water quality in agricultural areas is directly related to the land use, water and pesticide management practices. The contamination of drainage channels by the pesticide molinate is a great concern in the rice growing irrigation areas of south east Australia. Therefore, molinate concentration variations with different management practices were simulated in this study. The same farm fields as used in the model calibration were used for the management simulations.

In order to assess the sensitivity of the model to the various input parameters a series of simulations were conducted using the calibrated input file and varying significant parameter values by  $\pm 20\%$  of their original values. The volatilization coefficient is the most sensitive followed by the sediment bulk density, water/sediment partitioning coefficient and degradation rate in water. Parameters such as solubility and dispersion coefficient showed zero sensitivity.

The model was calibrated against molinate concentrations in a drainage channel that serviced 5 farms using data from an upstream monitoring point and a downstream monitoring point which were 1.9 km apart (Thomas *et al.*, 1998).

The RIVWQ model can be used in conjunction with surface runoff models to simulate the effects of land use, water management and pesticide management. However, observed field data are rare, therefore, only the effects of rice crop area on molinate concentrations in the drainage channel were investigated in this study. The rice crop area assumed for model simulation were 420 ha, 210 ha and 105 ha out of a total 900 ha area. Both the surface drainage flow rate and molinate concentration at the upstream point changed due to the rice crop area change.

The results of the model simulations suggest that the RIVWQ model can be effectively used for predicting pesticide fate in the drainage channels and exposure assessment in the agricultural environment. Thus, the model, in conjunction with surface runoff models, could be used to develop guidelines for the management of pesticide contaminated waters.

## 1. INTRODUCTION

Drainage water from irrigated agriculture frequently contains mixtures of pesticides which may enter natural water bodies directly or via a system of drainage channels. The environmental fate of pesticides is governed by complex interaction of many factors including the pesticide properties, agronomic practices, soil and hydrological conditions. The climatic conditions at the time of pesticide application and immediately following are also important.

Bowmer et al (1994) showed that pesticides used in irrigated agriculture in the Murrumbidgee Irrigation Area (MIA) of NSW, Australia, were present in drainage waters at concentrations often exceeding water quality guidelines. Toxicity of these chemicals to aquatic life remains a concern.

The large variability in biophysical and management conditions makes it very difficult to produce definitive guidelines. The experimental resources required to monitor a broad range of conditions are unavailable. As such the use of models to simulate varying biophysical and management conditions is useful in obtaining a broader spectrum of results that can be used to develop management guidelines.

Model selection is important to simulate the pesticide fate in the environment. Few pesticide water quality models are available for river systems. Examples include EXAMSII (Burns 1997) and WASP-5 (Ambrose *et al.* 1993). However, EXAMSII is unable to simulate time-varying discharges and mass loadings along the channel system, while WASP-5 a similar model also requires substantially more labour, computer time and disk storage.

A less detailed model developed for pesticide fate simulation in tributary systems is RIVWQ (Williams *et al.* 2004b). RIVWQ is straightforward in data setup, computation and file management. RIVWQ has been validated for northern Italy where it simulated stream flow and pesticide processes adequately (Miao *et al.* 2003). It was also successfully used for diazinon exposure assessment in the main drainage canal of the Sacramento River basin (Snyder and Williams, 2004). RIVWQ model can be used in conjunction with surface runoff models to simulate the effects of land use, water management and pesticide management. The objective of this study was to assess the RIVWQ model for its applicability in simulating pesticide fate in drainage channels of irrigation areas in south eastern Australia.

## 2. RIVWQ MODEL

RIVWQ was developed by Waterborne Environmental Inc. in 1999 to address the main pesticide dissipation pathways in streams whilst minimising input requirements. RIVWQ simulates the transport of organic chemicals in tributary stream systems based on the theory of constituent mass balance. Stream system geometry is represented using a link-node approach in which the prototype is divided into a number of discrete volumes (nodes or junctions) connected by flow channels (links). The model was written to be compatible with the pesticide runoff models PRZM, RICEWQ (Williams *et al.* 2004b), and GLEAMS (Knisel and Turtola 1999, Knisel, Leonard and Davis 1993) which operate on a daily time step. The latest version 2.02 is used in this study.

