



Continuous sampling of pesticides in waterways

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IN A RICE HULL

- ▶ Passive sampling devices offer a cheaper and more effective procedure for measuring pesticide concentrations in the aquatic environment over time than conventional manual sampling procedures
- ▶ Once the passive samplers are calibrated for each pesticide, their ability to determine time-integrated water concentrations will make it possible to link average water concentrations to water quality guideline values

With depleting water supply throughout Australia, more and more focus is being placed on water quality management by water users and the general community. Maintaining clean water is the only way forward to enable ecologically sustainable development of the nation. The National Water Quality Management Strategy (NWQMS) was introduced in 1992 as a response to community concerns about the condition of Australian water bodies.

The management of water quality in agricultural areas is important on a national basis, and in the rice growing areas, it is managed through the Land and Water Management Plans that have been implemented. This project was aimed at producing a new tool for assessing pesticide contamination in irrigation drainage waters of the rice growing regions using passive sampler technology.

State of flux

Our waterways are constantly changing; concentrations of contaminants can fluctuate on a daily or even hourly basis. Conventional methods to monitor contaminants (such as spot sampling and live organism deployment) are increasingly seen as inadequate in portraying a true picture of contaminant levels. Passive samplers, as an alternative method of sampling, are generating interest in many agricultural areas throughout Australia.

Spot sampling produces a single sample representative of a water body at a particular time and place. Although this technique is widely used throughout the world, it runs the risk of missing peak pesticide concentrations that may occur after a storm event or after aerial spraying of agricultural areas, as it only provides an instantaneous measure of contaminant concentration. Often we have to know what chemical we are analysing for in order to find it.

The uptake of contaminants by live organisms such as caged mussels or fish provides a more realistic picture of contamination. Over time, low concentrations of

contaminants are able to accumulate within the organism thus allowing detection of contaminants that may have otherwise been missed if spot sampling was used. On the down side, this technique also has many problems such as individual and species variability by sex, age and physiological state of the organism. Living organisms also require specific living conditions that are appropriate for the test organism. They are subject to variables such as mortality, reproductive development, growth, feeding needs, chemical stressors plus many others. On top of this, analysis of tissue residues can be a complex task that may require clean-up procedures, prior to testing.

Passive samplers for rice areas

Passive sampler technology provides a measure of time-averaged concentrations of contaminants in a water body giving a more accurate representation of water quality than is possible with spot sampling, and at a lower cost. It overcomes many of the problems associated with live organism deployment as the passive samplers effectively mimic bioaccumulation, though it too has some limitations. In developing a new tool for assessing pesticide contamination in irrigation drainage waters of the rice growing regions, the project also helped minimise some limitations of passive sampler technology, by broadening the type of contaminants that can be detected.

Our first calibrated passive sampler device was made from a polyethylene membrane bag containing a kerosene-like organic solvent (called TRIMPS). It absorbs pesticides that are not very water-soluble, otherwise known as hydrophobic, such as endosulfan (Thiodan™) and chlorpyrifos (Lorsban™). It has been used effectively in the cotton-growing region of northern New South Wales as this device can target the main insecticides used in the control of cotton pests.

Many other agricultural regions in Australia, such as the rice-growing area of southwestern New South Wales, use pesticides that range from not very water-soluble to very water-soluble, otherwise known as hydrophilic or polar.



Hence an approach that encompasses a wide range of pesticide types needed to be considered.

A modified passive sampler with a different sequestering medium was produced (called PIDS) and underwent both laboratory and field trials in the Murrumbidgee Irrigation Area (MIA). Though the modified polyethylene sampler broadened the range of detectable pesticides, further modification was still required to increase this range to allow for more water-soluble pesticides. The polyethylene membrane was replaced with the use of a cellulose membrane. Results in the laboratory were encouraging, increasing the uptake of more water-soluble pesticides significantly, though when subjected to field conditions the membrane broke down due to naturally occurring enzymes. The cellulose was stained with an enzyme inhibitor that hindered the degradation of cellulose and initial trials showed that the stained-cellulose passive sampler (called CIDS) was stable up to 21 days in the field.

All three types of samplers have been calibrated for a range of pesticides in a laboratory flow through system prior to deployment in the field. Calibration involves measuring the uptake into the solvent and the release from the solvent of the passive sampler for each individual pesticide. The results indicated that pesticide uptake is linear over 22 days of exposure time for each device and uptake is independent of pesticide concentration.

Large scale field study

In October and November of 2004 a large-scale study was undertaken in drainage canals of the MIA. Its aim was to investigate the relationship between pesticide concentrations in the drainage water, as measured by daily spot sampling, compared to those measured by the passive sampler devices.

