Simulating the Herbicide Molinate in Rice Paddies Using the RICEWQ Model

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EXTENDED ABSTRACT

Contamination of drainage channels and creeks with pesticides used in rice production is of concern in south-eastern Australia. Of major concern is the herbicide molinate that is detected in over 25% of water samples. This pesticide has been the focus of researchers and environmental protection authorities due to continuing frequent detection off-farm despite improved application methods and water management guidelines. The objective of this study was to assess the rice pesticide model RICEWQ version 1.7.2 for its applicability in simulating pesticide in runoff in south-eastern Australia. The model was successfully calibrated against field data on water depths and molinate concentrations from a rice field in the Murrumbidgee Irrigation Area. It was found that the calibrated model was able to simulate the field data in the supply bay adequately; however it is not capable of modeling rice fields with multiple bays, which are much more complex than a single bay situation.

Sensitivity analyses of the parameter values on molinate concentrations in ponded water, sediment and foliage were performed. Overall the application efficiency has a major impact and this impact is carried throughout the entire simulation. In ponded water the bulk density, mixing velocity, release rate for slow release formulation, pesticide solubility and water/sediment partition coefficient were relatively sensitive. In the sediment the release rate and the mixing depth, soil bulk density, degradation rate in the sediment, water/sediment partition coefficient and mixing velocity have large sensitivities. On the foliage only three parameters have non-zero sensitivities, the application efficiency, the wash-off coefficient and the degradation rate on foliage. The calibrated model was used to investigate water and pesticide management for a single bay. It was found that water management was critical to minimising molinate runoff. Using a 41 year weather sequence for Griffith in the Murrumbidgee Irrigation Area it was found that if water levels were maintained 5 cm below the drainage outlet there was little likelihood of surface runoff occurring.

Simulation of the registered label application methods and rates for molinate were undertaken. These compared application onto a dry bay, a ponded bay and application by ground rig, aerial, and Soluble Chemical Water Injection In Rice Technique (SCWIIRT) low pressure system. The greatest maximum concentrations of molinate in the ponded water occurred when molinate was applied directly onto the water. The maximum concentrations for application onto a dry bay were two orders of magnitude lower than for the applications onto a bay filled with water. However, the pesticide concentrations in water declined more rapidly for the application onto a water filled bay than for application onto a dry bay. Field trials are required to assess the accuracy of these results as no data comparing ponded water and dry bay applications is available.

The comparison of application methods was undertaken by adjusting the application efficiency parameter. This parameter determines how much active ingredient actually meets the target, e.g. enters the water column, with respect to instantaneous losses. This is important for molinate which is highly volatile. This was assigned as 60% (assumed) for the aerial application on dry bay, 70% (assumed) for the ground rig, 95% for aerial application (determined from the model calibration), and 100% (assumed) for the SCWIIRT. The results showed that after three weeks following application the pesticide concentrations in water for all scenarios were similar. Investigating the effect of application rate by increasing the rate by 60%, it was found that the period during which the water molinate concentration was above guideline level only increased by 11%. These modeling results indicate that the application amount is only critical to the concentration of molinate in runoff if it occurs in the first 30 days after application. The results regarding molinate concentrations in water with time and effects of different application rates suggest that poor application efficiency results in a major loss of chemical. If the application efficiency could be improved and application aimed at a target water concentration then lower application rates of molinate could potentially be as effective as current label rates.

1. INTRODUCTION

There are 2.5 million hectares of irrigated land in Australia, of which up to 120,000 ha are sown to rice annually and about 500,000 ha are in a rice growing rotation. The rice growing areas are within the Murray Darling Basin on the Murrumbidgee and Murray river basins. This rice is grown as ponded rice.

In rice production a large variety of pesticides are used. Rice production presents a challenging system for the management of pesticides due to rapid runoff from rainfall, variable management, and often close proximity of rice fields to surface waters such as drains, rivers and wetlands. Thus the opportunity for pesticide movement out of the rice paddy into the wider hydrological system is large.

Contamination of surface waters by pesticides has been detected at various sites across the rice growing areas. Three main irrigation companies in their annual reports all show frequent detection of rice pesticides in surface drains, to the point where some chemicals, such as molinate, are found in more than 25% of samples (Coleambally Irrigation Co-Op. Ltd., 2002). Molinate is a selective herbicide widely used around the world.