### 2.1. Water Balance

Water balance algorithm in RIVWQ uses a storage account method. The water balance equation in each node is given by Eq. (1).

$$O = \sum I + \frac{\partial S}{\partial t} \quad (1)$$

where  $O$  is outflow,  $I$  is inflow,  $S$  is storage of water in the control volume, and  $t$  is time. Inflow sources include upstream flows from all connecting links and incremental discharge from external sources. The flow velocity can be calculated by either geometric rating curves or Manning's equation. The model includes a Muskingum flood routing option. For relatively long channel length the Muskingum flood routing option should be used to account for travel time along the channel. For a detailed description see Williams *et al.* (2004b).

### 2.2. Pesticide Fate

The model tracks the total mass of chemical residues in the tributary stream systems from the loading points. The mass balance is calculated along each link of the node, as defined by users, and the governing equation applied to a control volume takes the following general form.

$$V \frac{\partial c}{\partial t} = \sum_{i=1}^{NC} (Q \cdot c) + \sum_{i=1}^{NC} (E_L \cdot A \frac{\partial c}{\partial x}) + \Delta s \quad (2)$$

where  $V$  is nodal volume of a stream segment,  $c$  is pesticide concentration,  $t$  is time,  $i$  is counter for links entering a node,  $NC$  is number of links or channels entering a node,  $Q$  is flow in a link,  $E_L$  is

dispersion coefficient,  $A$  is link cross-sectional area,  $x$  is longitudinal distance and  $\Delta s$  is rate of net addition of the pesticide mass due to external input or internal transformation processes.

Within each nodal volume, RIVWQ simulates transformation processes and simultaneously tracks the mass balance of each chemical in two media: the stream water column and benthic sediments. Chemical residue in water is assumed to be instantaneously diluted in each control volume. For a detailed description of the model see Williams *et al.* (2004b).

### 2.3. Inputs and outputs

Model inputs are provided through three files, a parameter file, a hydrology file and chemical mass or concentration file. The model outputs include stream flow rate and chemical concentrations in water and sediment at selected nodes on a daily basis.

## 3. MODEL CALIBRATION

### 3.1. Field Data

The model was calibrated against field data collected by Thomas *et al.* (1998). They monitored drainage water at the beginning of the irrigation season 16 October to 9 December, 1993 in a drainage channel receiving irrigation run off water from 5 farms in the Willbriggie area, 20km south of Griffith in the Murrumbidgee Irrigation Area. The 5 farms (labeled A to E) which all drained their run off into the same surface drain and the two monitoring points in the drainage channel are shown in Figure 1. This figure shows the farms but the pesticide delivery to the drain from the farms is not modeled in this exercise.

Pesticides monitored in the drain during the study period included molinate associated with rice growing. Daily composite samples were taken at the two locations in the drainage channel, the 'upstream site' and the 'downstream site'. These sites were 1.9 km apart. Between these two points there were no other inputs. The upstream site was located just below the junction of two drains that serviced the 5 farms that contributed drainage water. This modeling study only considers the load and fate of pesticide in the drainage channel. We use the observed data at the upstream and downstream points to test the model. We then varied the cropping area to derive loads and flow rates for analysis of possible effects on pesticide dissipation in the drainage channel.

The total area of the farms was of 900 ha, of which 420 ha was planted to rice, 100 ha maize, 40 ha soybean, and the rest fallow.

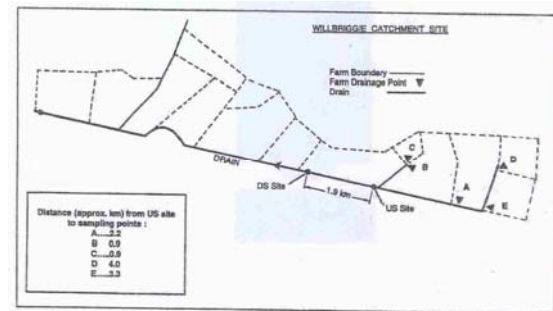


Figure 1. Layout of the study area

### 3. 2. CALIBRATION

The observed flow rates and pesticide concentrations at the upstream and downstream points were used in the calibration. The input values were flow rates and chemical concentrations at the upstream point. Calibration was undertaken to match the modelled downstream flow rates and pesticide concentrations to the observed values.