Three study sites were selected based on local knowledge of significant pesticide concentrations in past seasons (Figure 1). Each site received drainage water from irrigated farms between the towns of Leeton and Griffith. Two types of passive samplers (PIDS and CIDS) were deployed at each site. After a week of deployment, four replicate samplers were retrieved every third day at each site until the study was completed after three weeks. Solar powered trailers enabled us to collect a daily composite water sample that was then extracted in the laboratory and analysed for pesticides.

A cumulative mean water concentration for each pesticide could be determined and then compared against the concentrations found in the passive samplers. Environmental parameters such as temperature, pH, conductivity and water flow were measured hourly whilst turbidity was measured daily and rainfall was measured on a continuous basis.

The study indicated that the polyethylene samplers (PIDS) had good recovery in the field with more than 95% of the initial solvent being recovered in greater than 90% of all samplers deployed over the three-week period. Though the results for the stained-cellulose samplers (CIDS) were not as encouraging with 95% of the initial solvent being recovered in only just over 50% of the samplers in the three-week period. Most of the degraded CIDS were collected during the third week of the study and the low solvent volumes

prevented pesticide analysis.

Although previous studies had indicated stability up to three weeks, the higher temperatures in the study area caused the samplers to degrade at a quicker rate. Future deployment in similar conditions will reduce the deployment time of the CIDS samplers to a two-week period, as the study indicated that 95% of the initial solvent was recovered in almost 90% of the samplers during the initial two-weeks of deployment.

Peak values being missed

Ten pesticides were detected within the daily extracted water samples. The range of pesticide concentrations in the drainage water is shown in Table 1. The trigger values from *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* for the pesticides are also shown. The trigger value for each pesticide represents the threshold concentration at which any exceedences need to be investigated to ensure that no impact is occurring on the receiving ecosystem.

Murrumbidgee Irrigation conducted its monthly pesticide monitoring three days before our study and two days after our study was completed. Staff of MI reported concentrations below the trigger value for diuron, metolachlor and simazine on both days downstream from site 1. At site 2 they reported the presence of diuron at four times the trigger value for diuron in one of the samples, whereas the concentrations of metolachlor, simazine and the other pesticides measured were below the trigger value.

The results from our study indicated that the trigger value for diuron was exceeded on all 22 days at sites 1 and 2; the trigger value for simazine was exceeded on two days at site 1, and the trigger value for metolachlor occasionally at all three study sites (Figure 2). This demonstrates how easy it is

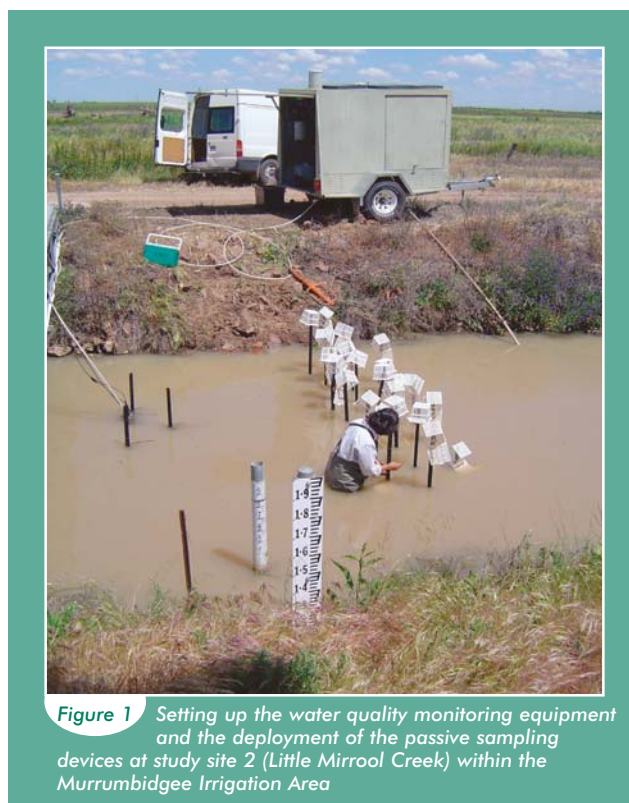



Figure 1 Setting up the water quality monitoring equipment and the deployment of the passive sampling devices at study site 2 (Little Mirrool Creek) within the Murrumbidgee Irrigation Area



to miss peaks in pesticide concentrations by using sporadic spot sampling.