This frequent detection of rice pesticides has led to concern from environmental regulators and the Australian Pesticides and Veterinary Medicines Authority (2003) when considering the re-registration of molinate. To try to reduce the environmental effects of molinate and other pesticides a variety of regulations are imposed upon rice farmers to try to contain the chemicals on farm. The most important of these is the "withholding period" which is the period after pesticide application when water must not be released from the farm. The length of this withholding period for molinate is 28 days in the Murrumbidgee Irrigation Area. Researchers have undertaken various studies to assess the dissipation rates of rice chemicals within rice fields. In southeastern NSW, Australia, in bays near the irrigation supply there was an average decrease of 99% in molinate concentration in water 19 days after application, but in bays at the drainage end the molinate concentration persisted above detection limits for much longer, up to 30 days. Bowmer et al., 1998). The current guidelines set for molinate in water in surface drains by the New South Wales Environmental Protection Authority are 0.0034 mg L^{-1} as a Notification level and 0.0145 mg L^{-1} as an Action Level (NSW EPA, 2004).

The large variability in biophysical and management conditions in the irrigation area makes it very difficult to produce definitive guidelines. The experimental resources required to monitor a broad range of conditions are unavailable. Thus 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.

Very few water quality models have been developed for rice production, and still fewer which deal with pesticides. There are two detailed process-based models aimed at researchers; PADDY (Inao and Kitamura, 1999) and RICEMOD (Linders and Alfarroba, 2001). A less detailed model developed for pesticide registration purposes in USA is RICEWQ (Williams et al., 2004). RICEWQ model was assessed by the Mediterranean-Rice group of the European Union and found to be the most suitable of those named above for the assessment of exposure risk of surface waters neighbouring rice paddies (Karpouzas and Capri, 2004). RICEWQ has been validated for northern Italy where it simulated runoff processes adequately (Capri and Miao, 2002; Miao et al. 2003a, 2003b). The objective of this study was to assess the rice pesticide model RICEWQ version 1.7.2 for its applicability in simulating pesticide in runoff in south eastern Australia.

2. RICEWQ MODEL

The RICEWQ was developed to evaluate the fate and pathways of pesticides in rice paddies. It was developed by Waterborne Environmental Inc. in 1999 to address the main pesticide dissipation pathways while minimizing input requirements. The model was developed specifically to simulate pesticide dissipation and runoff losses to receiving waters, and the latest version 1.7.2 is used.

Water balance algorithms account for inflow to and outflow from the paddy field. Inflow includes irrigation and rainfall while outflow includes runoff, evapotranspiration, and seepage. Irrigation is set at designated volumes by the user or set by an automatic irrigation facility that fills the bay to a set level when the water level in the bay drops to a critical level. The rate of filling is set by the user as an available irrigation flow rate. Drainage outflow occurs when the water level in the paddy field reaches a critical level and has an outflow rate given by the user. The model also allows seepage from the bay.

The model applies a conservation of mass approach to simulate the total mass of chemical residues in the paddy. RICEWQ tracks the fate of the chemical on the foliage, in the ponded water and in the bed sediment. The rate of chemical application is attenuated by an application efficiency to account for drift, off-target deposit, rapid volatilisation and other immediate losses that prevent the chemical entering the water column or depositing on foliage. The pesticide mass is then either volatilised, degraded (hydrolysis, photolysis, metabolism), partitioned to sediment or lost by mass transfer through surface runoff.

Partitioning to sediment occurs by direct partitioning, diffusion and settling of chemicals adsorbed to suspended sediment. These processes are represented simplistically, governed by rate terms input by the user. The model can track both parent and metabolite chemicals. For a detailed description of the model see Williams et al. (2004).

3. MODEL CALIBRATION

The model was calibrated against field monitored molinate concentration data after application in a rice paddy in October 2001 in the Murrumbidgee Irrigation area of New South Wales. Molinate is a herbicide that is used in the period October to November to control grass weeds.