In the flow rate calibration, Manning's equation and Muskingum flood routing option were used. For drainage channels Muskingum  $x$  coefficient was assumed to be 0.2 and Muskingum  $k$  coefficient can be estimated by dividing the length of channel reach by an assumed flow velocity, as per Miao *et al.* (2003). Channel geometry was obtained from field survey and Manning's roughness coefficient was obtained from literature values (Chow, 1959). Daily flow rates were measured only at the upstream point.

The comparison between observed upstream and modeled downstream flow rates is shown in Figure 2.

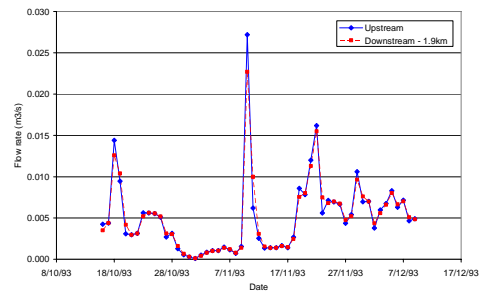
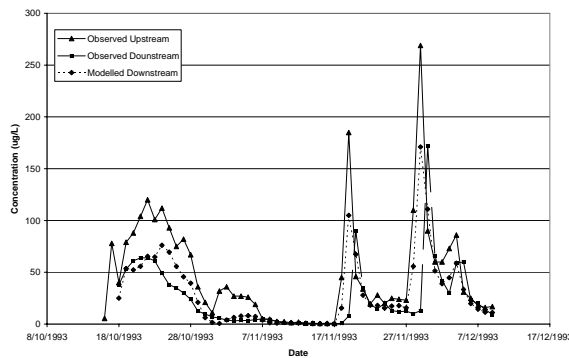


Figure 2. Observed upstream flow rate and model predicted downstream flow rate

Molinate is a herbicide widely used in rice culture. For the pesticide calibration several parameter values were taken from field data, literature, and general knowledge and the others were calibrated by a trial and error approach. The volatilization coefficient, solubility and degradation rate for molinate were obtained from a previous study (Christen et al, 2005). Soil properties for the channel were taken from Hornbuckle and Christen (1999).

The comparisons of the observed and modeled pesticide concentrations for molinate is shown in Figure 3. The concentrations at the upstream point are also presented for reference. In general, the model predicted the downstream chemical concentrations reasonably well even though there is some time lag between modelled and observed downstream concentrations.



**Figure 3.** Comparison of the model simulated and observed molinate concentration

In adjusting the calibration parameters we found that the model output was highly sensitive to the volatilisation coefficient. There was also sensitivity to the sediment bulk density, water/sediment partitioning coefficient and degradation rate in water. Model outputs showed no sensitivity to some parameters including solubility and the dispersion coefficient.

#### 4. MODEL SIMULATION

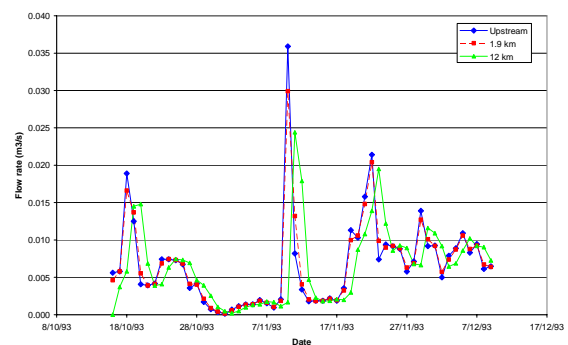
In order to assess the possible impacts of management changes such as increased drainage flows and changed concentrations in molinate in the drainage from the farms a series of four scenarios were developed as shown in Table 1.

**Table 1.** Simulation scenarios for load and fate

Scenario	Flow rate ratio	Pesticide loading ratio	Remarks
A	1.0	1.0	observed
B	1.0	0.5	50% load
C	0.76	0.5	50% load 76% flow
D	0.64	0.25	25% load 64% flow