The average pesticide concentration determined from the cellulose-membrane device (CIDS) for each time period was plotted against the cumulative mean drainage water concentrations, from the daily measurements. The graphs showed that for most points the daily water extraction of each pesticide was within two-fold of the average pesticide concentration derived from the passive samplers, displaying that both the calibrated passive sampler device and the daily water extraction produce the same total pesticide concentrations on average during the field study. The passive sampler technology is therefore shown to represent the average concentration in waterways over a 7-day to 22-day time period.

As the awareness of passive sampler technology as an important tool for sampling is increased, the improved sampling methodology will be able to yield more reliable measurements of contaminant concentrations under a wide range of environmental conditions. It will reduce the cost of monitoring since fewer analyses will be required throughout the year and it will hence enable increased monitoring, along with providing a means of detecting point and diffuse sources of pollution. It will be an important management tool in the agricultural industry, with the ability to detect when contaminated water is below and above trigger values thus indicating when it is suitable to release drainage water off-farm. 

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Table 1
Pesticide concentrations detected in MIA drainage waters, and the trigger values for each pesticide as determined by Australian and New Zealand Guidelines for Fresh and Marine Water Quality

Pesticide	Drainage water concentration µg/L	Trigger value µg/L
simazine	<0.001 to 15.7	3.2
bromacil	0.042 to 1.55	180
thiobencarb	0.175 to 1.8	2.8
molinate	0.02 to 2.04	3.4
diuron	0.003 to 32.9	0.2
flupyrifluorid	<0.0001 to 0.11	not available
metolachlor	<0.001 to 0.82	0.02
atrazine	<0.001 to 0.60	13
clomazone	0.2 to 6.42	not available
endosulfan sulphate	<0.0001 to 0.02	0.03

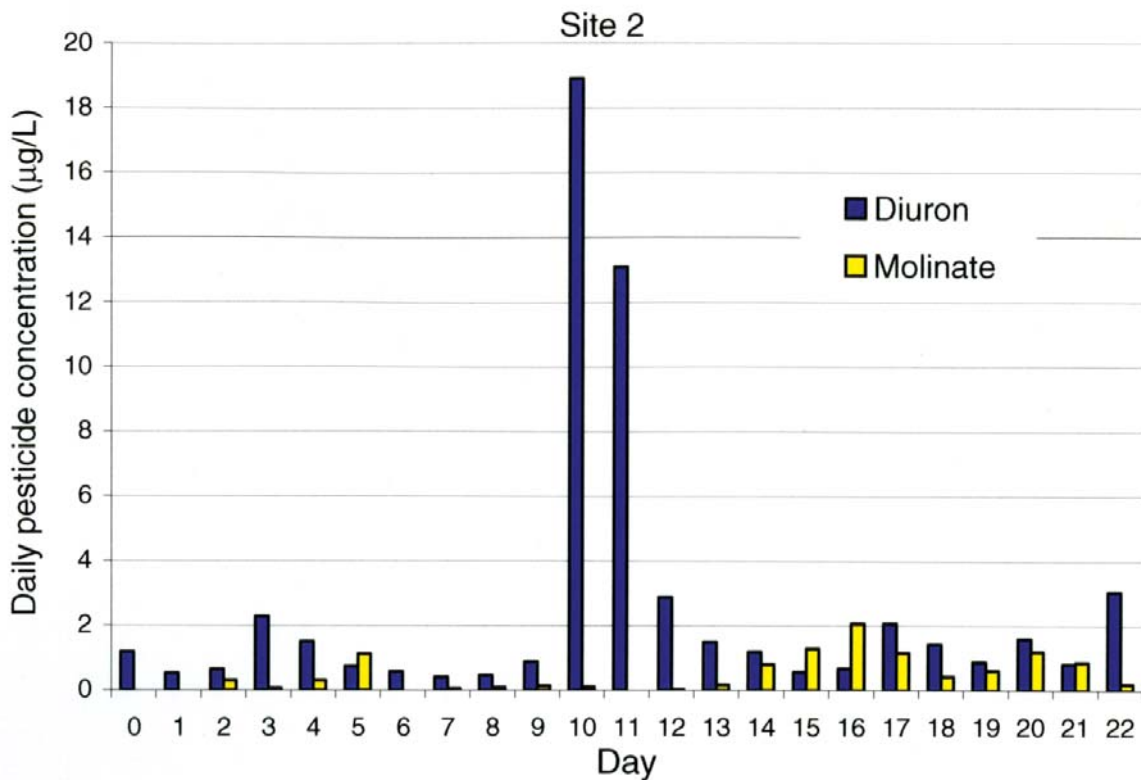


Figure 2 Daily measured water concentrations of diuron and molinate in a irrigation drain (site 2) in the Murrumbidgee Irrigation Area in October/November 2004. Values shown (µg/L) are from 24-h composite water samples.