The commercial rice farm consisted of an area of 18 ha of grey clay loams divided into 7 bays with a 'flow through' system of water management. The long term infiltration rate for these soils has been measured as 1-2 mm/day (Hornbuckle and Christen, 1999). The field was sown aerially on 15 October, 2001 and molinate was applied at a rate of 2.0 kg ha^{-1} (1.92 kg ha^{-1} active ingredient) on 17 October, 2001. Water was held for 4 days dropping from 11 cm to 9.4 cm over the period with no inflow or outflow of water. After the holding period, water was applied and maintained at 8 -16 cm water depth for 10 days with intermittent inflow and outflow. Water depth was measured manually using scaled rulers mounted at the top, middle and bottom of each bay.

Water was sampled from three different bays of the rice paddock in three replicates for molinate analyses (detection limit 0.25 ug/l). Also, the water depth in the bays using six depth measurements across the bay was monitored (Quayle and Oliver, 2005). In order to calibrate the model as accurately as possible the depth and molinate data from bay 1 (nearest the irrigation supply) was used rather than averaging all measurements across all three bays, as there were large variations in water depths and pesticide concentrations. Bay 1 was chosen because the data here was most comprehensive in number and timing of samples.

Model inputs are provided through two files, a meteorological file and a parameter file. The meteorological file has rainfall and pan evaporation on a daily basis. The model assumes that paddy evaporation is the same as that of open pan, which is appropriate for conditions in south eastern Australia (Humphreys et al., 1994). The model was calibrated in two steps firstly the water balance and then the pesticide balance.

3.1. Water balance calibration

In order to calibrate the water balance only the irrigation amounts were varied to match the observed ponded water depth. Initially irrigations were applied using the “fixed volume” facility, which allows input of specified amounts, in order to make the water balance as accurate as possible. Evaporation and rainfall were not altered and there was no surface drainage during this period.

The results of the model calibration were well matched to the observed water depths (Fig. 1). The ponded water depths had an average error of 0.9 cm between modelled and observed, the maximum error was 1.8 cm, and the root mean square error (RMSE) was 1.3 cm. The water balance for the fixed volume irrigation is investigated. Total inflow was 48.1 cm, of which 5.7 cm was rainfall and 42.4 cm was irrigation. Total outflow was 48.5 cm, of which 35.4 cm was evapotranspiration and 7.7 cm was seepage. The relative error of water balance was 0.8 %.

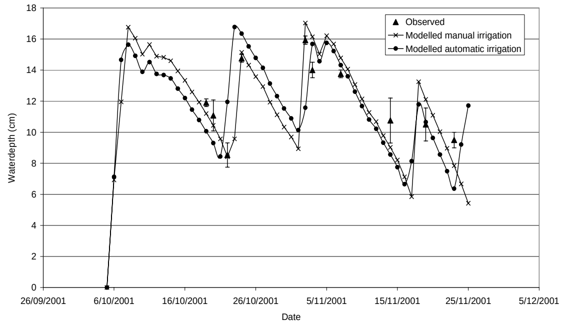

Figure 1. Observed and modelled water ponding depth after model calibration

Irrigations were also applied using the “automatic” facility, which fills the bay to a set level when the water level in the bay drops to a critical level. For this simulation two periods were identified, before the end of the first week in November and subsequent to this, as it appeared from the observed data there was a regime change at around this time. Initially the critical depth to trigger refill was set as 8.0 cm and fill level set as 16.0 cm. After the 1st week in November these were changed to 8.0 cm and 14.0 cm. Again only the irrigation amounts were varied to match the observed ponded water depth.

The modeled results of the automatic irrigation agreed well with the field measurements (Fig. 1). The water balance for the automatic irrigation was similar to the fixed volume irrigation.

3.2. Pesticide Calibration

After the water balance was adequately calibrated the pesticide balance was calibrated. The basic data used for the water balance calibration were again used and the soil and chemical parameters were added. Parameter values were taken from field data, literature, and general knowledge of rice growing. Only three parameters were completely unknown; the application efficiency, which concerns the amount of chemical that actually enters the water column, the mixing depth of sediment for direct partitioning and the mixing velocity which is associated with the mixing depth.