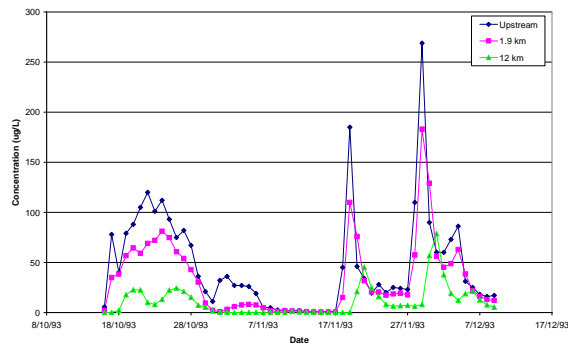
Using the calibrated RIVWQ model simulations were performed and the flow rates and concentrations at the downstream site (1.9km) and an arbitrary site that was located 12 km downstream were analyzed. Below the 1.9km site it was assumed there was no other inflow to the drain. The selection of a 12 km point is based upon the fact that many water quality license sites are about 10-12 km downstream of the farm area boundary in a main drainage channel, usually located just before the drain enters a natural waterway. The 12 km downstream point is purely arbitrary and no field observations are available.

At first, the observed values were used to simulate the flow rates and molinate concentration at downstream points (scenario A). Figure 4 shows the comparison of flow rates along the channel. Flow rates at the downstream site (1.9km) were very close to the upstream flow rates, while 12 km downstream the hydrograph is more spread out, with smaller peaks and a one or two day time lag.



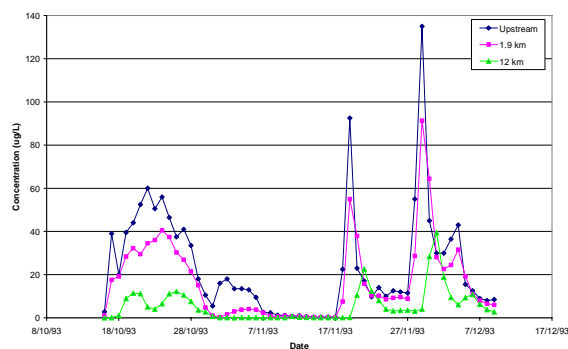
**Figure 4.** Modeled flow rates along the channel with observed rice area (420ha)

Figure 5 shows the comparison of molinate concentrations along the channel. Considering the half life of molinate was determined to be between 1.9-3.9 days and it took 2 days for water to travel 1.9 km (Thomas *et al.*, 1998), the molinate concentrations at 1.9 km and 12 km downstream appear fairly reasonable.



**Figure 5.** Modeled molinate concentrations along the drain with observed rice area (420 ha).

In the second scenario, the molinate loading at the upstream point were reduced by 50 % (scenario B). The concentration changes at the downstream point in this case were compared with the observed value case (scenario A). Here, the flow rates remained unchanged. Figure 6 shows molinate concentrations in the drainage channel for scenario B. Comparing Figure 6 with Figure 5 the pattern of concentration variations closely resemble each other, but with about 50 % reduced values in scenario B. This shows the linearity between the pesticide loading and concentration in the drain with the same flow rates. The dissipation of molinate along the channel reach is well represented in Figure 6, and the concentrations at the 12 km downstream point show an appropriate lag for the travel time.

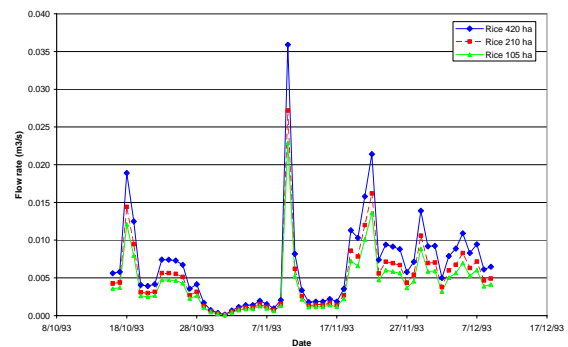


**Figure 6.** Modeled molinate concentrations with a 50 % reduction in pesticide loading

Scenarios C and D represent a change in land area planted to rice crop, in this case both the flow rate and pesticide loading were changed since when the rice area changes both drainage flow rates and pesticide loading will change. The surface water flow rate from the rice paddy was assumed to be 3 times larger than that of the other crops. The observed rice crop area was 420 ha in a total of

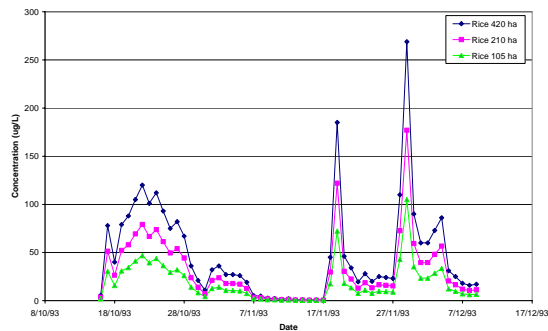
900 ha. Scenarios C, and D had rice paddy areas of 210 ha (50 % of the observed) and 105 ha (25 % of the observed), respectively. The molinate concentrations in water from the other crops are zero, since it is applied only to rice.

Modelled flow rate change due to the change of rice area is shown in Figure 7. Reduction of flow rates due to the reduction of rice crop area is well represented. The flow rates with a 50 % and 75 % rice crop area reduction showed linear reduction of flow rates from that of the observed rice crop area.

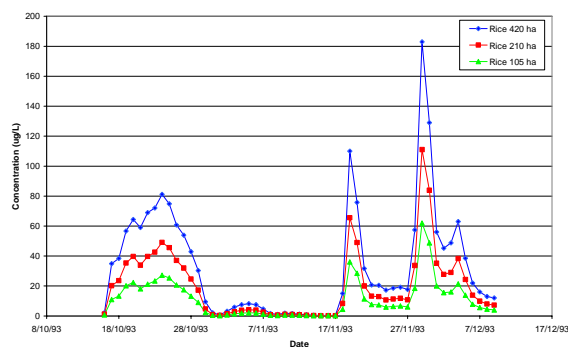


**Figure 7.** Modeled Flow rates at upstream point for scenarios C and D.

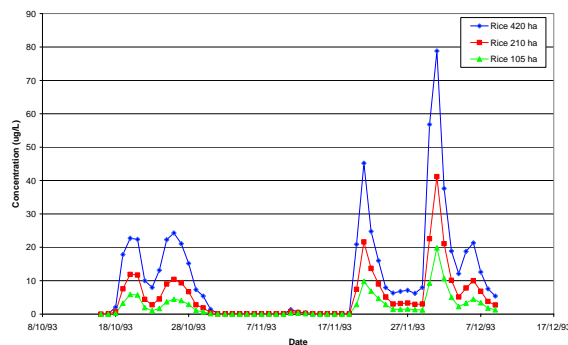
Figure 8 shows molinate concentrations with the reduced rice crop area are linearly related to the molinate concentrations for the observed rice area, 420ha. The ratios of inflow molinate concentrations for 210 ha and 105 ha to those for 420 ha rice area at the upstream point were 0.66 and 0.39, respectively. Molinate concentrations at the 1.9 km downstream point are smaller than those at the upstream point and clearly demonstrate the impact of changed rice areas, Figure 9. The molinate concentrations at the 12 km downstream point show a similar pattern to the upstream ones but with much smaller concentrations due to the pesticide dissipation along the drain reach, Figure 10.



**Figure 8.** Modeled molinate concentrations at the upstream point with different rice areas



**Figure 9.** Modeled molinate concentrations at the 1.9 km downstream point with different rice areas



**Figure 10.** Modeled molinate concentrations at 12 km downstream with different rice areas

## 6. DISCUSSION AND CONCLUSIONS

From this preliminary exercise it appears that RIVWQ model is a relatively simple model requiring limited input parameters compared to more detailed process based models. The model calibration was successful using field data and key parameters such as decay rate, volatilisation rates and soil water partitioning coefficient from a

previous study. Sensitivity analyses showed that the volatilisation coefficient is very sensitive followed by sediment bulk density, water/sediment partitioning coefficient and degradation rate in water.

Although the modeled appeared to perform adequately, the data sets used for testing were extremely limited. More field data is required to test the model under varied conditions before firm conclusions can be drawn as to its validity in this type of environment.

The modeled results showed that when rice areas were reduced both the surface drainage flow rate and molinate concentration at the discharge point changed and the model simulated the water flow rates and molinate concentrations with hydrograph decay, flow time lags and molinate dissipation of the form shown by field data and as would be expected under these conditions.

The results of the model simulation suggest that RIVWQ model could be used for preliminary predictions of pesticide fate in drainage channels and exposure assessment of the pesticide molinate in this environment. Discussions with water managers indicate interest in possible use of the model with further testing and field data to develop guidelines for the management of molinate in drainage waters.

## 7. ACKNOWLEDGMENTS

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