Firstly, calibration was undertaken to match the initial pesticide concentration sampled in the bay. This was done by altering the application efficiency. During this process the mixing depth for sediment partitioning was set to zero as the partitioning process occurs after the chemical is in the water column and thoroughly mixed, which takes about a day after application.

Calibration for application losses is necessary for most chemicals especially those with high volatility such as molinate. Since molinate was aerially sprayed with solid stream nozzles with liquid concentrate the drift losses are likely to be low. Calibration of the model led to a best fit value of 95% application efficiency to match the first sampling average concentration. The samples have a coefficient of variation of 8% and so the value of 95% seems reasonable. The model results show that the molinate lost to volatilisation on the first day is about 14% of the total mass entering the water.

After calibration of application efficiency the mixing depth of sediment for direct partitioning was varied across the range from 0 to 0.5cm and 0.1cm was selected with minimum error. The mixing depth and the mixing velocity, which is associated with the mixing depth, are linked parameters. Thus it was unnecessary to calibrate the mixing velocity once an appropriate calibration was achieved with the mixing depth. We have field dissipation rate data specifically from this study. Dissipation half-life for molinate in water was 2.7 days.

The results of the model calibration using the fixed volume irrigation for pesticide in the water are shown (Fig. 2). Note that the first water sample was taken one day after moninate application. It can be seen that the initial concentration in the water determined by RICEWQ matches observed data well and the slope of the decay determined by the model is similar to the observed. Analysis of the difference between modeled and observed concentrations showed that the largest differences occur soon after application, reducing to very small concentrations later. The maximum difference was 0.093 mg L^{-1}, the average difference was 0.032 mg L^{-1}, and RMSE was 0.048 mg L^{-1}.

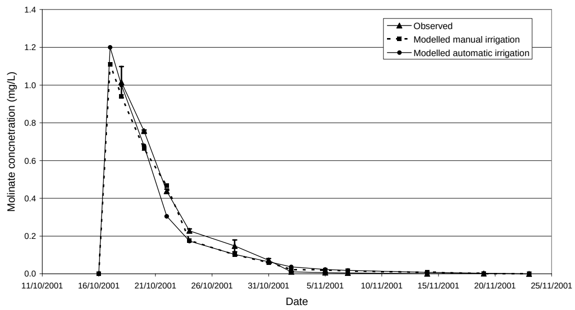

Figure 2. Observed and modelled molinate concentrations in ponded water.

The results of the model calibration using the automatic irrigation mode closely reflects the fixed volume irrigation. The overall results of the model calibration were very encouraging. With minimum calibration of the input parameters the modeled results adequately matched the observed data.

The model predicted pesticide mass balance per ha for the fixed volume irrigation was investigated Total effective application was 1.826 kg. Decay was 0.310 kg, volatilisation 1.320 kg, (which was 72% of the effective application) seepage loss 0.172 kg and residue at the end of simulation 0.120 kg, respectively. Relative error of the mass balance was 5.3 %. The pesticide mass balance for the automatic irrigation was also investigated. Basically there was no difference between the fixed volume irrigation and automatic irrigation in the pesticide mass balance.

4. SENSITIVITY ANALYSES

In order to assess the sensitivity of the model to the various input parameters a series of simulations were conducted using the calibrated fixed volume irrigation input file and varying each parameter by

± 50% of its original value except the application efficiency, which varied by ± 5% of its original value. The results for molinate concentrations were analysed at 0, 4, 15, 32 days after application, as the impact of a parameter change may occur early or late in the simulation.

On the day pesticides are applied the application efficiency is the most sensitive parameter followed by the release rate for slow release formulation and the fraction of pesticide intercepted by water and immediately transformed metabolite. At 32 days after application, the volatilisation coefficient is the most sensitive parameter followed by application efficiency, bulk density, mixing velocity, release rate for slow release formulation, and water sediment partition coefficient. The release rate may be important for slow release pesticides.

5. SCENARIO MODELLING

5.1. Water Management

Water management is critical in preventing runoff from rice fields that may be contaminated with pesticides. In order to test the importance of water management a set of irrigation regimes was developed which varied the depth of water in the rice paddy early in the season when molinate was applied. The irrigation regimes tested were to have a target irrigation depth of 1, 2, 3, 4 and 5 cm below the paddy overflow depth of 20 cm. This value was called “Difference between Irrigation target and overflow depth” (DIOD). The trigger irrigation depth to input water was set at 2.5 cm below the target irrigation depth. The scenarios were run for 41 seasons between 1962/1963 and 2003/2004.

Changing the target water management depth altered the concentration of pesticide in runoff when the DIOD was 4 cm or smaller. The results show that the maximum concentrations are above the NSW EPA Notification Level of 0.0034 mg L^{-1} when the DIOD was 4cm or smaller (Fig. 3).

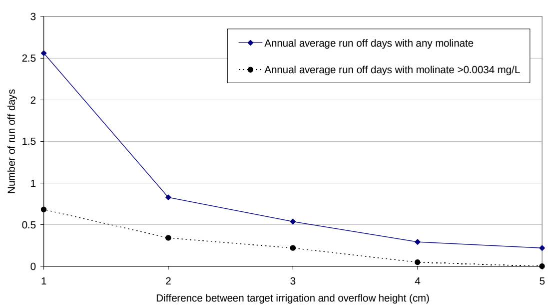

Figure 3. Average annual number of days where runoff water was contaminated with molinate

5.2. Pesticide management

In Australia pesticides can legally be applied by following the “Registered Label” directions. The registered label for the herbicide molinate directs that two rates (2.4 or 3.6 kg ha^{-1}) can be used depending upon the age and type of grass weeds (Nufarm, 2004). Molinate can be applied by normal ground rig to dry bays. When bays are flooded molinate can be applied by aircraft or alternatively by using a technique known as the Soluble Chemical Water Injection In Rice Technique (SCWIIRT) (Nufarm, 2004). This method was developed in the rice industry in Australia in 1993, and is a low pressure (<200kPa) application technique that “dribbles” the pesticide into the ponded water. This technique is intended to minimize losses and drift compared to aerial application techniques.

Using RICEWQ we can investigate the effect of these management options, scenarios in Table 1. These scenarios require that the application efficiency of the ground rig, dry bay aerial spray and SCWIIRT methods be estimated. These were assumed to be 70%, 60%, and 100%, respectively. A low efficiency (60%) for the dry bay aerial spray was selected due to the observation of extensive pesticide presence on the ground beyond the application area. Aerial spraying used solid stream nozzles with liquid concentrate molinate.

Table 1. Summary results for pesticide management scenarios

Scenario	Appl. method	Land condition	Efficiency (%)	Appl. rate (kg/ha)	Days above disch. limit
A	Ground rig	Dry	70	3.6	70
B	Aerial	Dry	60	3.6	68
C	SCWIIRT	Ponded	100	3.6	38
D	Aerial	Ponded	95	3.6	37
E	**SCWIIRT**	Ponded	100	2.4	31

The scenarios were run for 05/10/2001 to 31/03/2002, and the same climatic conditions and parameters were used as for the model calibration. For the dry bay scenarios, the irrigation was delayed until the day after spraying. The irrigation was controlled using the automatic mode in RICEWQ. The same irrigation control as in the model calibration was used. Initially the critical depth to trigger refill was set as 8.0 cm and fill level set as 16.0cm. After the 1st week in

November these were changed to 8.0 cm and 14.0 cm following the general agricultural practice. There were 2.0 cm rain on 23rd October and 1.8cm rain on 5th November.

Molinate concentrations in the ponded water following application for the scenarios are shown, note log scale (Fig. 4). The results show much higher concentrations for application on ponded water than on dry land for the first 30 days after application. After that the concentrations in the water applied on dry bed showed persistent higher values.

The molinate concentration in the water following application to a ponded bay by aerial and SCWIIRT method showed higher concentrations for the SCWIIRT application due to the assumed higher efficiency, 100%, as compared to the application efficiency of 95% for the aerial taken from the model calibration.

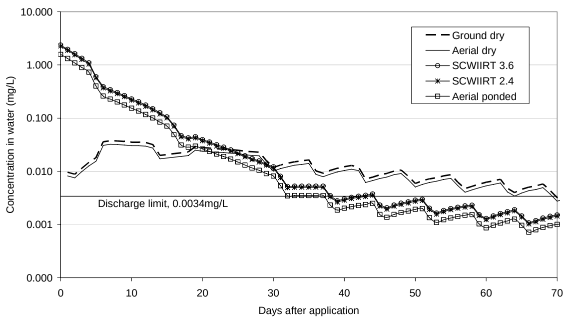

Figure 4. Modelled molinate concentration in ponded water.

Comparison of the molinate concentration in the ponded water for application to a dry bay and ponded bay by aerial application show that the concentration patterns between the two scenarios are quite different. The initial concentrations in water for the ponded application were much higher (2.2 mg L^{-1}) than for the dry bay (~ 0.01 mg L^{-1}). The level of concentration above the discharge limit persists 68 days in the dry bay application, as compared to 37 days for the ponded bay application. The high molinate concentration in the dry bay application for about 3 weeks after application is due to release of molinate from the sediment to the water column.

The pesticide application rate will have an impact on concentrations. A direct comparison can be made between scenarios C and E, where SCWIRRT application method is used and the application rates are 3.6 and 2.4 kg ha^{-1} for C and E respectively. This shows that at the higher rate the initial concentration is much higher, however after about six days the concentrations are very similar and the time until the water is below the discharge limit is only 7 days longer, 38 days vs. 31 days, for the higher rate of application.

The pesticide management and resulting water quality are summarised (Table 1). This shows that greatest maximum concentrations in paddy water occur when molinate is applied to ponded bay and increase with increasing application efficiency and application rate. The maximum concentrations for the dry bay application are two orders of magnitude lower than that of the applications onto a bay filled with water. However, the pesticide concentrations in water decline more rapidly for the water application than for the dry bay application.

When comparing pesticide application methods it is useful to compare the time required for the concentration in the water to reach an acceptable value for discharge, namely 0.0034mg/L. From Table 1 we can see that dry bay applications result in longer period above the discharge limit than ponded bay applications. The length of period above discharge limit is affected by the amount of chemical applied. Scenario C has an application rate of 3.6 kg/ha which is 50% higher than scenario E, and has 38 days above the discharge limit which is 23% longer than scenario E.

6. CONCLUSIONS

RICEWQ model is a fairly easy to use model requiring limited input parameters compared to more detailed process based models. The model calibration was successful with field data and key parameters such as decay rate, and volatilisation rate were available from the literature for molinate. However, there is little or no data on application efficiency from field trials.

The sensitivity analyses showed that the pesticide concentrations in ponded water were very sensitive to the application efficiency. Other key parameters such as release rate for slow release formulation, bulk density and mixing velocity were sensitive.

The field data used for calibration were from trials conducted on farmers properties. These results we believe are representative of the field conditions that would occur in the region generally. As such we can use RICEWQ to provide preliminary indications of the impacts of alternative application and management techniques.

RICEWQ was found to simulate simple water management conditions in a bay adequately. Using the calibrated model to run water management scenarios for 41 rice seasons, it was found that if the irrigation target depth was maintained at least 5 cm below the paddy overflow level there was negligible pesticide in runoff water

The label proscribed pesticide application methods for molinate were tested. The results showed that greatest maximum concentrations of molinate in water occur when the chemical is applied directly onto water and increase with increasing application efficiency and rate. The maximum concentrations for application onto a dry bay were two orders of magnitude lower than for the applications onto a ponded bay. However, the pesticide concentrations in water decline more rapidly for the application onto the water filled bay than for application onto the dry bay. It would be interesting to undertake some field trials to verify these results.

Comparison of application methods was made by adjusting the application efficiency. This ranged from 60% for aerial application on dry bay to 100% for the SCWIIRT system. In SCWIIRT ponded bay application the length of time above the discharge level only increased by 23% when the application rate was increased by 50%.

The results suggest that poor application efficiency results in a major loss of chemical. If the application efficiency could be improved and application aimed at a target concentration in water then lower rates of molinate could potentially be as effective as current label rates. This requires further research to determine water concentrations to control weeds.

Overall using RICEWQ has helped us to understand effects of water management and pesticide management on likely discharges to the environment. It is possible to further investigate management and environment impacts by looking at different seasonal conditions, soil types and application rates. This can be done relatively easily with this model and can be useful in giving preliminary indications of likely impacts of management or environmental changes.

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